Dual-mode fluorescence switching induced by self-assembly of well-defined poly(arylene ether sulfone)s containing pyrene and amide moieties†

Jeyoung Park, Jisung Kim, Myungeun Seo, Jinhee Lee and Sang Youl Kim*

Received 10th August 2012, Accepted 7th September 2012
DOI: 10.1039/c2cc35804b

A new class of fluorescent organogelators, pyrene-containing poly(arylene ether sulfone)s, showed two fluorescence switching modes in different gelation solvents. The THF gel exhibited excimer emission due to dimerization of the pyrene groups. In contrast, excimer emission was quenched after gelation in MC because of stacking among the pyrene groups.

Fluorescent organogelators have received considerable attention due to their potential applications in photonics, optoelectronics, light harvesting systems, and sensors. For fluorescent organogelators, pyrene moieties are commonly used to create π–π interaction sites and fluorescence probes during the gelation process. After completion of the sol-to-gel phase transition, gelation-induced enhanced excimer emission is observed in most cases due to aggregation of the pyrene moieties in a gel state, except one case of gelation-induced reduction of the excimer emission. Most of the supramolecular gels are formed from low-molecular weight organic gelators (LMWOGs), but polymeric molecules also form supramolecular gels, even though only a few. Advantages of polymeric gelators come from the polymeric nature of the molecules which support supramolecular gel stability and improve physical properties of gels by providing additional interaction sites along the polymer backbone. Recent developments in controlled polymerization techniques together with the effective modification method of polymer chains enable the systematic implantation of self-assembly motifs into polymeric molecules to fine tune the supramolecular assemblies.

In this study, the effects of tailored self-assembly motifs in polymer architectures were studied by using the well-defined poly(arylene ether sulfone)s (PAESs) containing pyrene and amide moieties. The behavior of these molecules strongly depends on the self-assembly motifs present and the polymeric architecture. To synthesize the well-defined PAES with amide and pyrene groups, chain-growth condensation polymerization (CGCP) was initiated from the amide initiators, in which the pyrene groups were introduced as π–π interaction sites and fluorescent probes. Interestingly, two different fluorescence switching modes were observed in different gelation solvents, for the first time to our knowledge. One mode involved gelation-induced enhancement of the excimer emission in tetrahydrofuran (THF), and the other mode involved gelation-induced fluorescence quenching in methylene chloride (MC). The contradictory results appeared to have been driven by a combination of the degree of hydrogen-bonding and pyrene stacking.

A synthetic scheme for the well-defined PAESs is shown in Scheme 1. Controlled polymerization was achieved with three types of initiators (Pyr1-1, Pyr2-1, and Pyr1-2), which were synthesized via an amidation reaction between 1-pyrenemethylamine and benzoic acid derivatives including a 2-fluoro benzotrifluoride moiety as an initiating site (Scheme S1 in the ESI†). CGCP of the AB type monomer I, 4-fluoro-4′-hydroxyphenyl sulfone potassium salt, was reported by Yokozawa and our group. Polymerization of the monomer I at 115 °C in sulfolane in the presence of the initiator and 18-crown-6 produced well-defined polymers without side reactions, such as self-polymerization of I or transesterification. The feed ratio of the monomer to the initiator was varied to control the molecular weight of the polymer. The compositions of the polymers produced in this series were labeled as Pnnm-I, where n, m, l indicate the number of pyrene groups, the initiating site per polymer, and the degree of polymerization (DP), respectively.

Scheme 1 Synthesis of PAESs initiated from the Pyr1-1, Pyr2-1, and Pyr1-2 initiators.
The chemical structures of the polymers were analyzed by $^1$H NMR spectroscopy, which revealed the peaks corresponding to the initiator and repeating units (Fig. S1, ESI†). The proton integration ratio of the initiator moiety to the end group (End/Init (NMR)) approached 1, indicating the absence of side reactions. The number average molecular weights ($M_n$ (NMR)) of the polymers obtained by NMR analysis agreed well with the theoretical values ($M_n$ (theor)). GPC analysis of the resulting polymers in DMF indicated that the polymers had a narrow molecular weight distribution with a polydispersity index (PDI) less than 1.3 (Fig. S2, ESI†). As the feed ratio of the monomer to the initiator increased to 18, the value of End/Init (NMR) exceeded 1 and the PDI broadened to 1.5, suggesting that transthenthenation or self-polymerization occurred. The characterization results are summarized in Table 1.

Self-assembly of the polymers was investigated by fluorescence spectroscopy, because pyrene is a prototypical chemosensor, which has a high fluorescence quantum yield in a wide excitation wavelength range. 

Table 1  Polymerization results, molecular weights, and gelation properties (10 g L$^{-1}$) of PAESs

<table>
<thead>
<tr>
<th></th>
<th>$M_n$ (theor)$^a$</th>
<th>$M_n$ (NMR)$^b$</th>
<th>DP (NMR)$^b$</th>
<th>End/Init (NMR)$^b$</th>
<th>$M_n$ (GPC)$^c$</th>
<th>PDI$^c$</th>
<th>State$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P11-05</td>
<td>1580</td>
<td>1820</td>
<td>6.0</td>
<td>1.06</td>
<td>2100</td>
<td>1.16</td>
<td>P</td>
</tr>
<tr>
<td>P11-10</td>
<td>2740</td>
<td>2960</td>
<td>10.9</td>
<td>1.20</td>
<td>3550</td>
<td>1.34</td>
<td>P G (5.7)$^f$</td>
</tr>
<tr>
<td>P21-05</td>
<td>1960</td>
<td>2030</td>
<td>5.3</td>
<td>1.03</td>
<td>2470</td>
<td>1.13</td>
<td>P</td>
</tr>
<tr>
<td>P21-10</td>
<td>3120</td>
<td>3320</td>
<td>10.9</td>
<td>1.07</td>
<td>3800</td>
<td>1.30</td>
<td>P G (4.7)</td>
</tr>
<tr>
<td>P12-09</td>
<td>2840</td>
<td>3090</td>
<td>10.1</td>
<td>1.03</td>
<td>3910</td>
<td>1.19</td>
<td>G (5.6) S</td>
</tr>
<tr>
<td>P12-18</td>
<td>4930</td>
<td>5400</td>
<td>20.1</td>
<td>1.15</td>
<td>5610</td>
<td>1.53</td>
<td>P G (4.4)</td>
</tr>
</tbody>
</table>

$^a$ On the basis of the feed ratio of the monomer to the initiator. $^b$ Determined by $^1$H NMR end-group analysis. $^c$ Determined by DMF-GPC (50 mmol of LiBr) using polystyrene standards (UV detector). $^d$ G: Gel, P: gel-like precipitate, S: soluble. $^e$ In parentheses: critical gelation concentration (g L$^{-1}$).

The fluorescence emission spectra of the initiators in THF were obtained. The fluorescence emission spectra displayed typical monomer emission peaks at 378, 388, 396, and 418 nm at low concentrations (<0.2 mM), and a broad band at 477 nm corresponding to the pyrene excimer emission, which gradually increased with the concentration. The ratio of the excimer peak intensity ($I_E$, 477 nm) to the monomer peak intensity ($I_M$, 396 nm) can be used to measure the efficiency of intramolecular excimer formation.$^{15}$ The value of $I_E/I_M$ increased as a function of the pyrene concentration more rapidly as the presence of pyrene groups in the initiators increased (Pyr2-1 > Pyr1-1 > Pyr1-2, Fig. S3, ESI†). This result clearly indicated that the fan-shaped Pyr2-1 more favored dimer formation than Pyr1-1 or Pyr1-2.

The fluorescence intensities of the polymers in MC (a good solvent for PAES) depended on the architecture and concentration (Fig. S4, ESI†). Interestingly, only the P11 polymers exhibited strongly red-shifted excimer emission at high concentrations (521 nm for P11-05 at [pyrene] = 12.6 μM, 533 nm for P11-10 at [pyrene] = 14.6 μM). It seems that the good solubility of Pyr1-1 in MC induced J-aggregate formation. A plot of the value of $I_E/I_M$ as a function of the pyrene concentration in the polymers is shown in Fig. 1. The order in which $I_E/I_M$ increased was P21 > P11 = P12. Noticeably, excimer formation was more significant in the case of P21-05 ($I_E/I_M$ of 33.6 at [pyrene] = 20 μM). The unique fan shape of Pyr2-1 as well as the enhanced solubility and the low entanglement of the short PAES chains in MC synergistically assisted the dimerization of pyrene.

We demonstrated previously that poly(arylene ether sulfone)s containing secondary benzamide initiators have unusual physical gelation properties in THF.$^{11}$ However, the transparent solutions of the polymers containing additional pyrene groups synthesized in this study did not turn into gels in THF at room temperature, with the exception of P12-09 (gelled). Instead, only a weak gel or gel-like precipitates formed, as observed by FE-SEM (Fig. 2a and Fig. S5a–g, ESI†). The poor solubility of the pyrene groups might hamper the intermolecular hydrogen bonding, which resulted in a short length of self-assembled fibers. The addition of 10% dimethyl sulfoxide (DMSO) to THF was helpful for inducing gelation of P11-10, P21-10, and P12-18, which have relatively long PAES chains (Fig. S5h, ESI†). Similar to the gelation behavior of the polymer in THF, only the P21 polymers formed a gel or gel-like precipitate in MC with the nanoribbon shape (Fig. 2b; Fig. S5i and j, ESI†). FE-TEM analysis of the gels revealed that the fibers were amorphous in both DMSO-THF and THF-MC with the nanoribbon shape (Fig. 2b; Fig. S5i and j, ESI†). The gelation behavior of the polymers is summarized in Table 1.

Remarkable phenomena were observed with the naked eye when these gels were exposed to illumination from a hand-held UV lamp at 365 nm. Gelation in THF enhanced the fluorescence, and the emission color changed from light blue to sky blue. However, gelation in MC quenched the fluorescence, yielding a dramatic color change from bright sky blue to a pale deep blue upon transition from the sol state (Fig. 2c and d). These intriguing properties were investigated by fluorescence spectroscopy. The enhanced fluorescence in the THF gel was
accompanied by an increase of \( I_E/I_M \) (7.2 times the value in the sol state), whereas quenched fluorescence in the MC gel was accompanied with a decrease of \( I_E/I_M \) (0.11 times the value in the sol state). The dual-mode fluorescence switching upon gelation in different solvents has not been reported previously.

The initiating moiety and polymer chain apparently self-assembled in different ways during gelation in THF or MC. FT-IR spectra of the polymer solutions were collected to investigate the hydrogen bonding structures (Fig. S7, ESI†). The amide I and amide II vibrational bands of P21-05 in THF were slightly red-shifted upon undergoing the sol-to-gel phase transition. The formation of a gel-like precipitate, rather than entire gelation, was attributed to this weak intermolecular hydrogen bonding. Gelation in MC favored the formation of strong hydrogen bonds, as indicated by the large red shift in the bands after gelation. Also, time-dependent \(^1\)H NMR spectra were collected (Fig. S8, ESI†). Upon sol-to-gel phase transition, the peaks corresponding to the amide protons disappeared and the peak corresponding to the methylene protons adjacent to the pyrene group shifted from 4.94 to 5.24 ppm (\( \Delta = 0.30 \) ppm) in MC-d3. These NMR results suggested that the strong hydrogen bonding in the MC gel induced consecutive association of the pyrene groups, rather than dimer formation, which resulted in fluorescence quenching. Powder X-ray diffraction patterns of the xerogels also support the above explanation (Fig. S9, ESI†). Only the MC xerogel showed a peak at 0.346 nm, indicative of ordering among the pyrene groups, resulting in fluorescence quenching in the MC gel.

The inclusion of self-assembly motifs in functional macro-molecules was important in this context for achieving self-assembled structures. This approach may be applicable to the generation of new supramolecular gels based on polymeric molecules.

This work was supported by NRF through ERC (R11-2007-050-04001-0) and NRL (R0A-2008-000-20121-0) programs.

Notes and references
