Metallosupramolecular Gels Made of Four-armed Poly(ethylene glycol)s Having Terpyridine Termini

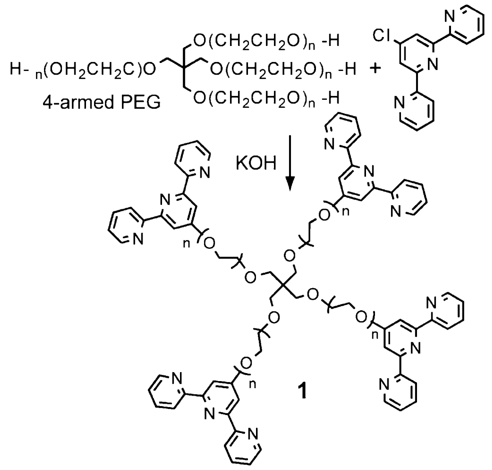
Mutsumi Kimura,*[1,2] Yasushi Nakagawa,[1] Naoya Adachi,[1] Yoko Tatewaki,[2] Tadashi Fukawa,[1] and Hirofusa Shirai[2]
[1]*Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University, Ueda 386-8567*
[2]*Collaborative Innovation Center of Nanotech FIBER (nanoFIC), Shinshu University, Ueda 386-8567*

(Received January 13, 2009; CL-090046; E-mail: mkimura@shinshu-u.ac.jp)

Four-armed poly(ethylene glycol) having 2,2′:6′,2″-terpyridine) termini was synthesized as a component unit and further utilized for preparation of metallosupramolecular gels by the addition of $FeCl_2$. The formed gels collapsed by the addition of NH_3.

Noncovalent intermolecular interactions such as hydrogen bonding, metal–ligand interactions, donor–acceptor interactions, and host–guest interactions allow the construction of self-assembling polymer systems (supramoleccular polymers) by connecting building monomer units having multiple association termini.[1] In contrast to the conventional polymers, these supramolecular polymers can dissociate into monomer units as a result of external stimuli. The supramolecular approach has been applied to the construction of functional gels. Meijer et al. have demonstrated reversible crosslinks and a virtual increase in molecular weight by using monomer units with two quadruple hydrogen bonding termini.[2] Okumura and Ito succeeded in the creation of new type of supramolecular gels based on polyrotaxane networks using freely movable crosslinkers.[3] Here, we report the preparation of supramolecular gels by the formation of metal complexes at the termini of four-armed poly(ethylene glycol)s (4-armed PEG). Terpyridine (tpy) ligands have been used as building ligands for well-defined metallosupramolecular structures through the formation of stable bis(terpyridine) metal complexes between two tpy ligands and one octahedrally coordinating transition-metal ion.[4] We selected the tpy ligands as terminates of metallosupramolecular gels.

Terpyridine-terminated 4-armed PEG **1** was prepared from 4′-chloro-2′,2′:6′,2″-terpyridine and hydroxy-terminated 4-armed PEG (Sigma-Aldrich, $M_n = 10000$ g/mol, $M_W/M_n < 1.2$) according to the literature method[5] (Scheme 1). A reaction of 4′-chloro-2′,2′:6′,2″-terpyridine with 4-armed PEG in the presence of powdered KOH and subsequent purification by size-exclusion chromatography (BioBeads SX-1 in THF) provided in a 77% yield. The synthesized **1** was characterized by ^{1}H NMR, gel-permeation chromatography (GPC), and MALDI-TOFMS. The proton resonance of 3′,5′ protons for tpy appeared at 8.1 ppm, revealing the formation of an ether bond. The GPC analysis showed that **1** had a single sharp and symmetrical elution pattern with $M_w/M_n < 1.2$. The GPC profile of **1** detected by a UV detector monitored at 270 nm agreed with that detected by a refractive index detector, indicating the incorporation of aromatic tpy ligands into the 4-armed PEG. Furthermore, the MALDI-TOFMS spectra exhibited a shift of about 1000 daltons for each single peak from the parent 4-armed PEG.[5] This shift of molecular weight corresponds to the masses of four tpy molecules. These results suggested that tpy ligands reacted almost completely with four termini in 4-armed PEG.



1

Scheme 1.

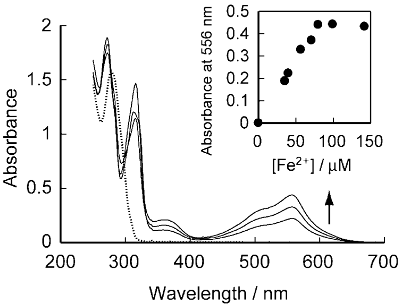


Figure 1. Effect of Fe^{2+} concentration on the absorption spectrum of **1** (40 μM) in metahnol: $[Fe^{2+}] = 0$ (dotted line), 40.0, 61.0, and 80.5 μM. Arrow indicates the direction of spectral change. The inset shows the relationship between Fe^{2+} concentration and the absorbance at 556 nm.

The formation of metallosupramolecular polymers can be monitored by UV–vis and ^{1}H NMR spectra. Figure 1 shows the UV–vis change of **1** by varying concentrations of Fe^{2+} in methanol. The UV–vis spectrum of **1** changed after the addition of Fe^{2+} ions, and a new metal-to-ligand charge-transfer (MLCT) band appeared at 556 nm, indicating the formation of octahedral $Fe(tpy)_2$ complex.[6] Furthermore, the absorbance at 556 nm increased with the Fe^{2+} concentration and then saturated. The content of $Fe(tpy)_2$ complex can be determined using the absorbance at the MLCT band based on the molar absorptivity of bis(2,2′:6′,2″-terpyridyl) iron(II) dihexafluorophosphate (22200 L mol^{-1} in CH_3CN). The content of $Fe(tpy)_2$ complex was above 95% for the total ligand concentration in **1**. The ^{1}H NMR spectrum of mixed CD_3OD solution of **1** and $FeCl_2$ confirmed the successful complexation. The proton signals in the aromatic region could be

Copyright © 2009 The Chemical Society of Japan

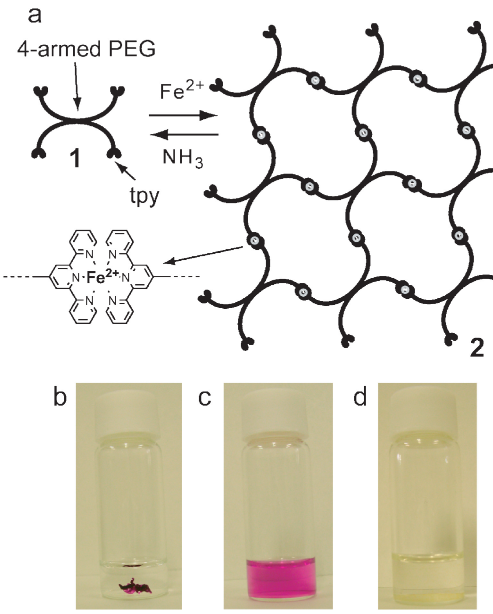


Figure 2. a) Schematic illustration of self-assembling process for the formation of metallosupramolecular gels and photographs of metallosupramolecular gel **2** before (b) and after the addition of ammonia after 10 min (c) and one night (d).

assigned to the complexed tpy protons, and their chemical shifts were in accordance with low-molecular-weight model complexes.[7] Signals of free tpy ligands were not detected in the ^{1}H NMR spectrum.

When 10 μL of methanol solution of $FeCl_2$ (0.54 M) was added to 100 μL of methanol solution of **1** (0.2 g/mL), a firm purple gel was formed, suggesting that a three-dimensional network structure was formed by the connection between two tpy ligands in different **1** with Fe^{2+} (Figure 2). The resulting gel **2** was washed with methanol to remove excess $FeCl_2$ and **1** and dried at 50 °C. The product yield was above 90% on the basis of the initial amount of **1** and $FeCl_2$.[7] The gel swelled in water and organic solvents such as methanol, toluene, and $CHCl_3$. When dried **2** was immersed in water for 10 h, **2** swelled to ca. 30 times the initial weight.

Differential scanning calorimetry traces of **1** and **2** exhibited one sharp transition peak at 40 and 34 °C, respectively. These transition peaks correspond to the melting points of **1** and **2**. The attachment of tpy segments and the formation of metal complexes decreases the melting point from the parent 4-armed PEG (59 °C).[8] Although the weight of **1** was completely lost at 450 °C under nitrogen atmosphere, the thermogravimetric analysis of **2** showed a weight loss of 94 wt % at 450 °C. This weight residue indicates the content of noncombustible inorganic component in **2**.

The formation of the complexes can be reversed by changing the pH value, applying electrochemical or thermal changes, or adding competitive chelators.[9] No changes in shape and color of **2** swelled in water could be observed by varying the pH value from 1 to 13 and heating up to 90 °C, which indicates the stability of the metallosupramolecular gels. On the other hand, the gel collapsed by the addition of aqueous NH_4OH solution, and the purple color disappeared after one night (Figure 2). UV–vis spectrum after the addition of NH_4OH returned to that of **1**. These results suggest that addition of NH_3 resulted in a decomplexation of $Fe(tpy)_2$ and that the dissociation of the connecting points induced the collapse of gels. The surface of a Pt electrode was modified with **2** by the depositing with **1** and $FeCl_2$. After the washing with methanol and drying, cyclic voltammograms of **2**-modified Pt electrode in water containing 0.1 M KCl indicates a reversible Fe^{2+}/Fe^{3+} couple at $E_{1/2} = +0.77$ V vs. Ag/AgCl.[10] This result indicates that the iron centers in the metallosupramolecular gel **2** are electrochemically equivalent and oxidizable at the same potential.

In conclusion, we have demonstrated the formation of metallosupramolecular gels by the connection of 4-armed PEG components through the self-assembly process between two tpy terminates and one Fe^{2+} ion. The narrowly distributed PEG arms may enable the creation of regulated size three-dimensional networks in metallosupramolecular gels. The size-selective molecular penetration or releasing in/from metallosupramolecular gels are currently in progress. In addition, the reversibility of the supramolecular connections will open new possibilities for the construction of stimulus-sensitive smart gel systems.

This work was supported by projects for "Creation of Innovation Center for Advanced Interdisciplinary Research Areas" in Special Coordination Funds for Promoting Science and Technology from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References and Notes

1 L. Brunsveld, B. J. B. Folmer, E. W. Meijer, R. P. Sijbesma, *Chem. Rev.* **2001**, *101*, 4071; A. Ciferri, *Supramolecular Polymers*, CRC, New York, **2005**; T. F. A. de Greef, E. W. Maijer, *Nature* **2008**, *453*, 171.
2 R. P. Sijbesma, F. H. Beijer, L. Brunsveld, B. J. B. Folmer, J. H. K. K. Hirschberg, R. F. M. Lange, J. K. L. Lowe, E. W. Meijer, *Science* **1997**, *278*, 1601.
3 T. Okumura, K. Ito, *Adv. Mater.* **2001**, *13*, 485.
4 U. S. Schubert, C. Eschbaumer, *Angew. Chem., Int. Ed.* **2002**, *41*, 2892, and related references therein.
5 P. R. Andres, R. Lunkwitz, G. R. Pabst, K. Böhn, D. Wouters, S. Schmatloch, U. S. Schubert, *Eur. J. Org. Chem.* **2003**, 3769; B. G. G. Lohmeijer, U. S. Schubert, *Angew. Chem., Int. Ed.* **2002**, *41*, 3825; M. Kimura, Y. Iwashima, K. Ohta, K. Hanabusa, H. Shirai, *Macromolecules* **2005**, *38*, 5055.
6 K. T. Potts, D. A. Usifer, A. Guadalupe, H. D. Abruna, *J. Am. Chem. Soc.* **1987**, *109*, 3961; U. S. Schubert, O. Hien, C. Eschbaumer, *Macromol. Rapid Commun.* **2000**, *21*, 1156.
7 MALDI-TOFMS spectrum of **2** gave exhibited no peaks corresponding to the cyclic oligomers.
8 H. Hofmeier, S. Schmatloch, D. Wouters, U. S. Schubert, *Macromol. Chem. Phys.* **2003**, *204*, 2197.
9 R. Farina, R. Hogg, R. G. Wilkins, *Inorg. Chem.* **1968**, *7*, 170; S. Schmatloch, M. F. Gonzálex, U. S. Schubert, *Macromol. Rapid. Commun.* **2002**, *23*, 957; H. Hofmeier, U. S. Schubert, *Macromol. Chem. Phys.* **2003**, *204*, 1391; B. G. G. Lohmeijer, U. S. Schubert, *Macromol. Chem. Phys.* **2003**, *204*, 1072.
10 R. Knapp, A. Schott, M. Rehahn, *Macromolecules* **1996**, *29*, 478; S. Kelch, M. Rehahn, *Macromolecules* **1997**, *30*, 6185; F. S. Han, M. Higuchi, D. G. Kurth, *J. Am. Chem. Soc.* **2008**, *130*, 2073.

Published on the web (Advance View) April 5, 2009; doi:10.1246/cl.2009.382