

Synthesis and Photophysical Properties of Fluorene or Carbazole-Based Alternating Copolymers Containing Si and Ethynylene Units in the Main Chain

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Abstract

Alternating copolymerization of 9,9-dihexyl-2,7-dibromofluorene, N-hexyl-2,7-dibromocarbazole (HCz) with diethynyldimethylsilane, diethynyldiphenylsilane, has been investigated using Sonogashira coupling reaction. Photophysical properties of the resulting copolymers were investigated with UV-Vis absorption and photoluminescence spectroscopy. All the copolymers in chloroform solution showed absorption peaks at 270 - 280 nm with shoulder peaks at around 380 nm derived from π - π^* transition or intra-molecular charge transfer through σ - π moiety, respectively. The chloroform solutions of the copolymers showed broad emission peaks at 415 - 425 nm. The emission wave lengths of the copolymers in the solid state (cast film) detected at 360 - 385 nm were remarkably blue-shifted in comparison with those in the chloroform solutions. Hydrosilylation reaction of the copolymers with 1,4-bis(dimethylsilyl)benzene yielded networked copolymers soluble in chloroform, indicating formation of branching polymers. The chloroform solutions of the HCz-based networked copolymers showed bimodal emission derived from new highly energy states in the σ - π conjugation.

Keywords

Fluorene, Carbazole, Alternating Copolymer, Si-Ethynylene, Photophysical Property, Network Polymer

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1. Introduction

A number of conjugated polymers have been developed due to their attractive features, especially phot- and electro-luminescence. One of the most useful applications of the conjugated polymers must be emission layers for organic light-emitting diodes (LEDs) [1] [2]. There are some advantages in the polymer electro-luminescence in comparison with inorganic electro-luminescence. The first is process ability to form the emission layer. The conjugated polymers with specific molecular structures show good solubility in organic solvents, and spin-coating or casting of the solutions makes it possible to form thin emission layer in the LED devices. Molecular design of the conjugated polymers can improve the solubility of the polymers in conventional organic solvents, for examples, incorporation of bulky side group and/or copolymerization. The second is control of the emission wavelength by the molecular design of the polymers. The emission wavelength is correlated with the conjugation length in the polymer electro-luminescence. The shortening or extension of the conjugation length of the polymers tends to induce blue-shift or red-shift of the emission wavelength, respectively. The third is geometrical variation of the polymers, such as conjugated polymers with networked, dendritic, or branched structure.

Incorporation of Si atom in the main chain of the π -conjugated polymers is effective to shorten the conjugation length [3]-[14]. Kim *et al.* reported the incorporation of Si atom into poly(p-phenylenevinylene), which showed blue-emission [3]. Masuda *et al.* synthesized poly(phenylene-ethynylene) containing Si atom in the main chain [4]. They observed the emissions of the polymers derived from not only π - π^* transition of the π -conjugation but intramolecular charge transfer through σ - π conjugation. We developed fluorene- and carbazole-based alternating copolymers containing Si-vinylene units in the main chain [15] [16]. These copolymers were synthesized by alternating copolymerization of dibromofluorene or dibromocarbazole with Si containing divinyl or diallyl compounds using Mizoroki-Heck reaction with a Pd catalyst. Incorporation of Si and unsaturated vinylene units in the main chain of the conjugated polymers was effective to improve solubility in the organic solvents. The incorporation of Si or vinylene units in the π -conjugated polymers played the opposite role for their photophysical properties. That is, the Si units shorten and vinylene units extend the conjugation length. The fluorene- and carbazole-based alternating copolymers containing Si-vinylene units in the main chain showed both the blue-shift and red-shift in the absorption and luminescence peaks depend on the state of the copolymers. As the next step, we came to an idea to incorporate Si-ethynylene units in the corresponding copolymers.

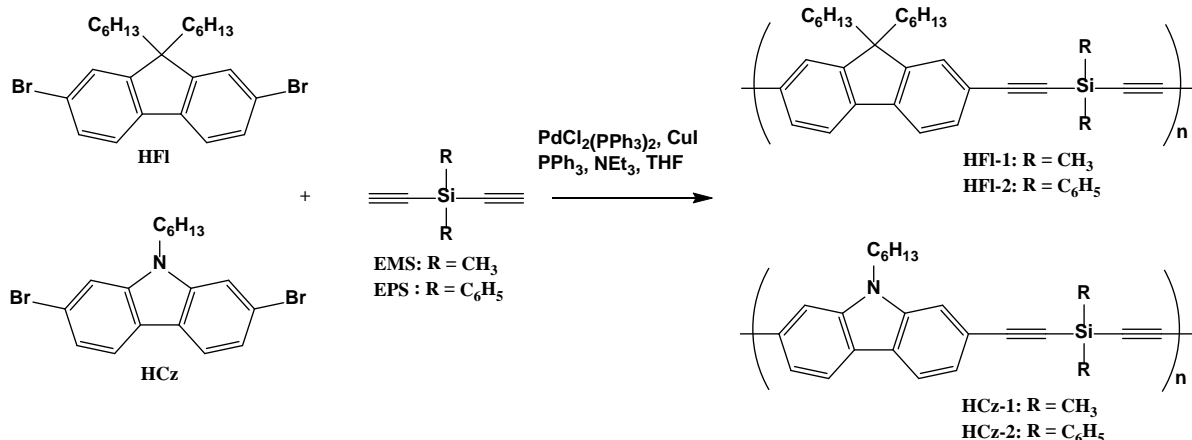
The conjugated network polymers with the σ - π conjugation have been synthesized by some synthetic methods [6] [17]-[19]. Neckers *et al.* synthesized dendritic poly(p-phenylenevinylene) containing Si-vinylene units, and reported the relationship between length of the p-phenylenevinylene unit and quantum yield [17]. Yamashita *et al.* synthesized σ - π conjugated network polymers by a hydrosilylation reaction between dihydrosilane compounds and diethynyl/triethynyl-benzene mixture, and reported increase of the absorption and fluorescence intensities with increasing of the crosslinking density [6]. Ishikawa *et al.* reported synthesis of the σ - π conjugated network copolymers by a crosslinking of poly[(silylene)diethynylene] with 1,4-bis(methylphenylsilyl)benzene using a hydrosilylation reaction [19]. This method is usable to synthesize the network polymers with the σ - π conjugation from the fluorene- and carbazole-based copolymers having Si-ethynylene units in the main chain synthesized in this report.

This paper reports the alternating copolymerization of 9,9-dihexyl-2,7-dibromofluorene (HFI) or N-hexyl-2,7-dibromocarbazole (HCz) with diethynylene Si compounds, diethynyldimethylsilane (EMS) or diethynyldiphenylsilane (EPS), by Sonogashira coupling reaction, as shown in **Scheme 1**, and the photophysical properties of the resulting copolymers. We also synthesize the network polymers by a hydrosilylation reaction of the obtained copolymers with 1,4-bis(dimethylsilyl)benzene (DMSB), and study the effect of the networking on the photophysical properties in comparison with the original linear copolymers.

2. Experimental

2.1. Materials

Dichlorodimethylsilane (Aldrich Co. Ltd.), dichlorodiphenylsilane (Tokyo Chemical Industry Co. Ltd.), and tetrahydrofuran (THF) solution of ethynylmagnesiumbromide (0.5 M) (Aldrich Co. Ltd.) were purchased and used as received. Palladium(II)dichlorobis(triphenylphosphine) ($\text{PdCl}_2(\text{PPh}_3)_2$) (Wako Pure Chemical Industries, Ltd.), CuI (Wako Pure Chemical Industries, Ltd.), triphenylphosphine (PPh_3) (Wako Pure Chemical Industries,



Scheme 1. Synthesis of fluorere or carbazole-based alternating copolymers containing Si and ethynylene units in the main chain.

Ltd.), THF (dehydrate grade, Kanto Chemical Co. Ltd.), and diethylether (dehydrate grade, Kanto Chemical Co. Ltd.) were commercially obtained, and used without further purification. Triethylamine (NEt₃) (Kanto Chemical Co. Ltd.) was dried with CaH₂ and distilled under a nitrogen atmosphere. HFl (Aldrich Co. Ltd.) was commercially obtained and used as received. HCz was synthesized according to the literatures [20]. Chloroform for photophysical properties analyses (Kanto Chemical Co. Ltd.) and tris(8-hydroxyquinoline)aluminum (Alq₃) (Wako Pure Chemical Industries, Ltd.) were commercially obtained, and used without further purification. DMSB was commercially obtained from Chisso Co. Ltd., and used as received. Toluene (Kanto Chemical Co. Ltd.) was dried over calcium hydride under refluxing for 6 h, and distilled under nitrogen atmosphere before use. Platinum-divinyltetramethyldisiloxane complex (Pt(dvs)) in vinyl terminated polydimethyl siloxane (Chisso Co. Ltd.) was diluted to 0.60 mM with distilled toluene and stored under nitrogen atmosphere.

2.2. Synthesis of EMS and EPS

A THF solution of ethynylmagnesiumbromide (0.5 M, 80 mL) was added dropwise to a diethylether solution (20 mL) of dichlorodimethylsilane, or dichlorodiphenylsilane (0.02 mol) at room temperature. The reaction mixture was refluxed at 40°C for 2 h, and cooled to room temperature. After the precipitates were filtered off, the solution was concentrated by evaporation. The obtained product was extracted with n-pentane, and n-pentane was removed off by evaporation under reduced pressure. The obtained products were pure enough by ¹H NMR spectroscopy. Yields of EMS and EPS were 52% or 65%, respectively.

2.3. Copolymerization

The copolymerization was carried out in a 100 mL glass reactor equipped with a magnetic stirrer. HFl or HCz (0.718 mmol), CuI (6.53 μmol), PPh₃ (6.53 μmol) were added to the reactor under nitrogen atmosphere. EMS or EPS (0.718 mmol), THF solution (2.5 mL) of PdCl₂(PPh₃)₂ (25.3 μmol) and NEt₃ (0.04 mmol) were introduced to the reactor, and the copolymerization was conducted at 60°C for 48 h. The copolymerization was terminated by adding a small amount of methanol. The polymer was precipitated in a large excess of methanol and recovered by filtration or decantation. The copolymer obtained was dissolved in chloroform and re-precipitated in methanol. The precipitate was recovered by filtration or decantation and dried in vacuo at 60°C for 6 h.

2.4. Synthesis of Network Copolymers

The reaction was carried out in a 100 mL glass reactor equipped with a magnetic stirrer. A copolymer (0.410 mmol of repeating unit), DMSB (0.205 mmol), and toluene solution of Pt(dvs) (10.4 μmol) were added to the reactor under a nitrogen atmosphere. The copolymerization was terminated by adding a small amount of methanol. The polymer was precipitated in a large excess of methanol and recovered by filtration. The precipitate was recovered by filtration and dried in vacuo at 60°C for 6 h.

2.5. Analytical Procedures

^1H and ^{13}C NMR spectra of the copolymers were recorded at room temperature on a JEOL-JNM-LA300 spectrometer in pulse Fourier transform mode. The sample solution was made in CDCl_3 as a solvent, and the resonance of CDCl_3 (7.24 ppm) was used as an internal reference. Molecular weight and molecular weight distribution of the copolymers were measured at 40°C by means of gel-permeation chromatography, SHIMADZU Prominence GPC System, using chloroform as a solvent and calibrated with standard polystyrene samples. UV-vis absorption spectroscopy was conducted with SHIMADZU UV-1600PC in a chloroform solution, 10^{-5} mol/L of the repeating unit of the copolymers. Photoluminescence (PL) spectroscopy was investigated with a SHIMADZU RF-1500 in a chloroform solution, 10^{-8} mol/L of the repeating units of the copolymer, or cast film from a chloroform solution, excited at the maximum absorption wavelength of the copolymers.

3. Results and Discussion

3.1. Synthesis of Alternating Copolymers

Copolymerization of HFI, HCz and EMS, EPS has been investigated with $\text{PdCl}_2(\text{PPh}_3)_2$ in THF at 60°C (Scheme 1). The results are summarized in Table 1. Although the molecular weights of the copolymers were relatively low, the corresponding copolymers were obtained in good yield. All the copolymers were soluble in conventional solvents such as acetone, chloroform, THF, toluene, and dimethylformamide.

3.2. Photophysical Properties of HFI-Based Copolymers

Photophysical properties of the HFI-based copolymers in chloroform solution were investigated with UV-vis absorption or PL spectroscopy. The UV-vis spectra of the HFI-based copolymers in chloroform are shown in Figure 1. The copolymers showed a strong absorption peaks at 280 nm with broad shoulder peaks at around 370 nm. The absorption peaks at around 370 nm should be derived from $\pi-\pi^*$ transition of the fluorene moiety, as detected in the reference polymer HFI-0. The absorption peaks at 280 nm, which was not detected in the reference polymer HFI-0, would be induced by intramolecular charge transfer through the $\sigma-\pi$ moiety in the copolymers, as previously reported [15]. All the absorption peaks of the present copolymers containing Si-ethynylene units were blue-shifted in comparison with those of the corresponding copolymers containing Si-vinylene units (HFI-i, HFI-ii) or HFI homo polymer (HFI-0) (Scheme 2, Table 2). The blue-shift in UV-vis spectra of the

Table 1. Results of copolymerization of HFI, HCz and EMS, EPS^a.

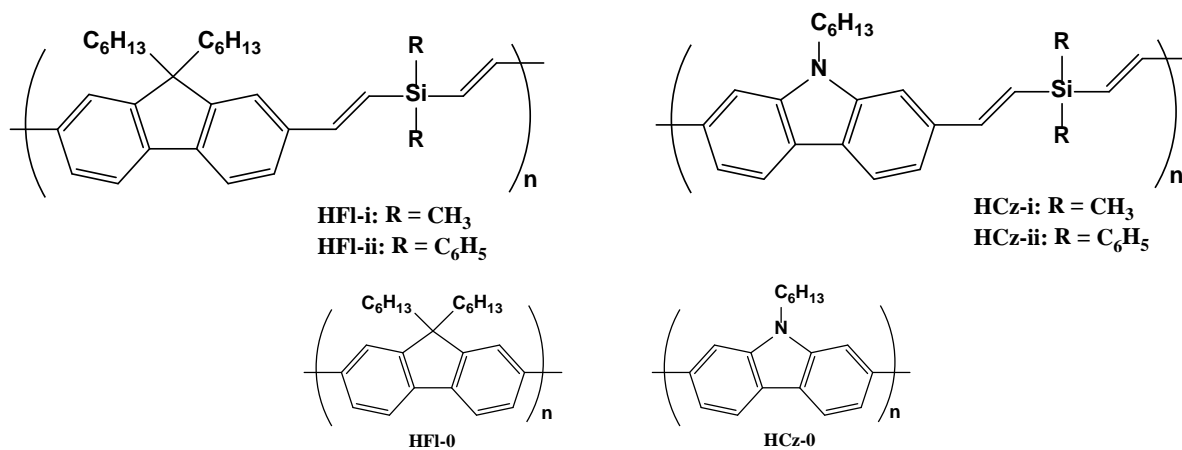
Sample	Monomer	Yield %	M_n^b	M_w/M_n^b
HFI-1	HFI/EMS	29	1900	1.9
HFI-2	HFI/EPS	40	2400	2.3
HCz-1	HCz/EMS	26	1300	3.3
HCz-2	HCz/EPS	52	1700	3.2

^aHFI, HCz = 0.718 mmol, EMS, EPS = 0.718 mmol, THF = 2.5 mL, $\text{PdCl}_2(\text{PPh}_3)_2$ = 25.3 μmol , PPh_3 = 6.53 μmol , NEt_3 = 0.04 mmol, CuI = 6.53 μmol , 60°C , 48 h, ^bDetermined by gel permeation chromatography using polystyrene standards.

Table 2. Photophysical properties of HFI-based copolymers containing Si-unsaturated units in the main chain^a.

Sample	Solution, λ_{max} (nm)		ϕ_{PL}^d	Film ^e , λ_{max} (nm)	
	Absorption ^a	Emission ^{b,c}		Absorption	Emission ^c
HFI-1	279 (372)	414	0.90	209 (348)	382
HFI-2	281 (376)	416	0.21	210 (377)	386
HFI-i ^f	411 (340)	460	0.98	414	471
HFI-ii ^f	345	454	0.95	342	466
HFI-0 ^f	377	414	0.23	382	422

^aEvaluated in chloroform (repeating unit: 10^{-5} mol/L), bracket: shoulder peak, ^bEvaluated in chloroform (repeating unit: 10^{-8} mol/L), ^cEmission was excited at λ_{max} of absorption, ^dQuantum efficiency measured using Alq_3 as a standard, ^ePolymer was casted from a chloroform solution (repeating unit: 10^{-3} mol/L), ^fRef [15].



Scheme 2. HFI- and HCz-based (co)polymers for reference.

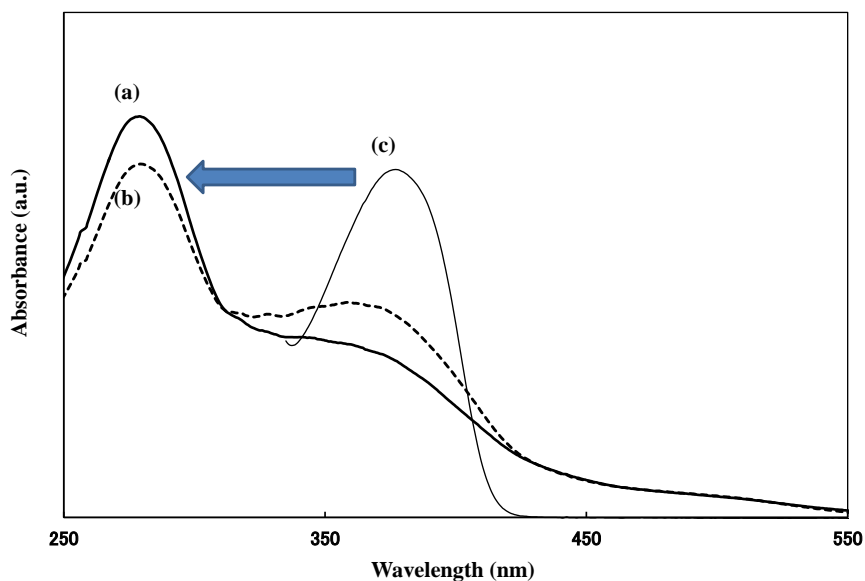


Figure 1. UV spectra of (a) HFI-1, (b) HFI-2, and (c) HFI-0 (reference) in chloroform solution, HFI unit: 10^{-5} mol/L.

present copolymers should be derived from shortening of the conjugation length by Si-ethynylene unit having short length and rigid structure.

Figure 2 shows the PL spectra of the HFI-based copolymers in chloroform. The copolymers showed broad emission peaks at around 415 nm. The emission wavelengths of the copolymers were almost same with the HFI homo-polymer (HFI-0). One explanation of the results is that both the shortening with Si and extension with ethynylene units of the π -conjugation length by σ - π moiety would cancel the shifts of the emission wavelength. The excitation spectra of the HFI-1, which were detected at the emission wavelength of 415 nm, showed the maximum emission intensity with excitation wavelength of 279 nm, which was λ_{max} of the absorption spectrum. The excitation with 372 nm, which was the shoulder peak of the absorption spectrum, just induced a weak emission at 415 nm. These results indicate that the emission at 415 nm should be derived from the intramolecular charge transfer through the σ - π moiety. The PL quantum yields of HFI-based copolymers, 0.9 (HFI-1) and 0.2 (HFI-2), were in range those of the reference (co)polymers. The PL spectroscopy of the copolymers was also investigated in the solid state, as the cast films prepared from the chloroform solutions at room temperature. The PL spectra of the HFI-1 and HFI-2 in the solid state are shown in **Figure 3**. The copolymers showed broad emission peaks at 380 nm, which was blue-shifted in comparison with that of HFI-0. Furthermore, the emission wavelengths in the solid state were blue-shifted in comparison with those in the chloroform solutions. These results

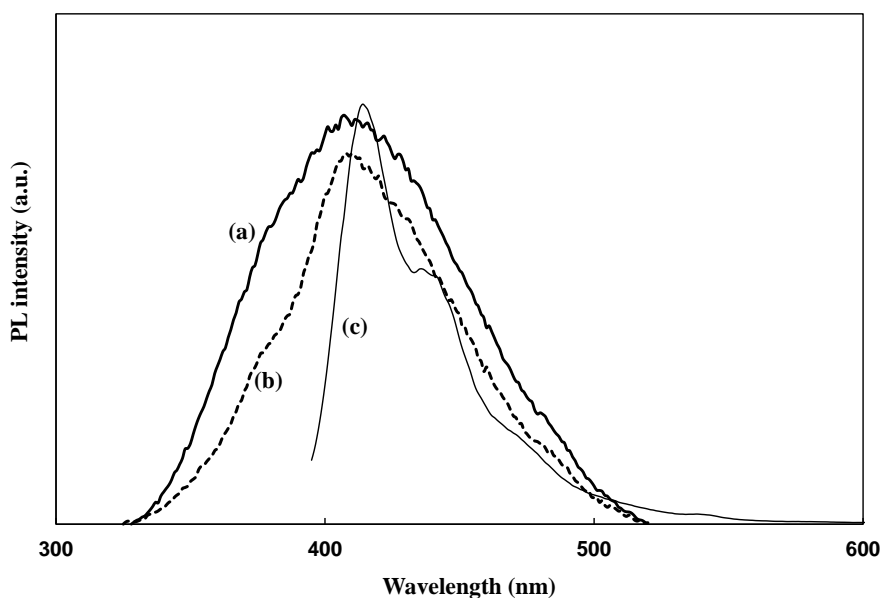


Figure 2. PL spectra of (a) HFI-1, (b) HFI-2, and (c) HFI-0 (reference) in chloroform solution, HFI unit: 10^{-8} mol/L.

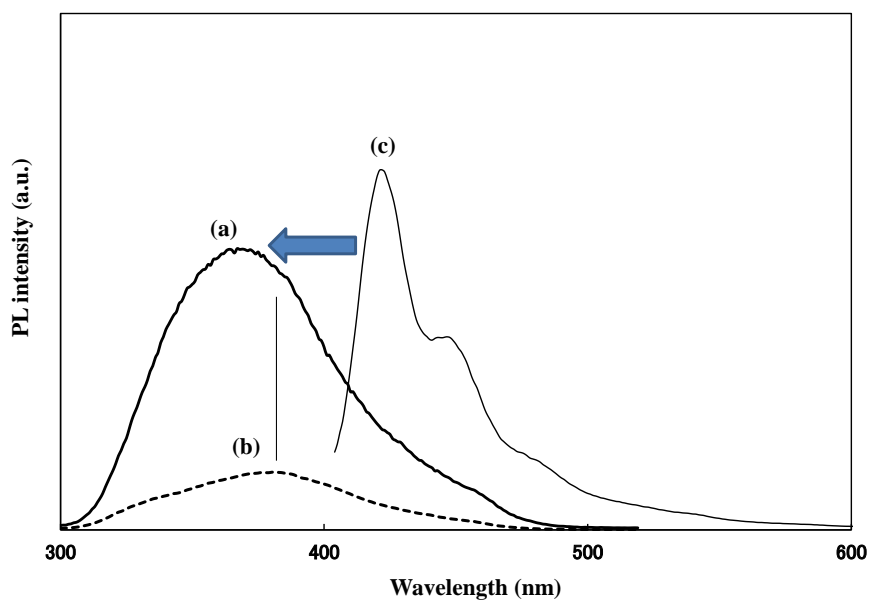


Figure 3. PL spectra of (a) HFI-1, (b) HFI-2, and (c) HFI-0 (reference) in solid state (cast film).

indicate that the aggregation of the HFI-1 and HFI-2 copolymers would form new high energy states. The reference copolymers with Si-vinylene units (HFI-i and HFI-ii) and homo-polymer HFI-0 (**Scheme 2**) showed the opposite tendency [15]. The Si-ethynylene units in the present copolymers should play an important role for the blue-shift of the emission wavelength in the solid state.

3.3. Photophysical Properties of HCz-Based Copolymers

Photophysical properties of the HCz-based copolymers in chloroform solution were studied with UV-vis absorption or PL spectroscopy. **Figure 4** shows the UV-vis spectra of the HCz-based copolymers in chloroform.

The chloroform solutions of the copolymers showed strong absorption peaks at 270 nm with broad shoulder peaks at around 360 - 380 nm. The absorption peaks at around 360 - 380 nm should be derived from the $\pi\text{-}\pi^*$ transition of the carbazole moieties, as detected in the reference polymer HCz-0 [15]. The absorption peaks at 270 nm would be induced by the intramolecular charge transfer through the $\sigma\text{-}\pi$ moiety, as shown in the HFI-based copolymers described above. The peak intensities of the shoulder peaks of the HCz-based copolymers were higher than those of the HFI-based copolymers. The result indicates that the intramolecular charge transfer through the $\sigma\text{-}\pi$ moiety should occur frequently in the HCz-based copolymers. All the absorption peaks of the present HCz-based copolymers containing Si-ethynylene units were blue-shifted in comparison with those of the corresponding copolymers containing Si-vinylene units (HCz-i, HCz-ii) or HCz homo-polymer (HCz-0) (Scheme 2, Table 3). The blue-shift in UV-vis spectra of the present copolymers should be derived from shortening of the conjugation length by Si-ethynylene units, as observed in the HFI-based copolymers.

Figure 5 shows the PL spectra of the HCz-based copolymers (HCz-1 and HCz-2) in chloroform. The copolymers showed broad emission peaks at around 425 nm. The emission wavelengths of the copolymers were red-shifted (about 10 nm) in comparison with that of the HCz homo-polymer (HCz-0). The extension of π -conjugation length with ethynylene unit would be more effective than the shortening of it with Si by the $\sigma\text{-}\pi$ moiety in the HCz-based copolymers. The PL quantum yield of HCz-based copolymers, 0.2 (HCz-1) and 0.5 (HCz-2), were lower than the reference (co)polymers. Figure 6 shows the PL spectra of the HCz-based copolymers in the solid state. The copolymers showed broad emission peaks at 360 nm, which were blue-shifted in comparison with that of HCz-0. The emission wavelengths in the solid state were blue-shifted in comparison with those in the chloroform solutions, as observed in the HFI-based copolymers. The reference copolymers with Si-vinylene units (HCz-i and HCz-ii) and homo-polymer HCz-0 (Scheme 2) showed the opposite tendency [15].

Table 3. Photophysical properties of HCz-based copolymers containing Si-unsaturated units in the main chain^a.

Sample	Solution, λ_{max} (nm)		$\phi_{\text{PL}}^{\text{d}}$	Film ^e , λ_{max} (nm)	
	Absorption ^a	Emission ^{b,c}		Absorption	Emission ^c
HCz-1	267 (363)	425 (373)	0.19	267 (377)	357
HCz-2	268 (377)	425 (371)	0.48	268 (396)	360
HCz-i ^f	332	454	0.47	334	477
HCz-ii ^f	349	454	0.94	349	482
HCz-0 ^f	373	414	0.79	377	433

^aEvaluated in chloroform (repeating unit: 10^{-5} mol/L), bracket: shoulder peak, ^bEvaluated in chloroform (repeating unit: 10^{-8} mol/L), ^cEmission was excited at λ_{max} of absorption, ^dQuantum efficiency measured using Alq₃ as a standard, ^ePolymer was casted from a chloroform solution (repeating unit: 10^{-3} mol/L), ^fRef [15].

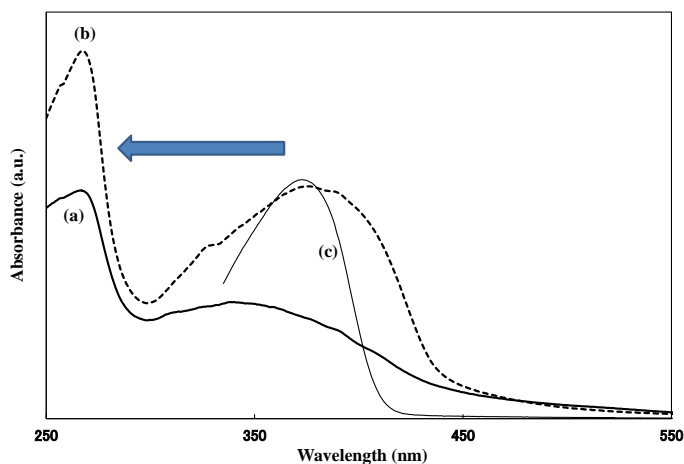


Figure 4. UV spectra of (a) HCz-1, (b) HCz-2, and (c) HCz-0 (reference) in chloroform solution, HCz unit: 10^{-5} mol/L.

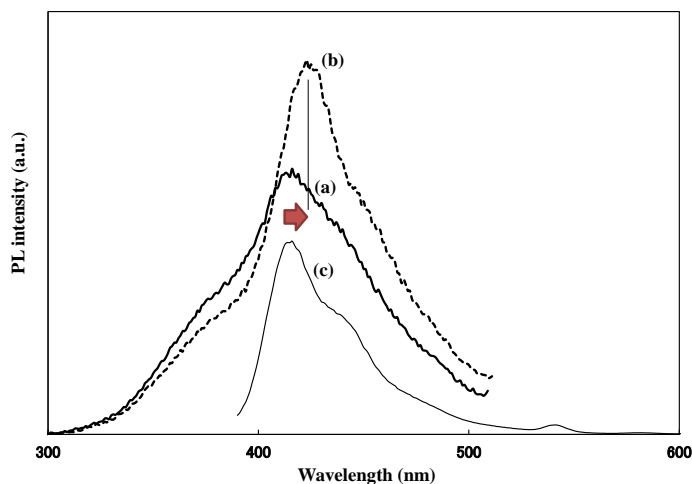


Figure 5. PL spectra of (a) HCz-1, (b) HCz-2, and (c) HCz-0 (reference) in chloroform solution, HCz unit: 10^{-8} mol/L.

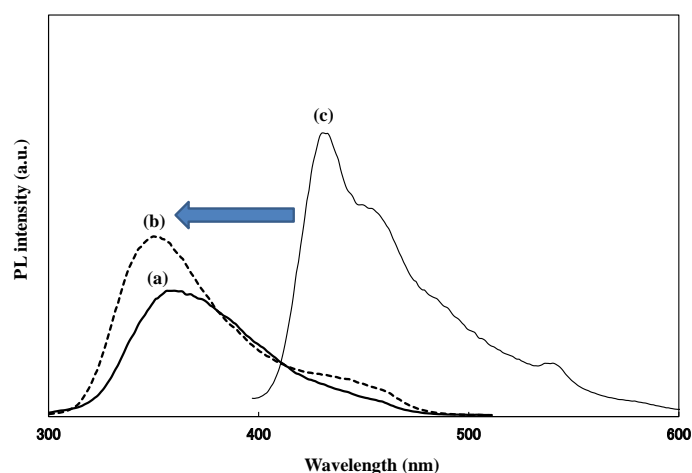


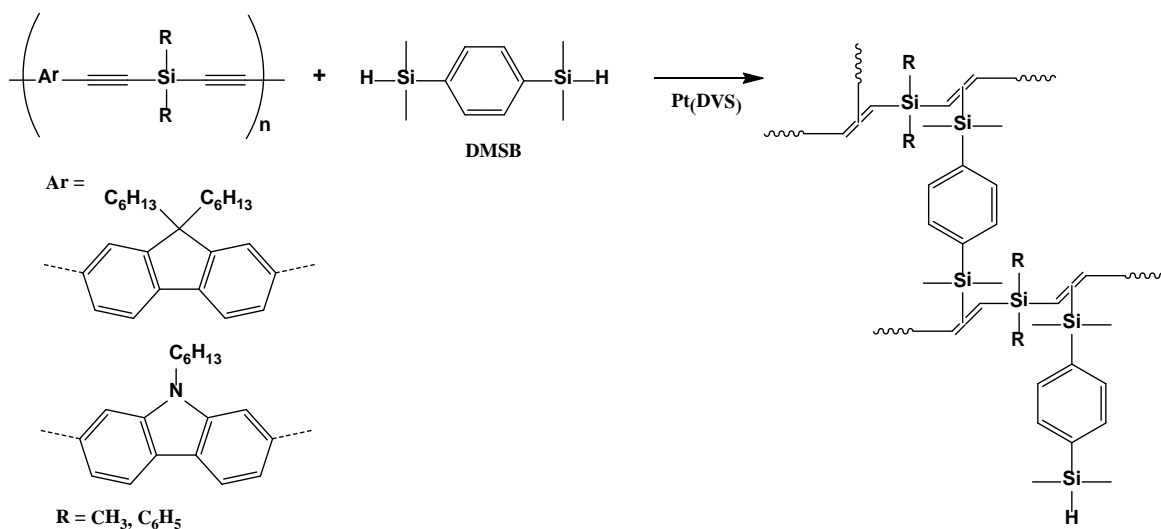
Figure 6. PL spectra of (a) HCz-1, (b) HCz-2, and (c) HCz-0 (reference) in solid state (cast film).

The results should be derived from the specific aggregation of the copolymers induced by Si-ethynylene units in the copolymers, as explained in the results of the HFI-based copolymers. The blue-shift factors, difference of the emission wavelengths in the chloroform solution and solid state, of the HCz-based copolymers (about 70 nm) were higher than those of the HFI-based copolymers (about 30 nm). The results indicate that the molecular structure of the HCz unit should be also important to form the new high energy state in the solid state. We have tried to investigate the solid structure of the copolymers by X-ray diffraction, although, we couldn't have the clear diffraction patterns of the copolymers. It remains as unsettled question what makes difference of the blue-shift factor between the HFI and HCz units in the copolymers. One possibility is that HCz units in the copolymers would effectively prevent from formation of the π -stacking, which causes red-shift of the emission wavelength, due to the electric repulsion between nitrogen atoms in the carbazole moiety.

3.4. Synthesis and Photophysical Properties of Network Copolymers with DMSB

The HFI and HCz based network copolymers were prepared by a hydrosilylation reaction with DMSB using Pt(dvs) catalyst, as shown in [Scheme 3](#). The resulting network copolymers were soluble in chloroform, and insoluble part was hardly detected. The result indicates that the reaction of the copolymers with low molecular weights could not form the infinite network structure and yielded the branching copolymers. The degree of the

branching, reaction conversion of the ethynyl groups in the copolymers, was determined by ^{13}C NMR spectroscopy. The results cleared that 1/2 to 2/3 part of the ethynyl groups in the copolymers reacted with DMSB. The HFI and HCz-based network copolymers showed the emission peaks at round 280 nm and 270 nm, respectively, as summarized in **Table 4**. The HFI-based network copolymers showed the almost same emission wavelengths with those of the original copolymers in chloroform. **Figure 7** shows the PL spectra of HCz-based network copolymers in chloroform, and those of original copolymers for the references. The HCz-1 network copolymer showed a main emission peak at 411 nm, which was slightly blue-shifted in comparison with that of the original polymer. In addition, a shoulder emission peak was newly detected in the network polymer at around 375 nm. In the case of the HCz-2 network copolymer, a main emission peak was newly detected at around 372 nm with a shoulder peak at around 426 nm. The excitation spectra of the HCz-2 network copolymer, detected at both the emission wavelengths 372 and 426 nm, showed the maximum emission intensity with excitation wavelength of 267 nm. These results indicate that the formation of the network in the HCz-based copolymers with DMSB should induce multiple energy states in the σ - π interaction.



Scheme 3. Synthesis of HFI, HCz-based network copolymers using a hydrosilylation reaction with DMSB.

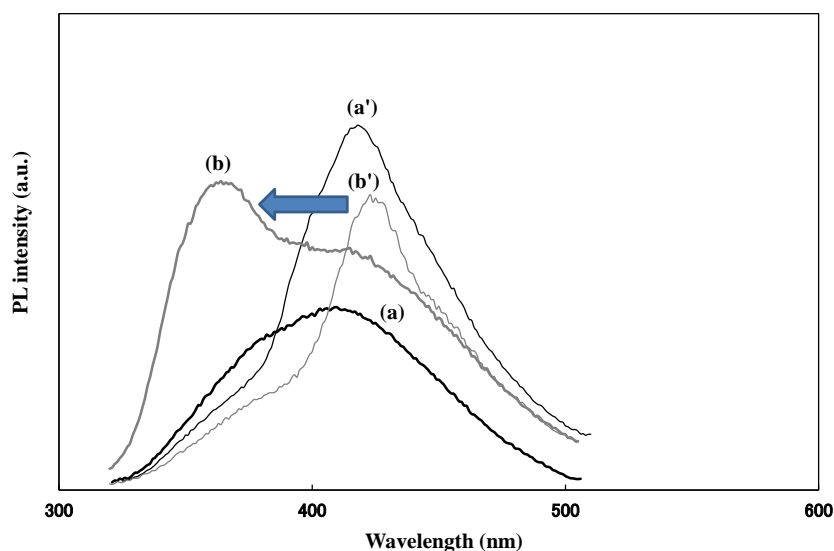


Figure 7. PL spectra of network polymers of (a) HCz-1, (b) HCz-2 with DMSB, and linear polymers (a') HCz-1, (b') HCz-2 (references) in chloroform solution, HCz unit: 10^{-8} mol/L.

Table 4. Photophysical properties of HCz-based copolymers containing Si-unsaturated units in the main chain^a.

Sample	Degree of Branching ^b	Solution, λ_{max} (nm)	
		Absorption ^c	Emission ^d
HFI-1/DMSB	0.50	276	415
HFI-2/DMSB	0.67	273 (334,350)	419
HCz-1/DMSB	0.66	267	419
HCz-2/DMSB	0.56	267 (327,345)	372 (426)

^aHFI, HCz: repanting units = 0.41 mmol, DMSB = 0.205 mmol, Pt(dvs) = 10.4 μmol (0.60 mM of toluene solution), 60C, 6 h, ^bDetermined by ¹³C NMR spectrum, bracket: shoulder peak, ^cEvaluated in chloroform (10⁻⁵ mol/L), bracket: shoulder peak, ^dEvaluated in chloroform (repeating unit: 10⁻⁸ mol/L), bracket: shoulder peak, emission was excited at λ_{max} of absorption.

4. Conclusions

The fluorene or carbazole-based alternating copolymers containing Si and ethynylene units in the main chain were successfully synthesized by Sonogashira coupling reaction of dibromo-fluorene or carbazole (HFI, HCz) and diethynylene Si compounds (EMS, EPS). The copolymers showed good solubility in conventional organic solvents such as acetone, chloroform, THF, toluene, and dimethyl foramide. The resulting copolymers showed bimodal absorption peaks and broad emission peaks in the chloroform solutions derived from the intramolecular charge transfer through the σ - π moiety. The emission peaks of the copolymers in the solid state showed remarkable blue-shift in comparison with those of the corresponding homo-polymers. The blue-shift in the emission peaks of the solid state copolymers should be induced by the higher energy states derived from intramolecular charge transfer through the σ - π moiety in the copolymer. The phenomenon was not observed in the reference (co)polymers. The Si-ethynylene unit in the copolymers should play an important role for the specific molecular aggregation of the copolymers in the solid state. The hydrosilylation reaction of the ethynyl groups in the copolymers with DMSB yielded the branched copolymers, which were soluble in organic solvents. The reaction of HCz-based copolymers with DMSB induced the emission at short wavelengths in the chloroform solution.

The present copolymers should be one of the useful conjugated polymers with fluorescence features. The modifications and reactions of the unsaturated ethynyl groups in the copolymers would enable us to control the wavelength in the emission and to form the conjugated polymers with geometrical variations. As the next step, we are looking carefully into the molecular structure of the copolymers in the solid state. We are also trying to apply the copolymers as emission layers for LEDs, and the results will be reported elsewhere.

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