Synthesis and Optical Properties of $\sigma-\pi$ Conjugated Organic–Inorganic Hybrid Gels

Naofumi Naga,¹ Hitomi Nagino,¹ Midori Iwashita,¹ Tomoharu Miyanaga,¹ Hidemitsu Furukawa²

¹Department of Applied Chemistry, College of Engineering, Shibaura Institute of Technology, 3-7-5 Toyosu, Koto-ku, Tokyo 135-8548, Japan

²Life-3D Printing Innovation Center, Soft & Wet Matter Engineering Laboratory, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992–8510, Japan

Correspondence to: N. Naga (E-mail: nnaga@sic.shibaura-it.ac.jp) or H. Furukawa (E-mail: furukawa@yz.yamagata-u.ac.jp)

Received 20 August 2014; accepted 28 January 2015; published online 4 March 2015 DOI: 10.1002/pola.27571

ABSTRACT: Organic-inorganic hybrid gels containing Si-vinylene units have been synthesized by a hydrosilylation reaction of trior tetra-ethynyl aryl compounds, 1,3,5-triethynylbenzene (TEB), 3,3',5,5'-tetraethynylbiphenyl (TEBP), or tetrakis(4-ethynylphenyl)methane (TEPM), and *bis*dimethylsilyl compounds, 1,1,3,3-tetramethyldisiloxane (TMDS) or 1,4-*bis*dimetylsilylbenzene (BDMSB), in toluene. Network structure of the resulting gels was quantitatively characterized by a scanning microscopic light scattering. The reactions yielded the gels having homogeneous network structure of 1.5–2.9 nm mesh size under the monomer concentrations that were relatively higher than the critical gelation concentration. The gels obtained from TEB showed broad absorption in the range from 340 to 370 nm, and emission in the

INTRODUCTION A number of π conjugated polymers have been developed due to their applicability to organic lightemitting diodes (LED). One of the advantageous properties of the conjugated polymers is solubility in organic solvents. This feature makes it possible to form thin layer of polymers for the LED devices via wet process. Molecular design of the conjugated polymers, such as incorporation of some kinds of side groups, is effective not only to improve the solubility in the organic solvents but to control the photophysical properties, quantum yield, and emission wavelength, of the polymers. Solutions of the fluorescent polymers are applicable for electrogenerated chemiluminescent cell of the light-emitting devices.^{1–11} There is concern for the leakage of liquid luminescent layers from the device cell. Physical gels and chemical gels, which are composed of organic solvent and conjugated polymer or crosslinked polymer with fluorescent molecule, for light-emitting devices have been developed to solve the issue.^{12–14}

Some organic–inorganic hybrid copolymers containing σ – π conjugated Si-vinylene units in the main chain have been developed in our laboratory. Mizoroki–Heck reaction of 9,9-dihexyl-2,7-dibromofluorene with disubstituted divinyl silane

range from 440 to 490 nm. The TEB-BDMSB gels showed remarkable red shift of the emission in comparison with that of the corresponding reaction solutions derived from the network formed by σ - π conjugation. The TEPM-TMDS, BDMSB gels exited by 280 nm showed not only the emission peak at around 360 nm derived from TEPM, but the broad peak at around 420 nm, which should be derived from interaction between phenyl groups of TEPM in the gels. © 2015 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2015**, *53*, 1360–1368

KEYWORDS: σ - π conjugation; gels; hydrosilylation; luminescence; organic-inorganic hybrid gels; pi interaction; photophysical property; scanning microscopic light scattering

compounds using a Pd catalyst produced the copolymers in good yield.¹⁵ These copolymers showed good solubility in conventional organic solvents and high photo luminescence (PL) quantum yield. We thought about to synthesize the gels composed by the network having Si-vinylene units. Two synthetic paths would be applicable to synthesize the gels. One is Mizoroki-Heck reaction of multiple brominated aryl compounds and divinyl disilane compounds with Pd catalysts. The residues of the Pd catalyst, however, dark-colored the gels, and made it difficult to investigate optical properties of the resulting gels. The other method is hydrosilylation reaction of multiple-ethynyl aryl compounds and disilane compounds with Pt catalysts. The Pt catalysts for the hydrosilylation reaction are almost colorless. Highly active catalysts for the reaction would yield the transparent clear gels, which should be suitable for investigation of the optical properties.

In this paper, we report the synthesis of organic–inorganic hybrid gels containing σ - π conjugated Si-vinylene units by hydrosilylation reactions of 1,3,5-triethynylbenzene (TEB), 3,3',5,5'-tetraethynylbiphenyl (TEBP), or tetrakis(4-ethynylphenyl)methane (TEPM), and 1,1,3,3-tetramethyldisiloxane

Additional Supporting Information may be found in the online version of this article.

© 2015 Wiley Periodicals, Inc.



SCHEME 1 Synthesis of σ - π conjugated organic-inorganic hybrid gels from TEB and TMDS or BDMSB using a hydrosilylation reaction with Karstedt's catalyst.

(TMDS) or 1,4-bisdimetylsilylbenzene (BDMSB) using a Pt catalyst, Karstedt's catalyst, as shown in Scheme 1. There should be some merits in the developed gels. The network of the designed gels is formed by the highly emissive parts of Si-vinylene units without small PL molecules, and there should be no leaking of the PL molecules from the gels. The gels are formed by a hydrosilylation reaction of the multifunctional aryl compounds as joint molecules and dimethylsilane compounds as linker molecules. This synthetic method yielded the gels with homogeneous network structure, as previously reported.¹⁶ The geometry or mesh size of the gels is controllable by the structure of the joint molecules or molecular size of the linker molecules, respectively. The network structure in the gel is quantitatively studied by a scanning microscopic light scattering (SMILS). The absorption and emission properties of the reaction systems before and after gelation are investigated with UV-vis and PL spectroscopy, and interrelation between network structure and the optical properties of the resulting gels is studied.

EXPERIMENTAL

Materials

TEB (Wako Pure Chemical Industries), diethynylbenzene (DEB) (Wako Pure Chemical Industries), TMDS (Chisso), and BDMSB (Chisso) were used as received. A poly(dimethylsilox-

ane solution) of platinum-divinyltetramethyldisiloxane complex (Karstedt's catalyst, **1**) was purchased from Chisso, and used without purification. Toluene was dried over calcium hydride by refluxing for 6 h and distilled before use under nitrogen atmosphere. TEBP or TEPM was synthesized by aryl-ethynyl coupling reaction of 3,3',5,5'-tetrabromobiphenyl or tetrakis(4-iodophenyl)methane and trimethylsilylethyne using *bis*(triphenylphosphine)palladium(II) dichloride, copper(I) iodide, and triphenylphosphine catalyst system following desilylation of methylsilylethynyl derivatives, according to the literature.¹⁷

Synthesis of σ - π Conjugated Organic-Inorganic Hybrid Gels

The mole ratio of ethynyl group in TEB, TEBP, or TEPM to Si–H group in TMDS or BDMSB was adjusted to 1.0. The solvent was filtered by a disk filter for getting rid of dusts. The resulting gels were measured in as-prepared state without further treatment at 25 $^{\circ}$ C.

Synthesis of TEB-TMDS Gel (Sample 1)

In a sample tube of 4 mm diameter (60 mm length), 12.0 mg (0.08 mmol) of TEB and 16.1 mg (21.3 μ L, 0.12 mmol) of TMDS were dissolved in a 179 μ L of toluene. Then a 60 μ L of toluene solution (0.6 μ mol/mL) of the catalyst **1** (36 μ mol) was added to the sample tube, and mixed in the





FIGURE 1 Ensemble-averaged relaxation time distributions as a function of the relaxation time of TEB-TMDS gels with the monomer concentration of 12.0 wt % (a), 14.0 wt % (b), and 16.0 wt % (c).

reaction system. After the sample tube was sealed by burning off, it was heated at 100 $^{\circ}$ C for 2 h without stirring. The reaction solution turned a slightly brawny cleared gel. The gels with different monomer concentrations and /or monomers were also conducted with the same procedure.

Synthesis of TEB-BDMSB Gel (Sample 5)

In a sample tube of 4 mm diameter (60 mm length), 12.0 mg (0.08 mmol) of TEB, and 23.3 mg (26.7 μ L, 0.12 mmol) of BDMSB were dissolved in a 225 μ L of toluene. Then, a 75 μ L of toluene solution (0.6 μ mol/mL) of the catalyst **1** (45 μ mol) was added to the sample tube, and mixed

TABLE 1 Network Structure of TEB–TMDS, BI	MSB Gels
---	----------

in the reaction system. After the sample tube was sealed by burning off, it was heated at 100 $^{\circ}$ C for 2 h without stirring. The reaction solution turned a slightly brawny cleared gel. The gels with different monomer concentrations and/or monomers were also conducted with the same procedure.

ANALYTICAL PROCEDURES

¹H NMR spectra of sol samples were recorded on a JEOL-JNM-LA300 spectrometer in pulse Fourier transform mode to determine the reaction conversion. The pulse angle of 45° was applied, and 32 scans were accumulated in 7 s of the pulse repetition. The spectra were recorded at room temperature with about 10 vol % of CDCl₃.

Quantitative determination of minute mesh size of the gels was performed with the SMILS system, as previously reported.^{18,19} The radius of mesh ξ (mesh size) was calculated from the relaxation time in SMILS analysis with Einstein–Stokes formula (1):

$$\zeta = \frac{16\pi n^2 \tau_{\rm R} K_{\rm B} \sin^2 \frac{\theta}{2}}{3\eta \lambda^2} \tag{1}$$

where n, $\tau_{\rm R}$, $K_{\rm B}$, θ , η , and λ are refractive index of toluene, ensemble-averaged relaxation time (s), Boltzmann constant (1.38 $\times 10^{-23}$ JK⁻¹), scattering angle (90°), viscosity coefficient of toluene at 298 K (5.6 $\times 10^{-4}$ Nm² s⁻¹), and wave length of incident ray (4.42 $\times 10^{-7}$ m), respectively.

UV-vis spectroscopy was conducted with Shimadzu UV-1600PC. PL spectroscopy was investigated with a Shimadzu RF-1500. Molecular weight and molecular weight distribution of a liner polymer were measured at 40 °C by means of a gel-permeation chromatography (Shimadzu Prominence GPC System) using chloroform as a solvent and calibrated with standard polystyrene samples.

Run	Monomer	wt %	${\tau_R}^a \times 10^{-6} \ s$	Mesh Size (nm)	σ^{b}	Reaction Rate (%)
1	TEB-TMDS	10.0	-	-	-	70.9
2	TEB-TMDS	12.0	4.73	1.3	0.049	
			150	40	0.085	
			1530	4000	0.089	
3	TEB-TMDS	14.0	4.50	1.2	0.038	
			950	2500	0.085	
4	TEB-TMDS	16.0	4.87	1.3	0.039	
5	TEB-BDMSB	6.0	-	-	-	56.0
6	TEB-BDMSB	8.0	4.91	1.0	0.27	
			59.5	23	0.31	
7	TEB-BDMSB	12.0	7.18	1.9	0.075	
			113	30	0.14	
8	TEB-BDMSB	16.0	5.73	1.5	0.036	

^a Relaxation time.

 $^{\rm b}$ Standard deviation of a peak of the ensemble-averaged relaxation time distribution.



FIGURE 2 Ensemble-averaged relaxation time distributions as a function of the relaxation time of TEB–BDMSB gels with the monomer concentration of 8.0 wt % (a), 12.0 wt % (b), and 16.0 wt % (c).

RESULTS AND DISCUSSION

Network Structure of Gels

The hydrosilylation reaction of TEB and TMDS or BDMSB was investigated with the catalyst **1** under the various monomer concentrations. Formation of the gel was confirmed by

TABLE 2 Network Structure of TEBP-	FMDS, BDMSB Gels
------------------------------------	------------------

the absence of fluidity of the reaction system. The reaction of TEB and TMDS more than 12.0 wt % (wt % of summation of TEB and TMDS in the reaction system) of the monomer concentration formed the gels. On the other hand, the reaction of the monomer concentration of 10.0 wt % yielded a viscous liquid. We will use the term of "critical gelation concentration" to refer the lowest monomer concentration that can form a gel. The reaction of TEB and BDMSB of 6.0 wt % did not form gel. The reaction of TEB and BDMSB more than 8 wt % of the monomer concentration formed the gels.

Reaction conversion of ethynyl group in the sol samples were determined by ¹H NMR spectroscopy. The conversions in the TEB-TMDS system (10.0 wt % Run 1) or TEB-BDMSB system (6.0 wt % Run 5) were 70.9 or 56.0%, respectively. Higher reaction conversion of the TEB-TMDS system can be explained by flexibility of the TMDS.

Figure 1 shows the ensemble-averaged relaxation time distributions as a function of the relaxation time of the TEB-TMDS gels. The network structure of the TEB-TMDS gels is summarized in Table 1. The ensemble-averaged relaxation time distributions of the gel with 12.0 wt % monomer concentration, which was the critical gel concentration of TEB-TMDS system, showed multiple relaxation peaks. The peaks at short relaxation time, less than 10^{-5} s, correspond to mesh sizes of about 1.2–1.3 nm. The mesh size gave roughly agreement with that of the expected mesh size derived from TEB and TMDS about 0.4–0.9 nm, calculated by a molecular mechanics method. On the other hand, the peak at long

Run	Monomer	wt %	${\tau_{\text{R}}}^a \times 10^{-6} \text{ s}$	Mesh Size (nm)	σ^{b}	Reaction Rate (%)
9	TEBP-TMDS	6.3	-	-	-	49.5
10	TEBP-TMDS	6.9	6.61	1.8	0.03	
			154	40.8	0.07	
			1800	4770	0.10	
11	TEBP-TMDS	7.2	6.62	1.8	0.03	
			406	108	0.12	
			7500	1990	0.15	
12	TEBP-TMDS	8.1	6.73	1.8	0.04	
			21000	5560	0.11	
13	TEBP-TMDS	9.0	6.33	1.7	0.03	
14	TEBP-BDMSB	6.1	-	-	-	45.4
15	TEBP-BDMSB	6.7	7.28	1.9	0.04	
			205	54.3	0.11	
			3170	841	0.32	
16	TEBP-BDMSB	7.0	6.80	1.8	0.03	
			3505	9300	0.22	
17	TEBP-BDMSB	8.8	5.73	1.5	0.04	
18	TEBP-BDMSB	13.3	6.30	1.7	0.03	

^a Relaxation time.

 $^{\rm b}$ Standard deviation of a peak of the ensemble-averaged relaxation time distribution.



Run	Monomer	wt %	${\tau_R}^a \times 10^{-6} \ s$	Mesh Size (nm)	$\sigma^{\rm b}$	Reaction Rate (%)
19	TEBP-TMDS	10.0	-	-	-	48.2
20	TEPM-TMDS	12.0	7.38	2.0	0.04	
			2420	642	0.15	
21	TEPM-TMDS	14.0	7.00	1.9	0.04	
22	TEPM-BDMSB	10.0				44.9
23	TEPM-BDMSB	12.0	6.81	1.8	0.03	
24	TEPM-BDMSB	14.0	6.74	1.8	0.03	

work structure.

TABLE 3 Network Structure of TEPM-TMDS, BDMSB Gels

^a Relaxation time.

 $^{\rm b}$ Standard deviation of a peak of the ensemble-averaged relaxation time distribution.

homogeneous network structure as observed in the TEB-TMDS

gels, described above. The monomer concentrations, which

form the sufficient network to occupy the space in the gels,

should be necessary to form the gels with homogeneous net-

The hydrosilylation reaction of TEBP or TEPM and TMDS or

BDMSB was also investigated with the catalyst 1 under vari-

ous monomer concentrations. The reactions of TEBP-TMDS

system of 6.3 wt % (Run 9) and TEBP-BDMSB system of 6.1

wt % (Run 14) did not form gel. The critical gelation concen-

trations of TEBP-TMDS or TEBP-BDMSB systems were about

7 wt %. The reaction conversions of ethynyl group in the

TEBP-TMDS system (6.3 wt % Run 9) or TEBP-BDMSB system (6.1 wt % Run 5) determined by ¹H NMR spectroscopy

The mesh size and mesh size distribution of the TEBP-TMDS

and TEBP-BDMSB gels determined by SMILS are summar-

ized in Table 2. The TEBP-TMDS or -BDMSB gels with rela-

tively low monomer concentrations (less than about 8 wt %)

showed a multimodal distribution of the ensemble-averaged

relaxation time, due to the formation of imperfect network

structure. The gels with relatively high monomer concentra-

tions, more than 9 wt %, formed the homogeneous network

were 49.5 or 45.4%, respectively.

relaxation time at around 1.5×10^{-4} s corresponded to the mesh size about 40 nm, which was much larger than that of the mesh size derived from TEB and TMDS. The structure should be derived from microgels. The relaxation peaks at around 10^{-3} s, which were derived from the large size of 2500–4000 nm, were detected in the gels with the monomer concentrations of 12.0 and 14.0 wt %. The large structure would be the fragments of the network due to the defect in the network. The gels generated at 16.0 wt % of monomer concentrations showed unimodal distribution of the ensemble-averaged relaxation time. The network structure in the gel should occupy all the space in the gel, as previously reported.¹⁶

Figure 2 shows the ensemble-averaged relaxation time distributions as a function of the relaxation time of TEB–BDMSB gels. The network structure of the TEB–BDMSB gels is summarized in Table 1. The gels obtained from the low monomer concentrations, 8.0 and 12.0 wt %, showed multimodality in the ensemble-averaged relaxation time distributions. The gels with 16.0 wt % monomer concentration showed a unimodal distribution of the ensemble-averaged relaxation time. Although the reaction conversion of the TEB–BDMSB system was lower than that of the TEB–TMDS system, the TEB–BDMSB gels with relatively high monomer concentration formed the gels with

FIGURE 3 UV–Vis spectra of TEB–TMDS system before gelation (i) and after gelation (ii), monomer concentration = 12.0 wt %.



FIGURE 4 PL spectra of TEB–TMDS system, $\lambda_{ex} = 304$ nm, monomer concentration; 12.0 wt % before (i) and after (ii) gelation, 16.0 wt % before (iii) and after (iv) gelation.



FIGURE 5 PL spectra of TEB–TMDS system, $\lambda_{ex} = 370$ nm, monomer concentration; 12.0 wt % before (i) and after (ii) gelation, 16.0 wt % before (iii) and after (iv) gelation.

with the mesh of 1.5-1.7 nm, as observed in the TEB systems.

Although the TEPM-TMDS or TEPM-BDMSB systems with 10.0 wt % of monomer concentration yielded a portion of gels, a small amount of fluid solvent was detected in the reaction systems (Run 19 or Run 22). These reaction systems containing 12.0 or 14.0 wt % of monomers produced the clear gels. The reaction conversions of ethynyl group in the TEPM-TMDS system (10.0 wt % Run 19) or TEPM-BDMSB system (10.0 wt % Run 22) determined by ¹H NMR

spectroscopy were 48.2 or 44.9%, respectively. Although these values were almost same with the TEBP system, the critical gelation concentrations of the TEPM systems were higher than those of the TEBP systems. The difference should be derived from differences in the geometry and/or the mobility of the tetra-ethynyl aryl compounds. Rigid structure of the crosslinking monomer is effective to decrease the critical gelation concentration, as previously reported.¹⁶ It is likely that the flexible structure of TEPM would prevent form forming an infinite network structure and increase the critical gelation concentrations in the reaction systems. The mesh size and mesh size distribution of the TEPM-TMDS and TEPM-BDMSB gels determined by SMILS are summarized in Table 3. The resulting gels showed a unimodal distribution of the ensemble-averaged relaxation time derived from the homogeneous mesh, about 2 nm, due to the relatively high monomer concentrations.

Optical Properties of the Gels

Absorption spectra of TEB–TMDS system before gelation and after gelation were collected by UV–vis spectroscopy. Figure 3 shows the UV–vis spectra of the TEB–TMDS system with 12.0 wt % of monomer concentration. The UV–vis spectra of the reaction system before gelation showed broad absorption ranged from 280 to 500 nm with shoulder peaks at around 304 and 370 nm derived from π – π * transition of the monomers.²⁰ After the gelation, the peaks slightly red shifted due to the extension of conjugation length via formed Si-vinylene units. The TEB–BDMSB system showed similar spectra

TABLE 4 Emission Wavelength of σ - π Conjugated Organic–Inorganic Hybrid Gels

				l ^a Before	∂a _m After	
Run	Monomer	wt %	Excitation(nm)	Reaction (nm)	Reaction(nm)	$\Delta \lambda_{ m em}^{ m b}$ (nm)
P ₁	DEB-BDMSB	12.0	376	472	475	3
2	TEB-TMDS	12.0	304	362, 411	373, 413	
			370	439	442	3
3	TEB-TMDS	14.0	370	442	450	8
4	TEB-TMDS	16.0	304	363, 413	373, 414	
			370	445	454	9
6	TEB-BDMSB	8.0	304	349, 443	357, 482	
			370	440	458	18
7	TEB-BDMSB	12.0	370	439	461	22
8	TEB-BDMSB	16.0	304	351, 442	356, 486	
			370	439	487	48
10	TEBP-TMDS	6.9	280	354	356, 410	
12	TEBP-TMDS	8.1	280		356, 407	
15	TEBP-BDMSB	6.7	280	356	358, 409	
18	TEBP-BDMSB	13.3	280		359, 407	
20	TEPM-TMDS	12.0	280		358, 418	
21	TEPM-TMDS	14.0	280	357	359, 424	
23	TEPM-BDMSB	12.0	280		356, 414	
24	TEPM-BDMSB	14.0	280	353	361, 421	

^a Emission wavelength.

 $^{\rm b}$ Red shift of emission wavelength TEB–TMDS, BDMSB gels after the reaction exited by 370 nm.

Materials



FIGURE 6 PL spectra of TEB–BDMSB system, $\lambda_{ex} = 304$ nm, monomer concentration; 8.0 wt % before (i) and after (ii) gelation, 16.0 wt % before (iii) and after (iv) gelation.

patterns those of the TEB-TMDS system. Emission property of the reaction systems before and after gelation was also investigated by PL spectroscopy. Figures 4 and 5 show PL spectra of the TEB-TMDS systems exited by 304 and 370 nm wavelengths, which were the shoulder peaks detected in the UV-vis spectroscopy (Figure 3), respectively. The emission wavelengths in the spectra are summarized in Table 4. The excitation of the TEB-TMDS systems before gelation by 304 nm wavelength generated the broad emission ranged from 320 to 600 nm with peaks at around 360 and 410 nm derived from the monomers, as shown in Figure 4. The former peak slightly red shifted ($\Delta \lambda_{em} = 3-9$ nm) after the gelation, whereas the latter peak did not change. The excitation of the TEB-TMDS systems before gelation by 370 nm wavelength generated the emission at around 440 nm, as shown in Figure 5.²¹ These emission peaks in the TEB-TMDS gels slightly red shifted ($\Delta \lambda_{em} = 2-11$ nm) in comparison with those of before gelation. Figures 6 and 7 show PL spectra of the TEB-BDMSB systems exited by 304 or 307 nm wavelengths, respectively. The TEB-BDMSB systems before gelation, which were excited by 304 nm wavelength, showed similar emission spectra to that of the TEB-TMDS systems. The excitation of the TEB-BDMSB gels



FIGURE 7 PL spectra of TEB–BDMSB system, $\lambda_{ex} = 370$ nm, monomer concentration; 8.0 wt % before (i) and after (ii) gelation, 16.0 wt % before (iii) and after (iv) gelation.



SCHEME 2 Structure of linear polymer DEB-BDMSB (P₁) for reference; M_n =4000, M_w/M_n =3.4.

by 304 nm showed strong emission at around 480 nm, which was newly appeared after the gelation, as shown in Figure 6. The emission peak could not be detected in the TEB-TMDS gels. The emission should be derived from interaction between the phenyl groups of BDMSB in the network. Chujo et al. developed through-space conjugated polymers containing π stack structure of paracycophane units in the polymer chain.²² These polymers showed high photo luminescence. One explanation for the emission appeared in the TEB-BDMSB gels may be that the phenyl groups of BDMSB form a kind of π stack structure in the high dense network structure of the gels. The excitation of the TEB-BDMSB gels by 370 nm generated the emission at around 458-487 nm. The emission wavelengths remarkably red shifted $(\Delta \lambda_{\rm em} = 18-48 \text{ nm})$ in comparison with those of the reaction systems before gelation, as shown in Figure 7.

The red shift of the emission wavelengths observed in the gels should be due to the extension of conjugation length with the σ - π conjugation formed by Si-vinylene units. The TEB-BDMSB gel showed remarkable red shift of the emission wavelength in comparison with that of the TEB-TMDS gel. Furthermore, the red shift value ($\Delta \lambda_{\rm em}$) exited by 370 nm drastically increased from 18 to 48 nm with increasing of the monomer concentration from 8.0 to 16.0 wt %. We synthesized a corresponding linear polymer by the hydrosilylation reaction of DEB-BDMSB (P₁) for a reference (Scheme 2). The linear polymer P₁ showed only a slight red shift of the emission, $\Delta \lambda_{\rm em} = 3$ nm, in comparison with that of the reaction system before polymerization.²³ The results indicate that the remarkable red shift in the emission spectra



FIGURE 8 Emission spectra of TEBP–TMDS system; before (i) or after (ii) gelation: monomer concentration: 6.9 wt %, TEBP–BDMSB system; before (iii) or after (iv) gelation: monomer concentration: 6.7 wt %, exited at 280 nm.



FIGURE 9 Emission spectra of TEPM-TMDS system; before (i) or after (ii) gelation: monomer concentration: 14.0 wt %, TEPM-BDMSB system; before (iii) or after (iv) gelation: monomer concentration: 14.0 wt %, exited at 280 nm.

of the TEB–BDMSB gels should be derived from the formation of network structure, two or three dimensional expansion, by the σ - π conjugation. The similar phenomenon was previously reported in a dendrimer having a σ - π conjugation moiety.²⁴ Increase of the monomer concentration in the TEB–BDMSB gels would form the high dense network structure with the small mesh size by the σ - π conjugation network, which should enhance the red shift of the emission wavelength in the gels.

The emission property of the TEBP, TEPM, and TMDS, BDMSB systems before and after gelation is also investigated by the PL spectroscopy. Figure 8 shows the PL spectra of the TEBP-TMDS and TEBP-BDMSB systems exited by 280 nm wavelength, which is a shoulder peak detected in the UV-vis spectroscopy of these systems. The emission wavelengths in the spectra are summarized in Table 4. The PL spectra of the TEBP systems before reaction showed an emission peak at around 356-359 nm derived from the TEBP monomer. The TEBP-TMDS and TEBP-BDMSB gels showed similar spectra patterns with those of the reaction solutions before gelation. Figure 2 shows the PL spectra of the TEPM-TMDS and TEPM-BDMSB systems exited by 280 nm wavelength, which is a shoulder peak detected in the UV-vis spectroscopy of these systems. The emission wavelengths in the spectra are summarized in Table 4. Both the TEPM-TMDS and TEPM-BDMSB gels showed the emission at around 360 nm derived from the TEPM monomer. Broad emission peaks newly appeared at around 420 nm after the gelation. The peaks were not observed in the TEPM monomer [Fig. 2(i,iii)] and TEBP systems gels (Fig. 8). The broad peaks appeared in the TEPM gels would be derived from a kind of π stacking interaction between the phenyl groups of TEPM in the gels, as observed in the TEB-BDMSB gels described above. TEPM has four phenyl groups per one molecule in three-dimensional structure with flexibility. The chemical structure and/or steric structure of TEPM should induce effective interaction between the phenyl groups in the network structure of the gels.

CONCLUSIONS

Synthesized from A hydrosilylation reaction of TEB, TEBP, or TEPM with TMDS or BDSMB with Karstedt's catalyst produced the organic–inorganic hybrid gels composed by σ - π conjugation network. The SMILS analysis of the gels cleared that the obtained gels containing high monomer concentration formed homogeneous network structure with 1-2 nm of mesh size. The TEB-BDMSB gels exited by 304 nm wavelength showed an emission at around 480 nm, which would be derived from interaction like a π stacking between phenyl groups of BDMSB in the gels. The TEB-TMDS, BDSMB gels which were exited by 370 nm wavelength showed blue emission ranged from 440-490 nm due to the σ - π conjugation in the network. The TEB-BDMSB gel showed wide red shift in the emission in comparison with that of the reaction solution before gelation. The red shift of the emission of the gels should due to the formation of the two- or three-dimensional $\sigma - \pi$ conjugation network. The TEBP-TMDS and TEBP-BDMSB gels showed similar spectra patterns with those of the reaction solutions before gelation. The TEPM-TMDS, BDMSB gels exited by 280 nm wavelength showed the broad peak at around 420 nm, which should be derived from interaction like a π stacking between phenyl groups of TEPM in the gels. The present organic-inorganic hybrid gels having σ - π conjugation network should be useful for the light-emitting devices, because the device can be easily prepared by the synthesis of the gels between sandwiched two electrodes with narrow gap. Application of the gels for a light-emitting device is now proceeding, and the results will be reported elsewhere.

REFERENCES AND NOTES

1 K. S. Santhanam, A. J. Bard, *J. Am. Chem. Soc.* 1965, *87*, 139–140.

2 H. A. Brilmyer, J. Bard, *J. Electroanal. Chem. Soc.* **1980**, *127*, 104–110.

3 J. Kim, L. R. Faulkner, J. Am. Chem. Soc. 1988, 110, 112-119.

4 J. Kim, L. R. Faulkner, J. Electroanal. Chem. 1988, 242, 107-121.

5 A. Kapturkiewicz, J. Electroanal. Chem. 1991, 302, 131-144.

6 H. Schaper, H. Kostlin, E. Schnedler, *J. Electrochem. Soc.* 1982, *129*, 1289–1294.

7 D. M. Hercules, R. C. Lansbury, D. K. Roe, *J. Am. Chem. Soc.* **1966**, *88*, 4578–4583.

8 K. Nishimura, Y. Hamada, T. Tsujioka, S. Matsuta, K. Shibata, T. Fuyuki, *Jpn J. Appl. Phys.* **2001**, *40*, L1323–L1326.

9 S. C. Chang, Y. Yang, Q. Pei, Appl. Phys. Lett. 1999, 74, 2081–2083.

10 S. C. Chang, Y. Li, Y. Yang, *J. Phys. Chem. B* **2000**, *104*, 11650–11655.

11 S. C. Chang, Y. Yang, F. Wudl, G. He, Y. Li, *J. Phys. Chem. B* **2001**, *105*, 11419–11423.

12 S. C. Chang, Y. Yang, Appl. Phys. Lett. 1999, 75, 2713–2715.

13 Y. Hamada, T. Tsujioka, K. Nishimura (SANYO Electric Co., Ltd., Japan), Electrochemiluminescent material, WO 2002066885-A1.

14 M. Yukawa (Semiconductor Energy Laboratory Co., Ltd.), Light-emitting device, light-emitting apparatus, electronic device and production of light-emitting device, JP2006-11403A 20 UV-vis and PL spectra of the monomers are available in the Supporting Information (Figures S1–S3).



15 N. Naga, N. Tagaya, H. Noda, T. Imai, H. Tomoda, *J. Polym. Sci., Part A Polym. Chem.* **2008**, *46*, 4513–4521.

16 N. Naga, E. Oda, A. Toyota, K. Horie, H. Furukawa, *Macro-mol. Chem. Phys.* **2006**, *207*, 627–635.

17 U. M. Wiesler, A. J. Berresheim, F. Morgenroth, G. Lieser, K. Müllen, *Macromolecules* 2001, *34*, 187–199.

18 H. Furukawa, K. Horie, R. Nozaki, M. Okada, *Phys. Rev. E* 2003, *68*, 031406–1.

19 H. Furukawa, M. Kobayashi, Y. Miyashita, K. Horie, *High Perform. Polym.* 2006, *18*, 837–847.

 ${\bf 20}$ UV-vis and PL spectra of the monomers are available in the Supporting Information.

21 Photos of TEB-TMDS gel are available in the Supporting Information (Figure S4).

22 Y. Morisaki, Y. Chujo, *Angew. Chem. Int. Ed.* **2006**, *45*, 6430–6437. **23** PL spectra of DEB-BDMSB system before and after polymerization are available in Supporting Information (Figure S5).

24 J. Kiu, R. Zheng, T. Matthias, Y. Tang, M. Häussler, J. W. Y. Lam, A. Qin, M. Ye, Y. Hong, P. Gao, B. Z. Tang, *Macromolecules* **2007**, *40*, 7473–7486.