Poly(p-phenyleneethynylene)–Silica Gel Hybrids without Any Compatibilizer

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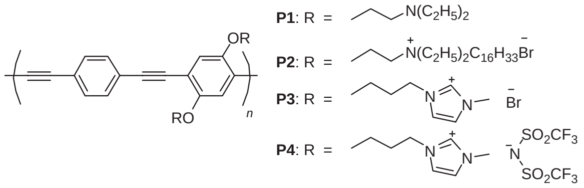
Poly(p-phenyleneethynylene) (PPE) and silica gel polymer hybrids were synthesized from the PPE together with tetramethoxysilane (TMOS) via a sol–gel method by utilizing cationic groups on the side chain of PPEs. Up to 10 wt % of the cationic PPE was able to disperse homogeneously into a silica matrix without any compatibilizer. Compared to amino and ammonium groups, PPE having imidazolium groups exhibited high dispersity in silica gel. The photoluminescence of the cationic PPE was reinforced against the thermal irradiation by the surrounding polymer hybrid matrix.

Recently, the construction of organic–inorganic hybrid materials with the molecular level homogeneity is an important and evolutionary way to combine the distinct properties of organic polymers and inorganic materials.[1–6] Especially, sol–gel reaction enables incorporating organic polymers or chromophores in the silica matrix owing to the low reaction temperature.[7] In our group, we have synthesized various organic–inorganic polymer hybrid materials by introducing a wide variety of organic polymers into the sol–gel reaction of alkoxysilanes.[3–5,8–10]

On the other hand, π-conjugated polymers have been paid many attentions in current materials researches due to their optical and electronic properties such as luminescence, conductivity, and non-linear optical property. Hybridizing π-conjugated polymers with silica gel has a potential expectation for creating novel materials. For example, Tolbert and co-workers synthesized an excellent PPE–silica polymer composite and demonstrated 2D hexagonal architecture derived from the rigid PPE backbone.[11] However, its hybridization with silica gel is strictly limited because of the incompatibility of the two components, hydrophobic π-conjugated polymers and hydrophilic silica matrix.[12,13] The contents of π-conjugated polymers were restricted to low, thus the properties of obtained hybrids derived from inorganic silica matrix rather than π-conjugated polymers. To educe an utmost characteristic of the π-conjugated polymers, it is crucial to increase the amount of π-conjugated polymers in the hybrid materials.

Generally, the isoelectric point of silica matrix is low to have a negative charge, so that a cationic group has higher miscibility to the matrix. Indeed, in the previous examples exemplified above, cationic groups were adopted for the hybridization. Though we achieved to synthesize homogeneous anionic PPE–silica polymer hybrid containing 10 wt % PPE, the employment of poly(N-vinylpyrrolidone) (PVP) as a compatibilizer was essential.[14] In this paper, we describe the synthesis and thermal stable photoluminescence properties of PPE–silica gel polymer hybrids by only introducing cationic groups on side chains of PPEs. To our best knowledge, this is the first report of the PPE–silica hybrid materials containing up to 10 wt % PPE without any compatibilizer.



Scheme 1. Structures of cationic PPEs for hybridization.

Cationic PPEs, **P1**,[15] **P2**,[16] **P3**,[17] and **P4**[18] as shown in Scheme 1, were synthesized as previously reported. **P1**–**P4** were characterized as 7–8-mer by ^{1}H NMR spectra in DMSO-d_6. **P1** has an amino group, **P2** has an ammonium group, **P3** has an imidazolium group with a hydrophilic bromide anion, and **P4** has an imidazolium group with a hydrophobic TFSI anion.

The polymer hybrids were synthesized via sol–gel reaction in the presence of above PPEs. Cationic PPEs were dissolved in methanol with TMOS and 0.1 M HCl aqueous solution (10 equiv to alkoxysilane). After being stirred at room temperature for 1 h, the mixture was placed in a polypropylene vessel covered with an aluminum foil having a few pinholes and left in air at 60 °C for 2 weeks, then subjected to photoluminescence spectroscopy using a Perkin-Elmer LS50B luminescence spectrometer at room temperature. The cationic PPEs incorporated organic–inorganic polymer hybrids were placed in a quartz cell and excited at 400 nm. The thickness of these samples was almost 400 µm. From the thermogravimetric analysis (TGA), the observed polymer content of Run 9 was in good agreement with the calculated value (ceramic yield: obs. (89.7%)/calc. (90.0%) = 99.7%, T_{d5} (decomposition temperature at 5% weight loss) = 301.2 °C).

Table 1. Hybridization results[a]

Run	Cationic PPE	PPE content/wt %	Appearance
1	**P1**	0.1	transparent
2	**P1**	1.0	transparent
3	**P1**	10	turbid
4	**P2**	0.1	transparent
5	**P2**	1.0	transparent
6	**P2**	10	turbid
7	**P3**	0.1	transparent
8	**P3**	1.0	transparent
9	**P3**	10	transparent
10	**P4**	0.1	translucent
11	**P4**	1.0	turbid
12	**P4**	10	turbid

[a]Conditions: Cationic PPEs were dissolved in MeOH with TMOS and 0.1 M HCl aq (10 equiv) as a sol–gel catalyst. The mixture was stirred at room temperature for 1 h, and the solvent was removed at 60 °C for 2 weeks.

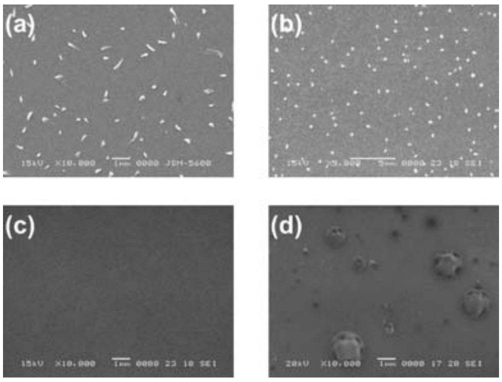


Figure 1. SEM images of (a) Run 3 (**P1**, 10 wt %), (b) Run 6 (**P2**, 10 wt %), (c) Run 9 (**P3**, 10 wt %), (d) Run 10 (**P4**, 0.1 wt %).

Table 1 shows the hybridization results. **P1**–**P3** exhibited enough dispersity to silica matrix (Runs 1, 2, 4, 5, and 7–9). In a previous report, even 0.1 wt % of PPV formed aggregations in silica matrix in case of employing PPV without any polar functional groups.[13] Compared to amino and ammonium groups, imidazolium groups demonstrated higher dispersity in silica matrix. Only in Run 9, up to 10 wt % of cationic PPE was dispersed homogeneously, though the same quantity of cationic PPE formed aggregations in Runs 3 and 6 (Figures 1a–1c). For the hybridization, (i) solubility in common organic solvents and (ii) dispersity to the silica matrix of PPEs are the two important factors. In **P1**, the solubility in the precursor solution was insufficient. **P2** has poor dispersity to silica matrix due to the long alkyl side chains, though the solubility was enough. In the case of Runs 10–12, the dispersity of imidazolium PPE was quite low, thus even 0.1 wt % PPE formed aggregations in Run 10 (Figure 1d). The hydrophobic TFSI anion would prevent the hybridization and accelerate aggregation formation of the PPE and silica domain. From this result, it was found the hydrophilicity of counter anions controlled the dispersity of cationic PPE to the silica matrix.

From the UV–vis reflection spectroscopy of Runs 7–9, as the PPE content increased, the reflection minima were red shifted (Run 7: 366 nm → Run 9: 382 nm). The intensity of photoluminescence spectra decreased to 1/4 and the maxima of photoluminescence spectra were red shifted as the PPE content increased (Run 7: 455 nm → Run 9: 488 nm). These results indicate the existence of the energy dissipation derived from the π-stacking of PPE main chains caused by the mutual approximations. The same tendency was observed also in Runs 1, 2, and Runs 4, 5.

Figure 2 represents the evaluation of the thermal durability of the imidazolium PPE–silica polymer hybrid (Run 9) with thermal treatment (120 °C for 2 h). The photoluminescence spectra of the polymer hybrid (Run 9, bold line) exhibited almost no significant changes, whereas that of the pristine imidazolium PPE (thin line) diminished as the half. This indicates that the PPE main chains were fixed in the polymer hybrid matrix and the molecular motions to form π-stackings were restrained. Indeed, it was reported that close contact of π-conjugated polymers induced spatial reorganization of polymer packing by heat (e.g. a change of adjacent polymer backbone from edge-on to face-on structure) and resulted in quenching of fluorescence.[19]

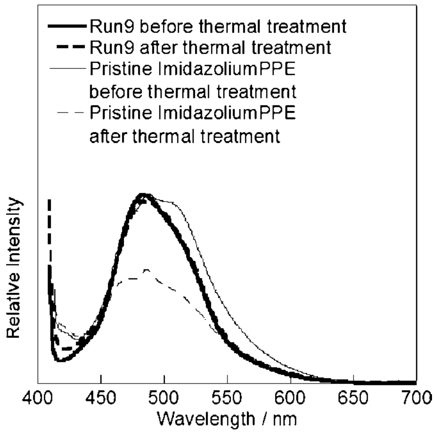


Figure 2. Photoluminescence spectra with thermal treatment.

In conclusion, we have successfully obtained the cationic PPE-incorporated organic–inorganic polymer hybrids with high contents (10 wt %) of PPE utilizing usual synthetic methods of polymer hybrids. Imidazolium groups exhibited high dispersity into the silica matrix, thus up to 10 wt % of PPE was able to be dispersed in silica matrix without any compatibilizer. The photoluminescence of cationic PPE was reinforced against thermal irradiation by surrounding silica matrix. This scheme enables to add promising processability to PPEs and other π-conjugated polymers for various applications such as optical waveguides or luminescent nanoparticles.

References and Notes

1 H. Dislich, *J. Non-Cryst. Solids* **1985**, *73*, 599.
2 B. M. Novak, *Adv. Mater.* **1993**, *5*, 422.
3 Y. Chujo, T. Saegusa, *Advances in Polymer Science*, Springer, Berlin/Heidelberg, **1992**, Vol. 100, p. 11.
4 Y. Chujo, R. Tamaki, *MRS. Bull.* **2001**, *26*, 389.
5 J. Miyake, Y. Chujo, *Chem. Lett.* **2008**, *37*, 312.
6 A. B. Descalzo, R. Martínez-Máñez, F. Sancenón, K. Hoffmann, K. Rurack, *Angew. Chem., Int. Ed.* **2006**, *45*, 5924.
7 *Sol–Gel Science, The Physics and Chemistry of Sol–Gel Processing*, ed. by C. J. Brinker, G. W. Scherer, Academic Press, Inc., San Diego, CA, **1990**.
8 T. Ogoshi, Y. Chujo, *Compos. Interfaces* **2005**, *11*, 539.
9 K. Adachi, A. K. Achimuthu, Y. Chujo, *Macromolecules* **2004**, *37*, 9793.
10 T. Ogoshi, Y. Chujo, *Macromolecules* **2003**, *36*, 654.
11 A. P.-Z. Clark, K.-F. Shen, Y. F. Rubin, S. H. Tolbert, *Nano Lett.* **2005**, *5*, 1647.
12 C. J. Wung, Y. Pang, P. N. Prasad, F. E. Karasz, *Polymer* **1991**, *32*, 605.
13 M. Kubo, C. Takimoto, Y. Minami, T. Uno, T. Ito, *Macromolecules* **2005**, *38*, 7314.
14 K. Kokado, Y. Chujo, *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 3749.
15 H. Peng, C. Soeller, J. Travas-Sejdic, *Chem. Commun.* **2006**, 3735.
16 Q.-L. Fan, Y. Zhou, X.-M. Lu, X.-Y. Hou, W. Huang, *Macromolecules* **2005**, *38*, 2927.
17 J. Chen, D. Zhang, Y. Liang, H. Zhou, *Synth. Commun.* **2006**, *36*, 2649.
18 Z. Fei, D. Kuang, D. Zhao, C. Klein, W. H. Ang, S. M. Zakeeruddin, M. Grätzel, P. J. Dysona, *Inorg. Chem.* **2006**, *45*, 10407.
19 J.-S. Yang, T. M. Swager, *J. Am. Chem. Soc.* **1998**, *120*, 5321.

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