

# Synthesis of Network Polymers Containing Si-Vinylene Units by Mizoroki-Heck Reaction

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## Abstract

Network polymers containing Si-vinylene units have been synthesized by Mizoroki-Heck reaction of cyclic siloxane or cubic silsesquioxane compounds with vinyl groups, as joint molecules, and dibromo aryl compounds, as linker molecules, using a Pd catalyst. The reaction of 1,3,5,7-tetravinyltetramethylcyclotetrasiloxane (TVMCTS) or octavinylsilsesquioxane (PVOSS) with *o*, *m*, *p*-dibromobenzene (DBB) or 4,4'-dibromobiphenyl (DBBP) yielded the corresponding network polymers, except TVMCTS-*o*DBB system. Optical properties of the network polymers were studied by UV-vis and photoluminescence spectroscopy, and absorption and emission derived from  $\sigma$ - $\pi$  conjugation of the Si-vinylene units were detected. Copolymerization of TVMCTS-DBB/bromobenzene yielded CHCl<sub>3</sub> soluble fraction due to formation of the network fragments. The network polymers of TVMCTS or PVOSS with 2,7-dibromofluorene (BFl) or 9,9-dihexyl-2,7-dibromofluorene were synthesized by the same procedures. Scanning electron microscope image of TVMCTS-BFl network polymer indicated formation of porous structure. The network polymers have been also synthesized by the reactions of multifunctional aryl bromide, as the joint molecules, with divinyl or dially silane compounds, as the linker molecules. The molecular structure of the multifunctional aryl bromide affected the emission wavelengths of the network polymers. In the case of the 2,2',7,7'-tetrabromo-9,9'-spirobifluorene-based network polymers, the emission spectra widely ranged from 450 to 500 nm, which were sensitive to molecular structure of the divinyl or dially silane compounds.

**Keywords:** network polymer, Si-vinylene unit, Mizoroki-Heck reaction, optical properties

## 1. Introduction

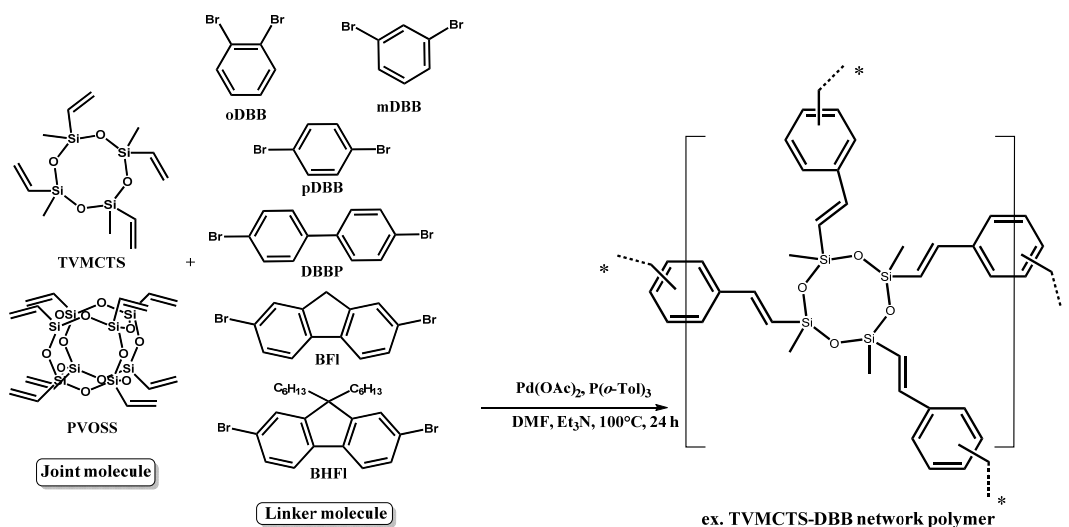
Many kinds of  $\pi$ -conjugated polymers have been developed due to their characteristic photophysical features and application to organic light-emitting diodes (for example Burroughes, Bradley, Brown, Marks, Mackay, Friend, Burns, & Holmes, 1990). Among the  $\pi$ -conjugated polymers, poly(*p*-phenylene-vinylene), poly(thiophene), poly(*p*-phenylene), poly(fluorene), and poly(carbazole) are typical polymers that show high photoluminescence quantum yield. The copolymers based on these  $\pi$ -conjugated polymers have been synthesized to control the photophysical properties and/or increase solubility in organic solvents.

We have synthesized fluorene or carbazole-based alternating copolymers containing Si-vinylene units (Naga, Tagaya, Noda, Imai, & Tomoda, 2008; Naga, Ohkura, Tagaya, & Tomoda, 2011; Naga & Saito, 2016). The copolymers were obtained with Mizoroki-Heck reaction of dibromofluorene or dibromocarbazole with Si-containing divinyl or diallyl compounds. For example, the copolymerization of 9,9-dihexyl-2,7-dibromofluorene (BHFl) with divinyl dimethylsilane (VMS) using palladium(II) acetate catalyst yielded the corresponding alternating copolymer in good yield. The copolymers showed absorption peaks derived from intramolecular charge transfer through the  $\sigma$ - $\pi$  moiety.

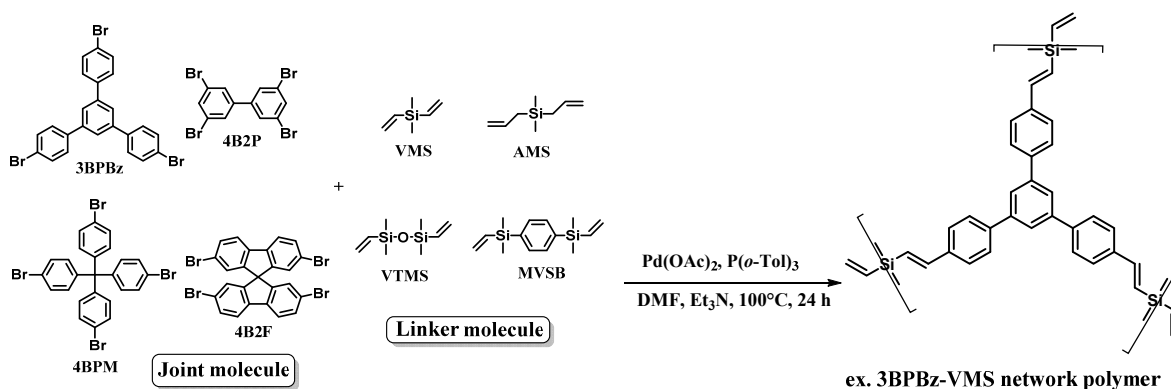
Geometric variations of the conjugated polymers, such as hyper-branched, dendritic, and network structures, have been also investigated (for examples Jiang, Su, Trewin, Wood, Campbell, Niu, Dickinson, Ganin, Rosseinsky, Khimiyak, & Cooper, 2007; Dawson, Laybourn, Clowes, Khimiyak, Adams, & Cooper, 2009; Liu, Lam, & Tang, 2009; Hu, Lam, & Tang, 2013). Neckers et al. reported synthesis of Si containing unsaturated star polymers by hydrosilylation reaction of 1,3,5-triethynylbenzene (TEB) and (*p*-(dimethylsilyl)phenyl)acetylene (Wang, Kaafarani, & Neckers, 2003). Some organic-inorganic hybrid gels containing  $\sigma$ - $\pi$  conjugated Si-vinylene units in the network were developed in our laboratory by the hydrosilylation reaction of TEB and 1,1,3,3-tetramethyldisiloxane or 1,4-bisdimethylsilylbenzene in toluene (Naga, Iwashita, Nagino, Miyanaga, & Furukawa, 2015). Although, the hydrosilylation reaction is one of the

effective methods to synthesize the network structures containing Si-vinylene units, the multifunctional ethynylene compounds, such as TEB, should be necessary. We thought about to synthesize the network polymers having Si-vinylene units using Mizoroki-Heck reaction. This method should widen the applicable monomers and make it possible to synthesize variety of network polymers having Si-vinylene units.

In this paper, we report synthesis of the network polymers containing Si-vinylene units by Mizoroki-Heck reaction of multi-functional siloxane compounds with vinyl groups and dibromo aryl compounds using a Pd catalyst, as shown in Scheme 1. The reaction of multifunctional aryl bromide with divinyl or diallyl silane compounds also conducted to yield the network polymers, as shown in Scheme 2. Absorptive and emissive properties of the network polymers were investigated with UV-vis and photoluminescence (PL) spectroscopy.



Scheme 1. Synthesis of network polymers by Mizoroki-Heck reaction of cyclic siloxane or cubic silsesquioxane compounds with vinyl groups-dibromo aryl compound systems



Scheme 2. Synthesis of network polymers by Mizoroki-Heck reaction of multifunctional aryl bromide-divinyl, diallyl silane systems

## 2. Method

### 2.1 Materials

1,3,5,7-Tetravinyltetramethylsiloxane (TVMCTS) (Chisso Co., Ltd.) and octavinyl octasilsesquioxane (PVOSS) (Aldrich Chemical Co., Ltd.) were used without further purification. 1,2-Dibromobenzene (oDBB), 1,3-dibromobenzene (mDBB), 1,4-dibromobenzene (pDBB), 4,4'-dibromobiphenyl (DBBP), bromobenzene (BB), 2,7-dibromofluorene (BFI), and BHF1 were commercially obtained from Tokyo Chemical Industry Co., Ltd., and used as received. 1,3,5-Tris(4-bromophenyl)benzene (3BPBz), 3,3',5,5'-tetrabromo-1,1'-biphenyl (4B2P), tetrakis(4-bromophenyl)methane (4BPM), 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (4B2F) (Tokyo Chemical Industry Co., Ltd.), VMS (Aldrich Chemical Co., Ltd.), diallyldimethylsilane (AMS) (Tokyo Chemical Industry Co., Ltd.), 1,1',3,3'-tetramethyl-1,3-divinyl disiloxane (VTMS) (Chisso Co., Ltd.), and 1,4-bis(dimethylvinylsilyl)benzene (MVSb) (Shin-etsu Chemical Co., Ltd.) were commercially obtained and used without further purification. Palladium(II) acetate

(Pd(OAc)<sub>2</sub>) (Aldrich Chemical Co., Ltd.), tri-*o*-tolylphosphine (P(*o*-Tol)<sub>3</sub>) (Kanto Chemical Co., Ltd.), triethylamine (NEt<sub>3</sub>) (Kanto Chemical Co., Ltd.), and N,N-dimethylformamide (DMF) (dehydrated grade, Kanto Chemical Co., Ltd.) were commercially obtained and used as received.

## 2.2 Synthesis of Network Polymers

Synthesis of the network polymers was carried out in a 10 mL ample tube equipped with a magnetic stirrer. A reaction of TVMCTS with DBB is described as a reference. DBB (1 mmol), P(*o*-Tol)<sub>3</sub> (0.12 mmol), and Pd(OAc)<sub>2</sub> (0.02 mmol) were added to the ample tube under a nitrogen atmosphere. After the addition of TVMCTS (0.5 mmol), DMF (2.0 mL), and NEt<sub>3</sub> (1.5 mmol), the ample tube was sealed by burning off. The reaction was conducted at 100°C for 24 h. The polymerization was terminated by adding a small amount of methanol. The polymer was precipitated in a large excess of methanol and recovered by filtration. The polymer obtained was washed by chloroform and dried in vacuo at 50°C for 6 h. Other network polymers were synthesized by the same procedures with the molar ratio of vinyl or allyl to Br was 1.0.

## 2.3 Analytical Procedures

FT-IR spectra of the network polymers were recorded on a Jasco FT/IR-410 spectrometer in pulse Fourier transform mode as KBr discs. <sup>1</sup>H NMR spectra of CHCl<sub>3</sub> soluble fractions of TVMCTS-DBB/BB polymers were recorded on a JEOL-JNM-LA300 spectrometer in pulse Fourier transform mode in CDCl<sub>3</sub>. The pulse angle was 45° and 32 scans were accumulated in 7 s of the pulse repetition. UV-vis absorption spectroscopy was conducted with SHIMADZU UV-2450. Photoluminescence (PL) spectroscopy was investigated with a SHIMADZU RF-5300PC. Scanning electron microscope (SEM) images were acquired by JEOL JSM-7400F.

## 3. Results and Discussion

### 3.1 Network Polymers from TVMCTS, PVOSS-DBB, DBBP

Mizoroki-Heck reaction of TVMCTS or PVOSS with DBB or DBBP has been investigated with Pd(OAc)<sub>2</sub> catalyst in DMF at 100°C, as shown in Scheme 1. Polymerization results are summarized in Table 1. The reaction of TVMCTS with pDBB and DBBP yielded the polymers in good yields. The yield of the TVMCTS-mDBB polymer was much lower than that of the TVMCTS-pDBB polymer. Furthermore, the polymer was not obtained in the reaction of TVMCTS with oDBB. The sterically hindered *o*- and *m*- positions of Br in DBB should decrease the reaction conversion, which would cause the low polymer yields. The reactions with PVOSS yielded the polymers in good yields independent of the molecular structure of the dibromo aryl compounds used. Large number of vinyl groups, 8 groups per one molecule, should effectively form the network structure.

FT-IR spectra of TVMCTS-mDBB, pDBB, and DBBP are shown in Figure 1 (a), (b), and (c), respectively. The broad peaks derived from Si-O-Si structure of TVMCTS were detected at around 1050 cm<sup>-1</sup>. The peaks derived from phenyl groups were detected at around 1500 cm<sup>-1</sup> (C=C stretching of phenyl) and 750-800 cm<sup>-1</sup> (C-H vending of disubstituted phenyl). The peaks derived from the unsaturated C=C units connected to Si, and Si-C units were detected at 1600 cm<sup>-1</sup>, and 1275 cm<sup>-1</sup>, respectively. These results clear the formation of the network polymers by Mizoroki-Heck reaction of TVMCTS with mDBB, pDBB, and DBBP. The network polymers with PVOSS showed similar spectral profiles derived from the corresponding network structure.

Absorptive and emissive features of the network polymers (solid state) were studied with UV-vis and PL spectroscopy. The UV-vis and PL spectra of TVMCTS-pDBB, TVMCTS-DBBP, and PVOSS-pDBB are shown in Figure 2. The λ<sub>max</sub> wavelength of the spectra are summarized in Table 1. The network polymers showed broad absorption ranged from about 300 to 400 nm. Excitation of the network polymers with the λ<sub>max</sub> wavelength of the absorption showed relatively sharp emission peaks. The network polymers with pDBB and DBBP showed the emission at longer wavelength than those with oDBB or mDBB. The red-shift of the network polymers with pDBB and DBBP would be due to the long and linear conjugated structure in the network derived from these *p*-substituted linker molecules.

Table 1. Synthesis and optical properties of TVMCTS, PVOSS-DBB, DBBP network polymers<sup>a</sup>

Run	Joint	Linker	Yield %	λ <sub>max</sub> nm	
				absorption <sup>b</sup>	emission <sup>b,c</sup>
1	TVMCTS	mDBB	41	342	383
2	TVMCTS	pDBB	95	320	461
3	TVMCTS	DBBP	95	353	450
4	PVOSS	oDBB	87	312	365
5	PVOSS	mDBB	100	319	370
6	PVOSS	pDBB	100	354	457
7	PVOSS	DBBP	100	335	450

<sup>a</sup>Conditions: linker molecule (1 mmol), P(*o*-Tol)<sub>3</sub> (0.12 mmol), Pd(OAc)<sub>2</sub> (0.02 mmol), TVMCTS (0.5 mmol) or PVOSS (0.25 mmol), DMF (2.0 mL), NEt<sub>3</sub> (1.5 mmol), 100°C for 24 h. <sup>b</sup>Evaluated in solid state. <sup>c</sup> Excitation with  $\lambda_{\text{max}}$  of absorption.

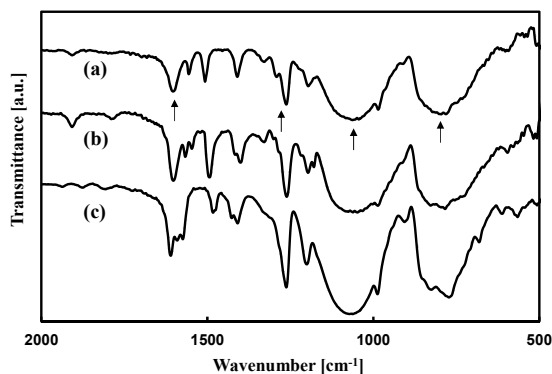


Figure 1. FT-IR spectra of (a) TVMCTS-mDBB, (b) TVMCTS-pDBB, and (c) TVMCTS-DBBP network polymers

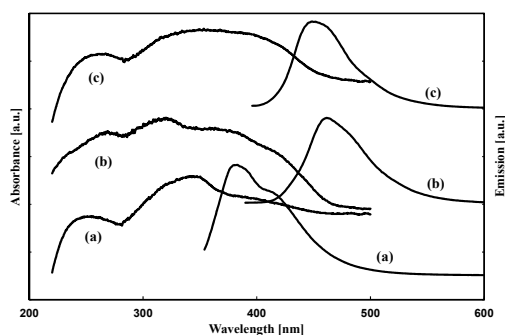


Figure 2. UV-vis (left) and PL (right) spectra of (a) TVMCTS-mDBB, (b) TVMCTS-pDBB, and (c) TVMCTS-DBBP network polymers (solid state)

### 3.2 Network Polymers from TVMCTS-pDBB/BB and TVMCTS/VTMS-pDBB Systems

Network polymers have been synthesized from TVMCTS-pDBB/BB systems. The results are summarized in Table 2. The network polymers contained chloroform soluble fraction, and its amount slightly increased with increasing of the BB feed ratio. Molecular structure of the chloroform soluble fraction was studied by <sup>1</sup>H NMR spectroscopy. Figure 3 shows the <sup>1</sup>H NMR spectrum and chemical shift assignment of the chloroform soluble fraction of a TVMCTS-pDBB/BB network polymer (Run 10). The peaks derived from vinylene units and methyl group connected to Si were detected at 6.0, 4.7 and 1.5 ppm, respectively. These results indicate that the molecular structure of the chloroform soluble fraction is parts of the network structure. Incorporation of mono-functional BB prevents from formation of infinite network, and yields the small fragments. The network polymers were also synthesized from TVMCTS/VTMS-DBB systems. Although the chloroform soluble fraction of the network polymers was detected, the fractions were small. Absorptive and emissive features of the TVMCTS-pDBB/BB network polymers of the chloroform soluble fractions were studied with UV-vis and PL spectroscopy in chloroform, as shown in Figure 4. Intensity of the absorption peak at around 300-320 nm in UV-vis spectra increased with increasing of the BB feed ratio in the reaction system. The fragments derived from the defect structure, which shows the absorption at long wavelength, would increase with increasing of the BB feed ratio.

Table 2. Synthesis and optical properties of TVMCTS–pDBB/BB, TVMCTS/VTMS–pDBB network polymers<sup>a</sup>

Run	Joint		Linker		Yield %	CHCl <sub>3</sub> sol. <sup>b</sup> wt%	$\lambda_{\max}$ nm	
	mmol		mmol				absorption <sup>c</sup>	emission <sup>c,d</sup>
	TVMCTS	VTMS	pDBB	BB				
8	0.30		0.56	0.06	97	10	271	424
9	0.27		0.47	0.15	81	15	271	430
10	0.23		0.31	0.31	60	16	264	443
11	0.28	0.03	0.59		78	-	-	-
12	0.23	0.08	0.55		72	5	287	447
13	0.16	0.16	0.47		63	7	280	451

<sup>a</sup>Conditions: P(*o*-Tol)<sub>3</sub> (0.125 mmol), Pd(OAc)<sub>2</sub> (0.025 mmol), DMF (2.0 mL), NEt<sub>3</sub> (1.56 mmol), 100°C for 24 h.

<sup>b</sup>CHCl<sub>3</sub> soluble fraction. <sup>c</sup>Evaluated in CHCl<sub>3</sub>. <sup>d</sup>Excitation with  $\lambda_{\max}$  of absorption.

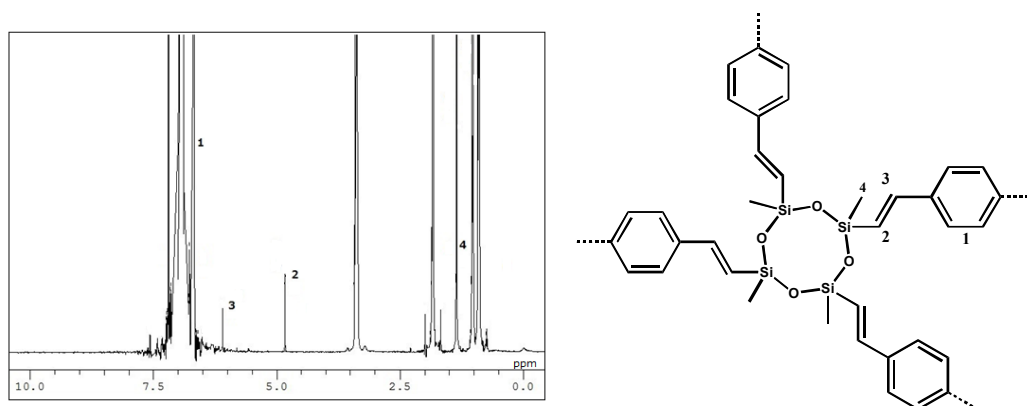
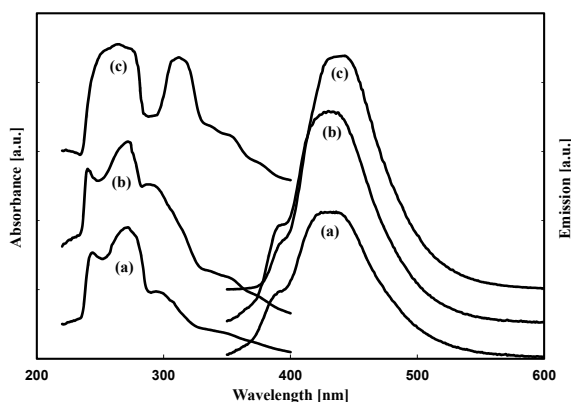
Figure 3. <sup>1</sup>H NMR spectrum of TVMCTS-DBB/BB polymer (Run 10), and assignment

Figure 4. UV-vis (left) and PL (right) spectra of network polymers of chloroform soluble fraction of TVMCTS-pDBB/BB network polymers (chloroform solution), (a) Run 8, (b) Run 9, and (c) Run 10

### 3.3 Network Polymers from TVMCTS, PVOSS-BFI, BHF1

Network polymers have been synthesized from TVMCTS, PVOSS-BFI, BHF1 systems, as shown in Scheme 1, to introduce the fluorescent fluorene units into the network. The results are summarized in Table 3. The corresponding network polymers were obtained in good yields.

FT-IR spectra of TVMCTS-BFI, TVMCTS-BHF1 network polymers are shown in Figure 5 (a) and (b), respectively. The broad peaks derived from Si-O-Si structure of TVMCTS were detected at around 1050-1100 cm<sup>-1</sup>. The peaks derived

from phenyl groups of fluorene units and unsaturated C=C units connected to Si were detected at around  $1450\text{ cm}^{-1}$  (C=C stretching of phenyl) and  $1650\text{ cm}^{-1}$ , respectively. These results clear the formation of the network polymers by Mizoroki-Heck reaction of TVMCTS with BFI and BHF1. The network polymers with PVOSS showed the similar spectral profiles derived from the corresponding network structure.

Absorptive and emissive features of the network polymers (solid state) were investigated with UV-vis and PL spectroscopy. The  $\lambda_{\text{max}}$  wavelengths of the absorption and emission spectra are summarized in Table 3. The spectra of the network polymers showed broad absorption peaks at around 315 nm or 350 nm, and emission peaks at around 450 nm or 480 nm. Definite correlation between the molecular structure and the absorption or emission wavelengths was not detected in these network polymers. The results indicated that the hexyl substituent of fluorene unit has little effect on the optical properties of the network polymer.

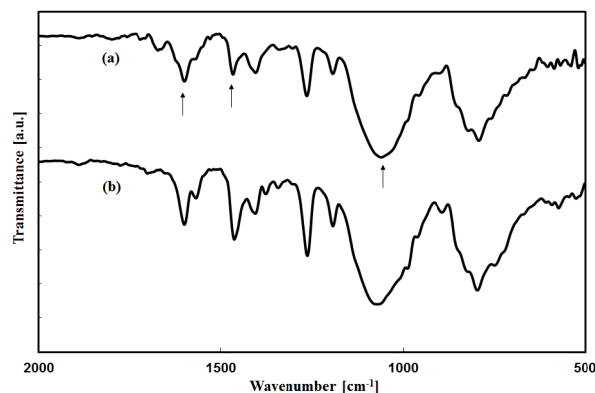


Figure 5. FT-IR spectra of (a) TVMCTS-BFI, and (b) TVMCTS-BHF1

Table 3. Synthesis and optical properties of TVMCTS, PVOSS-BFI, BHF1 network polymers<sup>a</sup>

Run	Joint	Linker	Yield %	$\lambda_{\text{max}}$ nm	
				absorption <sup>b</sup>	emission <sup>b,c</sup>
14	TVMCTS	BFI	54	316	449
15	PVOSS	BFI	51	352	451
16	TVMCTS	BHF1	64	318	477
17	PVOSS	BHF1	47	315	454

<sup>a</sup>Conditions: BFI or BHF1 (1 mmol), P(*o*-Tol)<sub>3</sub> (0.12 mmol), Pd(OAc)<sub>2</sub> (0.02 mmol), TVMCTS (0.5 mmol) or PVOSS (0.25 mmol), DMF (2.0 mL), NEt<sub>3</sub> (1.5 mmol), 100°C for 24 h. <sup>b</sup>Evaluated in solid state. <sup>c</sup>Excitation with  $\lambda_{\text{max}}$  of absorption.

SEM images of TVMCTS-BFI and TVMCTS-BHF1 network polymers are shown in Figure 6. TVMCTS-BFI network polymer showed the texture derived from porous structure. By contrast, the texture of TVMCTS-BHF1 network polymer indicated smooth surface. One explanation for this result is effect of the substituent of BHF1 on the network formation. The bulky hexyl group of BHF1 would prevent from forming rigid network structure.

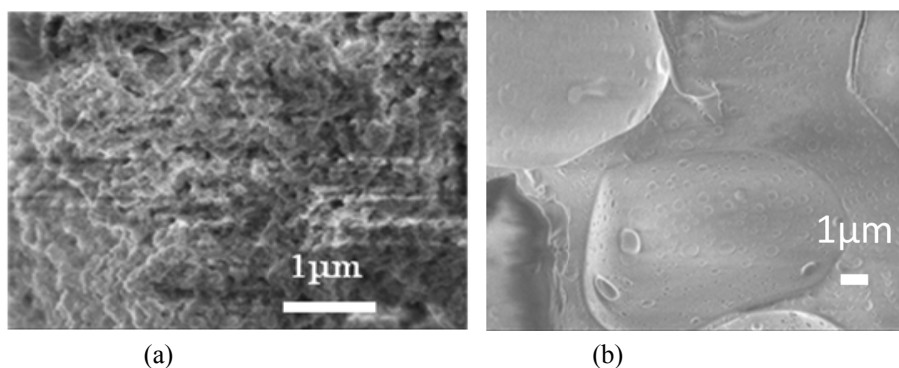


Figure 6. SEM images of (a) TVMCTS-BFI, and (b) TVMCTS-BHF1 network polymers

### 3.4 Network Polymers from Multifunctional Aryl Bromide and Divinyl, Diallyl Silane Compounds

Network polymers containing Si-vinylene units were also synthesized by the Mizoroki-Heck reaction of multifunctional aryl bromide (3BPBz, 4B2P, 4BPM, or 4B2F) with divinyl or diallyl silane compounds, VMS, AMS, VTMS, MVSB, as

shown in Scheme 2. The corresponding polymers were obtained in middle to good yields, 27-94% as summarized in Table 4. Figure 7 shows FT-IR spectra of 3BPBz-VMS, AMS, VTMS, MVSB network polymers. All the network polymers showed the peaks derived from stretching of C=C in vinylene, stretching of C=C in phenyl group, stretching of CH<sub>3</sub>-Si-CH<sub>3</sub>, and C-H vending of phenyl group, at around 1600 cm<sup>-1</sup>, 1500 cm<sup>-1</sup>, 1250 cm<sup>-1</sup>, and 840-820 cm<sup>-1</sup>, respectively. The spectrum of 3BPBz-AMS network polymer (Figure 7 (b)) or 3BPBz-MVSB network polymer (Figure 7 (d)) showed the peak derived from vending of Si-CH<sub>2</sub>-CH= or stretching of Si-aryl at around 1150 cm<sup>-1</sup> or 1130 cm<sup>-1</sup>, respectively. Molecular structure of the other network polymers was also confirmed by the FT-IR spectra.

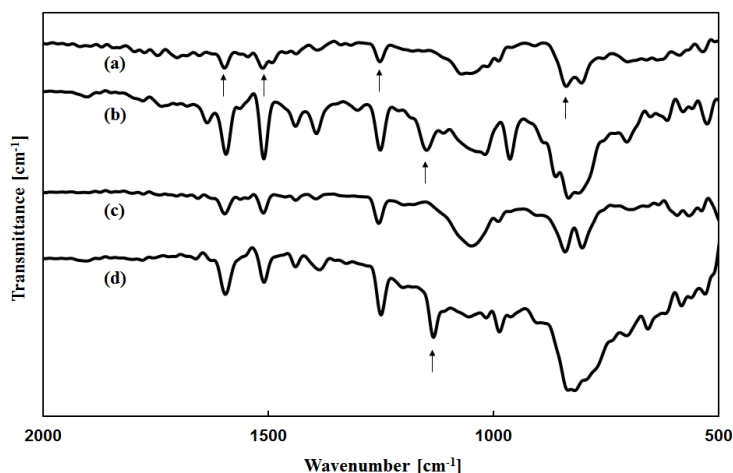


Figure 7. FT-IR spectra of (a) 3BPBz-VMS, (b) 3BPBz-AMS, (c) 3BPBz-VTMS, and (d) 3BPBz-MVSB network polymers

Table 4. Synthesis and optical properties of multifunctional aryl bromide-divinyl, diallyl silane network polymers<sup>a</sup>

Run	Joint	Linker	Yield %	$\lambda_{\max}$ nm	
				excitation <sup>b</sup>	emission <sup>b,c</sup>
18	3BPBz	VMS	84	378	428
19	3BPBz	AMS	94	362	430
20	3BPBz	VTMS	71	396	439
21	3BPBz	MVSB	69	390	435
22	4B2P	VMS	51	374	421
23	4B2P	AMS	32	---	---
24	4B2P	VTMS	68	371	416
25	4B2P	MVSB	52	363	411
26	4BPM	VMS	93	263	341
27	4BPM	AMS	87	263	344
28	4BPM	VTMS	69	258	342
29	4BPM	MVSB	57	264	341
30	4B2F	VMS	49	450	489
31	4B2F	AMS	64	419	463
32	4B2F	VTMS	80	458	496
33	4B2F	MVSB	27	385	448

<sup>a</sup>Conditions: linker molecule (0.188 mmol or 0.25 mmol), P(*o*-Tol)<sub>3</sub> (0.0375 mmol), Pd(OAc)<sub>2</sub> (0.0075 mmol), joint molecule (0.125 mmol), DMF (0.5 mL), NEt<sub>3</sub> (0.47 mmol), 100°C for 24 h. <sup>b</sup>Evaluated in solid state. <sup>c</sup>Excitation with  $\lambda_{\max}$  of absorption.

Emission spectra of the network polymers (solid state) are shown in Figure 8. The excitation wavelength was determined by fluorescence excitation spectrum. The averaged maximal emission wavelength of the emission spectra, which were excited with 280-380 nm at intervals of every 10 nm, was used as the excitation wavelength, as summarized in Table 4. 1,3,5-Triphenylbenzene, biphenyl, tetraphenylmethane, and 9,9-spirofluorene, which are moieties of the network structure in the network polymers with 3BPBz, 4B2P, 4BPM, and 4B2F, showed the emission peak with  $\lambda_{\text{max}}$  at 352 nm, 322 nm, 323 nm, and 310 nm, respectively. These wavelengths were different from those of the corresponding network polymers. These results indicate that the emission of the network polymers should be affected by the  $\sigma$ - $\pi$  conjugation formed by Si-vinylene unit. Figure 8 (i) shows the emission spectra of 3BPBz-based network polymers. The emission spectra showed maximal peaks at around 430 nm. In the case of the 4B2P-based network polymers, Figure 8 (ii), the polymer with VMS, VTMS, and MVSb showed the emission peaks with the  $\lambda_{\text{max}}$  at around 410-420 nm. By contrast, 4B2P-AMS network polymer did hardly show emission, Figure 8 (ii)-(b). Methylene units between Si and vinylene in AMS should disturb formation of conjugation in the network, as previously reported in the similar liner polymers (Naga, Tagaya, Noda, Imai, & Tomoda, 2008). The 4BPM-based network polymers showed the emission peaks with the  $\lambda_{\text{max}}$  at around 340 nm independent of the structure of divinyl or dially-silane compounds (Figure 8 (iii)). These wavelengths were shorter than those of the 3BPBz and 4B2P-based network polymers due to the short excitation wavelength. In the case of the 4B2F-based network polymers, the  $\lambda_{\text{max}}$  of the emission spectra widely ranged from 450 to 500 nm, and depended on molecular structure of the divinyl or dially silane compounds (Figure 8 (iv)). One possibility to explain the results would be difference of the emission wavelengths, as summarized in Table 4. We studied the effect of the excitation wavelength on the emission wavelength of the 4B2F-based network polymers with fixed excitation wavelengths of 380 and 410 nm. The results cleared that the excitation wavelength did not affect the emission wavelength of those network polymers. The difference of the emission wavelengths of the 4B2F network polymers should be derived from the molecular structure of the divinyl or dially silane compounds. Substituent in 9,9-spirofluorene molecule is sensitive to the emission wavelengths, as reported in some 9,9-spirofluorene molecules (for example Abdel-Awwad, Luan, Messow, Kusserow, Wiske, Siebert, Fuhrmann-Lieker, Salbeck, & Hillmer, 2015). The molecular structure of the divinyl or dially silane compounds in the network structure with 4B2F should strongly affect the emission wavelengths.

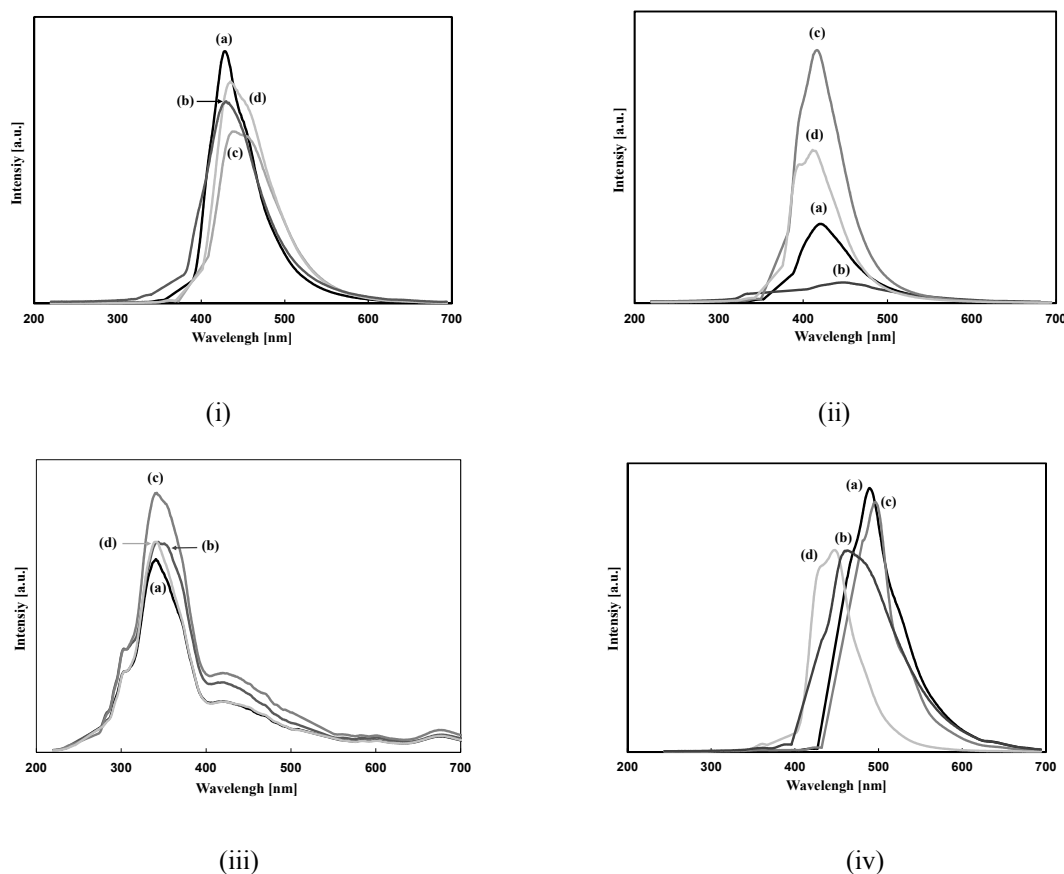


Figure 8. PL spectra of (i) 3BPBz-, (ii) 4B2P-, (iii) 4BPM-, and (iv) 4B2F- based network polymers with (a) VMS, (b) AMS, (c) VTMS, and (d) MVSb (solid state)



#### 4. Conclusions

Mizoroki-Heck reaction of cyclic siloxane or cubic silsesquioxane compounds with vinyl groups, TVMCTS, PVOSS, as the joint molecules, and dibromo aryl compounds, as the linker molecules, gave the corresponding network polymers. The network polymers showed the emission derived from the  $\sigma$ - $\pi$  conjugation. Molecular structure of the dibromo aryl compounds affected the emission wavelengths of the network polymers. Long conjugation structure with DBBP or BFI, and straight substituted structure with pDBB of the dibromo aryl compounds induced the long emission wavelengths. Copolymerization with mono-functional BB produced the  $\text{CHCl}_3$  soluble fraction in the resulting network polymers. The SEM image of TVMCTS-BFI network polymer indicated formation of porous structure. The network polymers were also synthesized by the reaction of multifunctional aryl bromide, as the joint molecules, with divinyl or dially silane compounds, as the linker molecules. The emission wavelengths were depended on the molecular structure of the multifunctional aryl bromide. The emission wavelengths of 4B2F-based network polymers were sensitive to the structure of the divinyl or dially silane compounds, and widely ranged from 450 to 500 nm.

Mizoroki-Heck reaction of multi-functional siloxane compounds having vinyl groups with dibromo aryl compounds, or multifunctional aryl bromide with divinyl or dially silane compounds is one of the useful methods to synthesize the network polymers containing Si-vinylene units. The network polymers synthesized by the present methods would be widely usable due to their features: porosity, photophysical properties, thermal stability, and chemical resistance. Such experiments are under way, and the results will be reported elsewhere.

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