4614 *Macromolecules* **2009**, *42*, 4614–4621
DOI: 10.1021/ma900556f

Macromolecules
ARTICLE

A Photocurable, Photoluminescent, Polycarbosilane Obtained by Acyclic Diene Metathesis (ADMET) Polymerization

Jitendra S. Rathore[†] **and Leonard V. Interrante***

Department of Chemistry and Chemical Biology, Rensselaer Polytechnic Institute, Troy, New York 12180-3590. [†] *Current address: IBM Almaden Research Center, Advanced Organic Materials Division, 650 Harry Road, San Jose, CA 95120*

Received March 15, 2009; Revised Manuscript Received April 19, 2009

ABSTRACT: The synthesis and study of a novel thermosetting, blue photoluminescent, cyclolinear polycarbosilane (CLPCS) are reported. This cyclolinear polycarbosilane, in which disilacyclobutane (DSCB) rings alternate with *trans*-stilbene units (i.e., $[-\{cyclo\text{-Si}(CH_3)(CH_2)_2Si(CH_3)\}-C_6H_4-CH{=}CH-C_6H_4-]_n$ (S-CLPCS), was prepared by via acyclic diene metathesis (ADMET) polymerization. The polymer showed excellent solubility in common organic solvents and blue photoemission with a high emission quantum yield ($\Phi \approx 0.65$). Spin-coated polymer films were thermally or photochemically cross-linked to yield tough, insoluble films, which showed no significant decrease in photoluminescence intensity relative to that of the initial polymer film prior to cross-linking. The effect of the DSCB spacers on the processability and optical properties of the polymers was investigated by preparing a series of alkylene-spaced polycarbosilane analogues and model compounds.

Introduction

Organosilicon polymers with well-defined fluorophores in their backbone have received considerable attention as conducting polymers and also as electroluminescent materials for potential use in light-emitting diodes.[1−7] The photophysical properties of these polymers are determined by the choice of the fluorophores and by the spacers that separate the fluorophores, which, in the case of certain silylenes and unsaturated organic groups, can extend the conjugation length through $\sigma-\pi$ conjugation and become part of the light-absorbing and -emitting chromophore. This can lead to thermally and/or photoinduced charge delocalization along the polymer backbone as well as appreciable red shifts in the emission spectra.[8−10] Although the extent of $\sigma-\pi$ conjugation in these polymers is generally agreed to be slight, some of these polymers have exhibited significant electrical conductivity when doped with acceptors such as $FeCl_3$ and SbF_5. The introduction of silylene spacers, especially dialkylsilylenes, has also been shown to improve the solubility and processability of such typically rigid-rod-like, fluorophore-containing polymers.[4,11−13]

Condensation-based strategies[1,3,4] and hydrosilylation reactions[14−25] are some of the most common synthetic routes to fluorophore-containing organosilicon polymers; however, recently, acyclic diene metathesis polymerization (ADMET) has been reported by Peetz et al. to provide a convenient route to silylene- and siloxane-containing photoluminescent polymers and macrocycles.[26] This work, which employed distyryl-functional silylenes and siloxanes to produce linear polymers containing alternating *trans*-stilbene and silylene linkages and macrocyclic oligomers, extended the original studies of Wagener and co-workers, who employed ADMET to develop a variety of novel organosilicon polymers.[27−30]

In 2004, we reported the synthesis of a unique class of thermally cross-linkable organosilicon polymers, i.e., cyclolinear polycarbosilanes (CLPCS), using the ADMET route.[31−34] These polymers, which contain four-membered 1,3-disilacyclobutane (DSCB) rings linked by alkylene chains, i.e., $[-\{cyclo\text{-Si}(CH_3)(CH_2)_2Si(CH_3)\}-(CH_2)_n-]_n$, are soluble in common organic solvents and undergo ring-opening at above ca. 200 °C to form thermally stable, insoluble cross-linked films.[35−37] The resultant hydrophobic, low-permittivity ($k = 2.4$) films were found to have excellent thermomechanical properties and have been suggested for use as low-*k* dielectric materials in electronics processing.[33]

We report here the further extension of the ADMET strategy to the preparation of fluorophore-containing CLPCS in which the alkylene $\{(CH_2)_n\}$ bridges are replaced by *trans*-stilbene linking groups. The incorporation of this fluorophore between the DSCB rings results in a processable photoluminescent polymer that can be spin-coated and thermally or photochemically cross-linked to yield insoluble, thermally stable thin films. Starting from a distyryl-substituted DSCB, blue-photoluminescent, *trans*-stilbene-bridged oligomeric and polymeric cyclolinear carbosilanes (S-CLPCS) were obtained in high yield. In addition, we have prepared stilbene-containing, alkylene-spaced $\{(CH_2)_n\ n = 1, 2\}$, carbosilane oligomers and model compounds and studied their optical and photoluminescent properties.

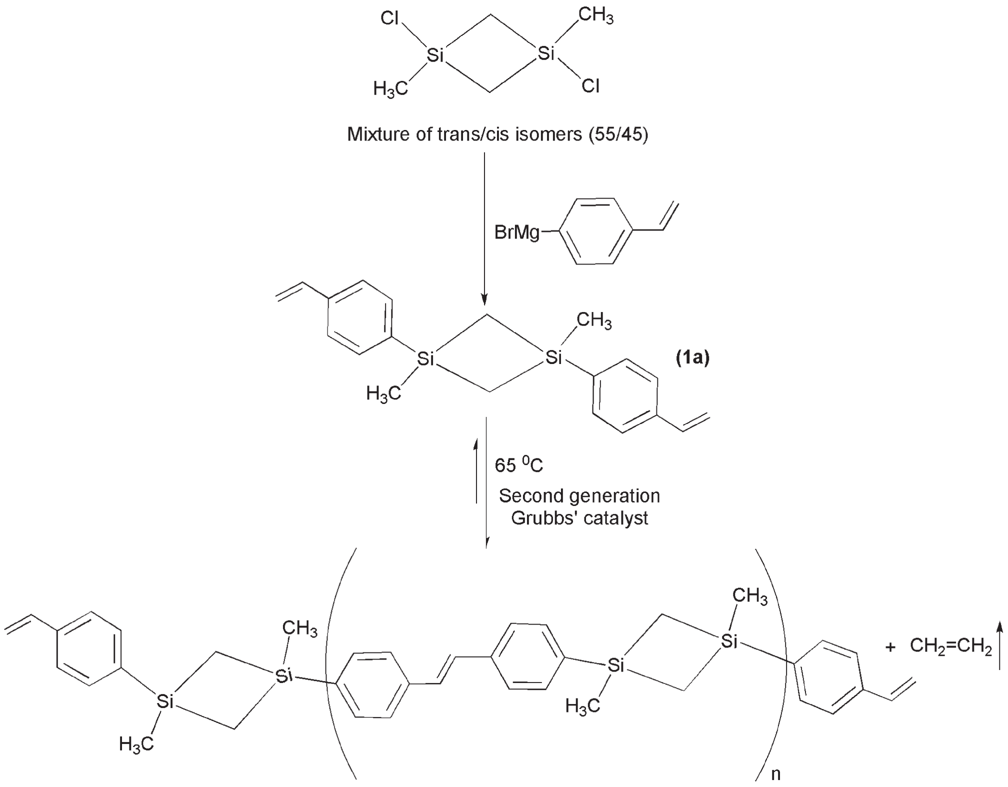
Results and Discussion

Synthesis and Characterization of *trans*-Stilbene Cyclolinear Polycarbosilane {S-CLPCS (2a)}. 1,3-Disilacyclobutanes, $[SiRR'CH_2]_2$, are strained 4-membered ring compounds that undergo facile, thermally induced or transition metal-catalyzed ring-opening polymerization (ROP) to form poly(silylenemethylene)s, e.g., $[SiRR'CH_2]_n$.[35] Therefore, the incorporation of such species in a cyclolinear polymer by ADMET polymerization provides a challenge so as to avoid significant ring-opening during polymerization. We have found that the typical Grubbs (Ru) and Schrock (Mo) metathesis catalysts can be used effectively for this purpose if the temperature of the reaction is

---

*Corresponding author: e-mail interl@rpi.edu.

Scheme 1. Synthesis of S-CLPCS (2a)



controlled.[31-34] Our prior work employed 1,3-dibutenyl-1,3-dimethyl- and -diallyl-1,3-dimethyl-1,3-disilacyclobutane as monomers and involved reduction with toluene sulfonhydrazide to yield the fully saturated $[-\{cyclo\text{-Si(CH}_3)(\text{CH}_2)_2\text{Si(CH}_3)\}-(\text{CH}_2)_n-]_n$ cyclolinear polymers. The same methodology, without the reduction step, was applied successfully to the 1,3-distyryl-1,3-dimethyl-1,3-disilacyclobutane (monomer **1a**) (trans/cis mixture; 55/45) using the second-generation Grubbs catalyst (Scheme 1) to yield the corresponding $[-\{cyclo\text{-Si(CH}_3)(\text{CH}_2)_2\text{Si(CH}_3)\}-\text{C}_6\text{H}_4-\text{CH}{=}\text{CH}-\text{C}_6\text{H}_4-]_n$ S-CLPCS (**2a**) in high yield.

The polymerization of **1a** was performed under an inert atmosphere at 65 °C, resulting in a sticky liquid product (for details; see the Experimental Section). Gel permeation chromatography (GPC) of the product (Figure S1a, Supporting Information) indicated a broad peak with a polydispersity index (PDI) of 1.8 (M_n = 5400) and a degree of polymerization (DP) $\approx$ 18, which is surprisingly high considering the rigid-rod-like *trans*-stilbene in the polymer backbone. Presumably, the DSCB rings impart sufficient flexibility to the growing polymer chains, allowing them to remain in solution with the monomer and exhibit sufficient mobility to build up relatively high molecular weights. In fact, the final polymer (**2a**) has a low T_g (vide infra) and showed excellent solubility in common organic solvents, such as chloroform, benzene, toluene, and methylene chloride. The solubility and molecular weight enhancing effect of the DSCB rings are further demonstrated by comparison with the corresponding alkylene-bridged oligomers (vide infra).

The ^{1}H NMR spectrum of the product showed a peak at $\delta \sim 7.1$ ppm indicative of *trans*-stilbene protons.[26] The ^{13}C NMR spectrum evidenced the virtual disappearance of the signal at 114.29 ppm, attributable to the terminal vinylic carbons, and a shift in the nonterminal vinylic carbon signals from δ 134.2 to δ 127.4 ppm, indicating selective formation of *trans*-stilbene groups (>99%). The ^{29}Si NMR spectrum of **2a** showed two distinct peaks at δ −1.76 and δ −1.52 ppm, which were assigned to the *cis*- and *trans*-DSCB isomers, respectively (Figure S2, Supporting Information).

Two specific oligomers (the dimer and tetramer) were separated from this product by HPLC and were identified by matrix-assisted laser desorption time-of-flight (MALDI-TOF MS) using dithranol as a matrix and AgTFA as an ionizing agent (for details; see Experimental Section). In the case of the tetrameric oligomer, the loss of one methyl group (calcd m/z = 1300, 1298; exptl m/z = 1285, 1283) was evidenced in the spectrum; however, the dimeric oligomer (calcd m/z = exptl m/z = 719, 721) showed no such loss of methyl groups during MALDI-TOF analysis (Figures S3a and S3b, Supporting Information).

Differential scanning calorimetry (DSC) and GPC analysis of **2a** was carried out after removal of relatively lower molecular weight species by precipitation of the polymer from chloroform solution using an excess of methanol. GPC indicated a DP of ca. 27, and the DSC showed a clear second order transition at $T_\text{g} \approx -27$ °C (Figure 1a) followed by a broad exothermic peak centered at 223 °C, which is associated with the ring-opening and the irreversible cross-linking of the polymer. The energy released during the cross-linking process can be estimated by calculating the area under the exotherm and was found to correspond to $\approx$42.45 kJ/(mol of DSCB rings in the polymer), very close to the value exhibited by the dimer and tetramer and consistent with prior studies of the related polymethylene-bridged CLPCS.[31] Moreover, TGA analysis of **2b** showed no appreciable weight loss up to $\approx$500 °C, with a significantly higher char yield ($\approx$80%) on pyrolysis to 1000 °C under N_2 as compared to the char yield in air ($\approx$ 50%) (Figure 1b). Isothermal TGA plots were also recorded at 400, 450, and 500 °C under N_2. A gradual weight loss of 3−8% was observed at 400 and 450 °C over a 10 h period. At 500 °C,

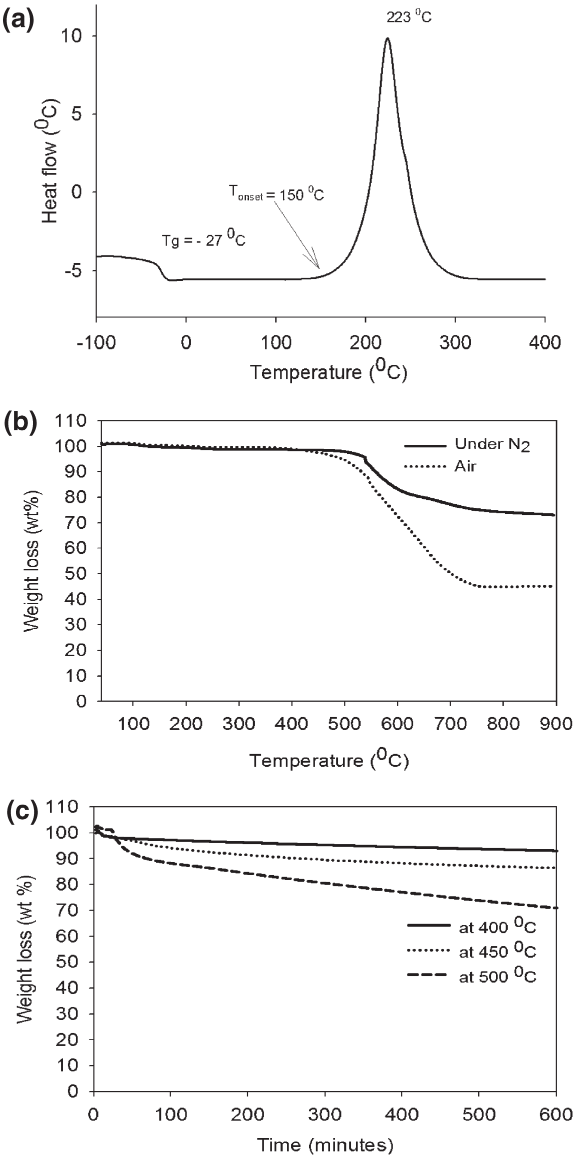
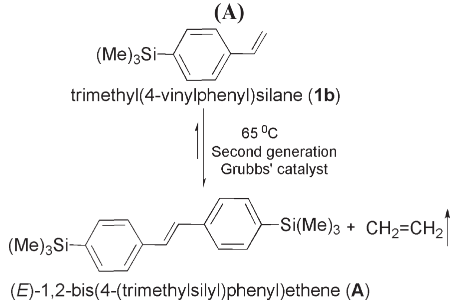


Figure 1. (a) DSC plot of S-CLPCS. (b) TGA plot of **2b** under N_2 and in air. (c) Isothermal TGA plots.

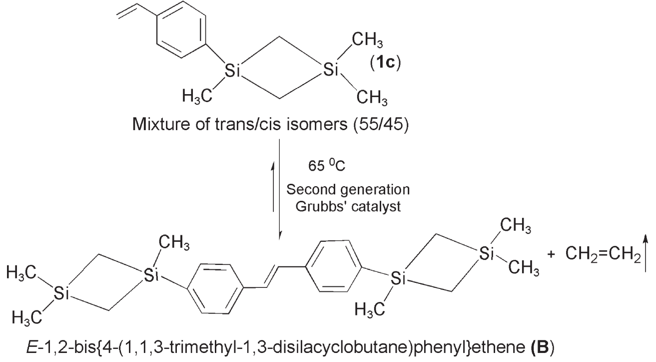
the isothermal TGA plot displayed a total weight loss of 30% after 10 h (Figure 1c).

Synthesis and Characterization of Model Compounds and Oligomers. To gain better insight into the optical and photoluminescence properties of polymer **2b**, we prepared model compounds that are structurally similar to the chromophore units present in the **2b** backbone. Compound **A**, which employs trimethylsilyl as the terminal groups, was prepared by the second-generation Grubbs-catalyzed ADMET dimerization of trimethyl(4-vinylphenyl)silane (**1b**) (Scheme 2) (see Experimental Section). The ^{1}H NMR spectrum of **A** shows an isolated single peak at δ 7.11 ppm consistent with *trans-vinylic* protons (Figure S4, Supporting Information).[26] The other model compound **B** consists of the *trans*-stilbene fluorophore bonded on both sides to 1,1,3-trimethyl-substituted DSCB rings, thus closely resembling the arrangement of DSCB rings around the *trans*-stilbene fluorophore in the **2b** backbone. Compound **B** was synthesized by the ADMET dimerization of 1,1,3-trimethyl-3-styryl-1,3-disilacyclobutane (**1c**) (Scheme 3); however, around 15% (calculated by ^{1}H NMR) of **1c** remained unreacted even after 48 h of stirring at 65 °C. The isolation of the pure **B** (GC purity ≈99%) was carried out by purifying the crude reaction mixture by means of column chromatography (for details, see Experimental Section).

Scheme 2. Preparation of (*E*)-1,2-Bis{4-(trimethylsilyl)phenyl}ethene (A)



Scheme 3. Synthesis of *E*-1,2-Bis{4-(1,1,3-trimethyl-1,3-disilacyclobutane)phenyl}ethene (B)



In addition, S-CLPCS oligomeric analogues having *trans*-stilbene as fluorophores and alkylene units {$(CH_2)_n$, n = 1, 2} as spacers were prepared to study the effects of the spacers on the overall property profile of the stilbene-containing polymers (Scheme 4). Oligomer mixture **C** {$(CH_2)_n$, n = 1} was prepared by ADMET polymerization of bis(dimethyl-(4-vinylphenyl)silyl)methane (**1d**) and was isolated as an off-white powder. The product was partially soluble in $CHCl_3$ (≈70 wt %) and cyclohexane (≈60 wt %), after filtration from undissolved solid. The partial solubility of oligomer mixture **C** implies that higher molecular weight fractions remained insoluble and could not be analyzed by ^{1}H NMR spectroscopy or GPC. The ^{1}H NMR spectrum of **C** manifested typical *trans*-vinylic proton signals (δ 7.1 ppm) (Figure S5, Supporting Information); additionally, the residual terminal-vinylic proton peaks were also observed in the region of δ 5−6 ppm. A DP ≈ 7 was calculated by integrating the terminal protons signals in the ^{1}H NMR spectrum of oligomer **C**. Also, the GPC of **C** showed a broad PDI of 1.7 and DP ≈ 7, in agreement with the ^{1}H NMR integration results. A similar ADMET strategy was adopted to prepare the ethylene-bridged {$(CH_2)_n$, n = 2} oligomer mixture **D** using the monomer (**1e**) [bis(dimethyl(4-vinylphenyl)silyl)ethane]. **D** exhibited slightly better solubility as compared to oligomer mixture **C** showing ≈75 wt % solubility in $CHCl_3$ and ≈70 wt % oligomer solubility in cyclohexane, again leaving an insoluble higher molecular weight fraction. The limited solubility of the alkylene-bridged oligomers in contrast to the excellent solubility of **2b** highlights the role of the DSCB spacers in improving the solubility of the stilbene-containing polymers.

Optical and Photoluminescence Properties (Solution). The UV−vis spectra of polymer **2b**, the model compounds (**A**, **B**), and the alkylene-spaced oligomers (**C**, **D**) showed very

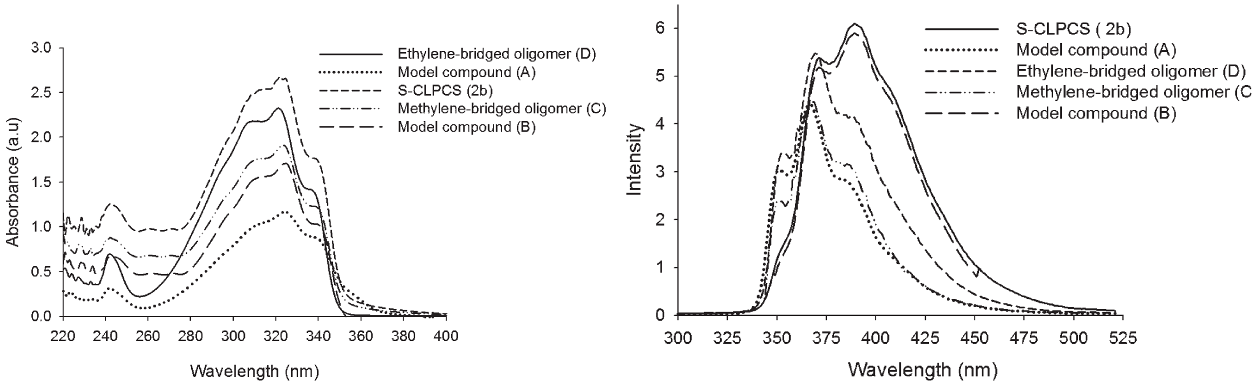


Figure 2. (a) UV−vis absorbance plots. (b) Emission plots for compound **A**, compound **B**, oligomer **C**, oligomer **D**, and S-CLPCS.

Scheme 4. Synthesis of the Methylene- and Ethylene-Bridged Oligomers C and D

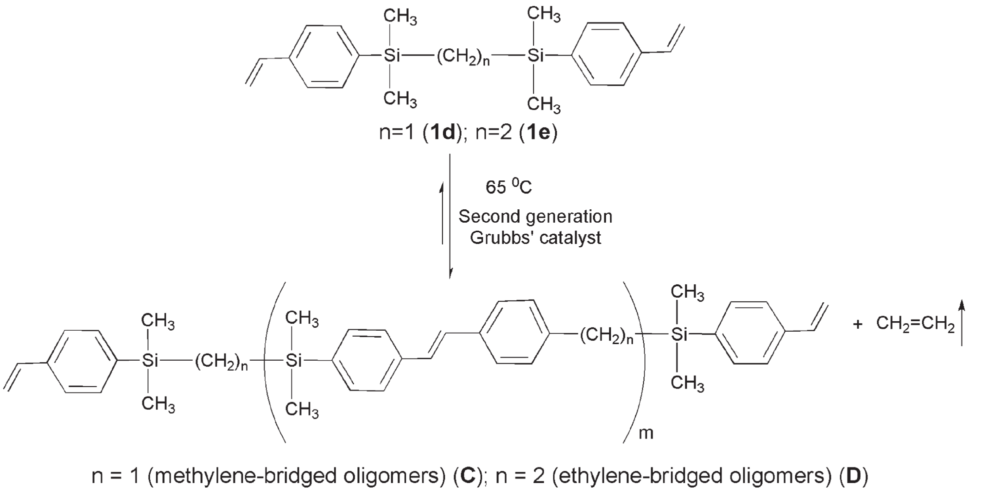


Table 1. Summary of UV Maxima (λ_{max}, nm), Extinction Coefficient (ε), Emission Maxima (λ_{max}), and Emission Quantum Yields (Φ)

entry	UV−vis (λ_{max}, nm)	extinction coefficient[a] (ε, L mol^{-1} cm^{-1})	emission (λ_{max}, nm)	quantum yield[b] (Φ)
2b	326	1.57×10^7	395	0.65
A	321	5.19×10^6	366	0.14
B	324	1.37×10^7	390	0.30
C	326	1.25×10^7	372	0.21
D	326	1.21×10^7	370	0.29

[a] Calculated on the basis of number of moles of fluorophore units {$-Si(R_1R_2)-C_6H_4-CH{=}CH-C_6H_4-Si(R_1R_2)-$} present in the polymers or oligomers. [b] Measured relative to Rhodamine solution in water (see Experimental Section).

similar absorption spectra with absorbance maxima (λ_{max}) in the region of 321−326 nm (Figure 2a, Table 1). The fluorophore $-Si(R_1R_2)-C_6H_4-CH{=}CH-C_6H_4-Si(R_1R_2)-$ present in the aforementioned polymer and model compounds showed a red shift of ≈25−30 nm as compared to the UV absorbance of *trans*-stilbene ($\lambda_{max} \approx 295$ nm). This indicates some $\sigma-\pi$ interaction between the σ-orbitals of silicon and π-orbitals of the *trans*-stilbene, as was suggested previously.[8−10,26,36]

The emission spectra of these species exhibited somewhat greater differences in both peak positions and emission quantum yields (Figure 2b). **A** exhibited a maximum at 366 nm and a fluorescence quantum yield of $\Phi = 0.14$. The emission maxima of the alkylene-bridged oligomer mixtures **C** and **D** (**C**, $\lambda_{max} = 372$ nm; **D**, $\lambda_{max} = 370$ nm) and emission quantum yields {Φ(**C**) = 0.21 and Φ(**D**) = 0.29} were found to be quite similar to one another and only slightly different from that of **A**. In general, these data correspond closely to the results obtained by Peetz et al. for their silylene-bridged *trans*-stilbene polymers.[26] On the other hand, the emission spectra of a solution of **2b** showed a maximum centered at $\lambda_{max} = 395$ nm, red-shifted by ca. 20 nm relative to these other compounds and polymers. Moreover, the emission quantum yield of the **2b** solution ($\Phi = 0.65$) was 2−3-fold higher as compared to the model compounds and oligomers. Compound **B**, which also contains DSCB rings, shows a similar red shift in its emission spectra ($\lambda_{max} = 390$ nm), but its emission quantum yield is apparently considerably lower ($\Phi = 0.30$). A comparison of the emission quantum yields of **2b** solutions with similar silicon-containing systems having fluorophores, such as paracyclophane,[37] phenylenevinylene,[4,38] biphenylene,[4] and phenylene,[4] indicates relatively higher yields for polymer **2b**. It must be noted that emission quantum yields are dependent on a number of factors (e.g., the solvents, the standards used for the emission measurements, the excitation wavelength, etc.) as well as the type and arrangement of the fluorophores;[4,11−13,37,38] however, it appears that the incorporation of the terminal Si atom in the $-Si(R_1R_2)-C_6H_4(CH)_2C_6H_4-Si(R_1R_2)-$ fluorophore into disilacyclobutane rings has a significant effect on the emission properties of these systems, perhaps due to the relative proximity of the second Si atom in the DSCB ring and/or the increased flexibility in the polymer chains.

Optical and Photoluminescent Properties (Thin Films). As was mentioned previously, one of the interesting characteristics of the CLPCS is their tendency to undergo thermally induced cross-linking to yield insoluble thin films

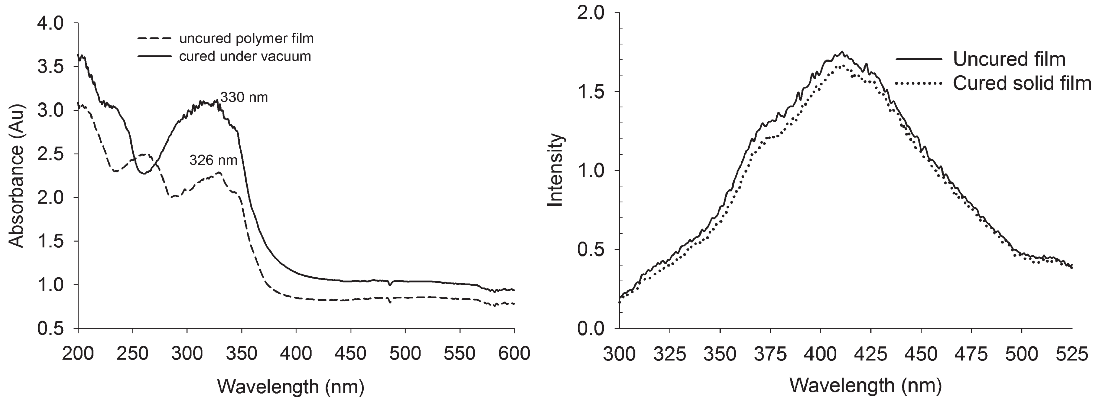
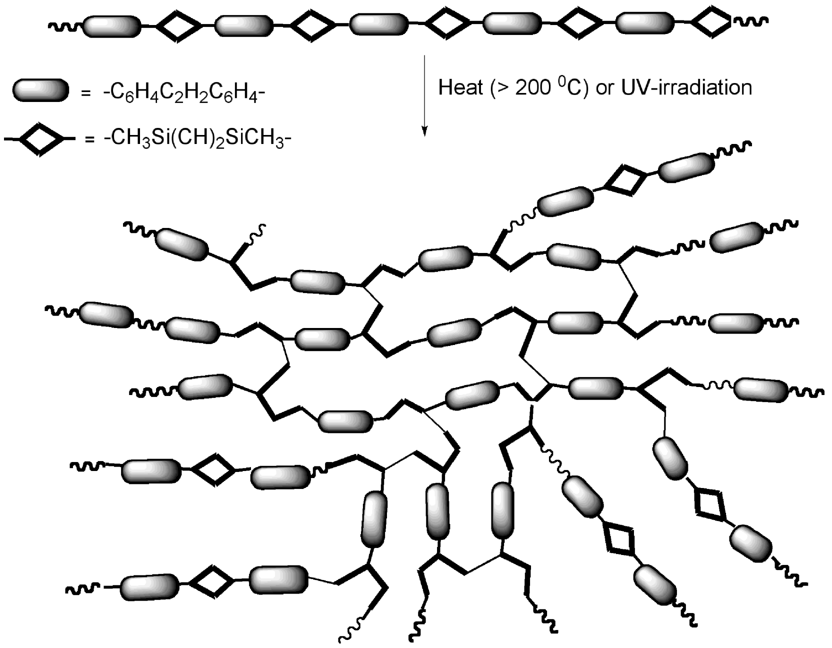


Figure 3. (a) UV−vis spectra of the S-CLPCS films. (b) Emission spectra of the S-CLPCS films.

Scheme 5. Illustration of the Thermal and Photochemical Cross-Linking of the S-CLPCS Films



(Scheme 5). To evaluate the optical and photoluminescent characteristics, spin-coated **2b** thin films (≈200 nm) on transparent potassium bromide pellets were cured at 250 °C/1 h under vacuum (shrinkage ≈ 5%). The resultant films remained smooth and apparently uniform with no observed cracking. Moreover, no apparent swelling or dissolution was observed when the coated pellets were immersed in organic solvents, e.g., chloroform, cyclohexane, and toluene. The curing process of the as-spun films was quantitatively measured via FT-IR spectroscopy by analyzing the intensity of the sharp peak at 930 cm^{-1} (C−H bending) which, upon ring-opening, shifts to 1050 cm^{-1} (broad). The FT-IR spectrum of the thermally cured films indicated ≈65% ring-opening. UV−vis spectra of the above thermally cured films were analyzed directly by UV−vis spectrophotometry, revealing a broad UV absorbance band with a maximum at around 330 nm (Figure 3a). These films displayed intense blue-light emission ($\lambda_{\max}$ = 410 nm) upon excitation at 266 nm with a frequency-quadrupled neodymium-doped yttrium aluminum garnet laser (Figure 3b). As is evident in this figure, the films did not show any significant drop in the emission intensity after curing at 250 °C for 1 h under vacuum. However, changing the curing conditions to 350 °C/1 h under vacuum led to the complete cross-linking of the polymer and a total loss of emission for the resultant films. We also investigated the photochemical cross-linking of **2b** films (200 nm) on potassium bromide pellets under an inert atmosphere. To study the FT-IT spectra of the photochemically cross-linked films, as-spun films (200 nm) on potassium bromide pellets were cured for 2 h under an argon atmosphere in a UV chamber equipped with an ultraviolet ozone-free lamp (254 nm wavelength). The FT-IR analysis of the photochemically cured films indicated partial cross-linking ≈60% (shrinkage ≈4%), and the films were found to be adherent to the pellets (Figure S6, Supporting Information). The UV−vis and emission profile of the partially UV cured films were found to be essentially identical to that of the thermally cured films.

Conclusions

We have reported an efficient, ADMET-based route to fluorophore-containing organosilicon polymers (S-CLPCS) that showed excellent solubility in common organic solvents and could be processed into thin films by spin-coating from solution. The S-CLPCS solutions displayed blue emission with high emission quantum yields (Φ = 0.65) as compared to model compounds, polymers, and oligomers containing similar fluorophore units. The polymer films were thermally and photochemically cross-linked to yield solid, blue-photoluminescent films. No appreciable drop in the emission intensity was noted for the thermally or photochemically cured films. Moreover, the effect of the DSCB as spacers in improving the processability of the polymer was evidenced by preparing alkylene-spaced oligomers.

Experimental Section

Materials. 4-Bromostyrene, Rhodamine B solution, and magnesium powder were purchased from Sigma-Aldrich Chemical Co. and were used as received. 1,3-Diisopropoxy-1,3-dimethyl-1,3-disilacyclobutane was procured from Starfire Systems, Inc., Malta, NY, and was chlorinated using previously reported procedure.[39] The second-generation Grubbs catalyst (Ru) was obtained from Strem Chemical Co. Trimethylsilyl chloride and bis(chlorodimethylsilyl)ethane were purchased from the Gelest Chemical Co. and used without further purification.

Instrumentation. All of the NMR spectra were recorded on a Varian Unity-500 MHz NMR instrument. ^{1}H and ^{13}C NMR spectra were referenced internally to the solvent peak, and the ^{29}Si spectra were referenced externally to TMS. The molecular weight of the polymers was measured on a Waters GPC system equipped with a refractive index detector (Waters 2410) and three Styragel columns packed with 5 μm particles (HR1: effective molecular weight 100−5000; HR3: effective molecular weight 500−30 000; HR4: effective molecular weight 5000−500 000) using THF as the eluent at a flow rate of 1.0 mL/min. The column temperature was set at 30 °C. Molecular weights were reported relative to polystyrene standards, and a third-order calibration curve was used to measure the molecular weight of unknown samples. The HPLC apparatus consists of a dual piston pump (Knauer, K-501), a six-port sample injector (Rheodyne, 7125) equipped with a 100 μL injection loop, and a variable wavelength UV/vis absorption detector (Spectra-Physics, SP 8480) and operated at a wavelength of 260 nm. FT-IR experiments were performed on Thermo Electron Corp. Nicolet 4700 instruments. Thermogravimetric analysis (TGA) was conducted on a Mettler Toledo TGA/SDTA851^e instrument (ramping rate = 20 °C/min). DSC measurements were carried out with a TA 2920 instrument from −120 to 430 °C (heating rate 10 °C/min). The UV absorption spectra were recorded using a Jasco v-530 UV/vis spectrophotometer. The UV chamber used for photochemical curing is equipped with an ultraviolet ozone-free lamp (254) nm wavelength (300 W/inch), Jelight Co., Model 42. Typically, the UV chamber was placed inside a glovebox, and the films were cured in the UV chamber under an argon atmosphere with UV dose of 300 J/s for 2 h. FT-IR spectra were obtained on liquid samples sandwiched between sodium chloride IR crystal windows using a Nicolet 4700 infrared spectrophotometer. MALDI mass spectra were obtained using a Bruker Daltonik Ultraflex III MALDI-TOF mass spectrometer (Bruker Daltonik, Bremen, Germany). Ionization was performed by a Nd:YAG "smart" laser beam. Dithranol was used as the matrix. Ionization was performed by using AgTFA as an ionizing agent. Calibration of the mass range in linear mode was performed using a protein standard mixture. All the emission spectra were recorded by excitation with a frequency-quadrupled neodymium-doped yttrium aluminum garnet laser with emission wavelength of 266 nm at room temperature.

Emission Quantum Yield Measurement. Emission quantum yields were measured by using Rhodamine B solution as the standard. The quantum yield of an unknown is related to that of a standard by eq 1. The subscript u refers to the unknown and s to the standard, and the other symbols have the following meanings: Φ is the quantum yield, A is the UV−vis absorption at the excitation wavelength, F is the integrated emission area across the band, and η is the index of refraction of the solvent containing the unknown (η, chloroform for unknown) and the standard (η_0, water for known) at the sodium D line and the temperature of the emission measurement.

$$\Phi_u = A_s F_u / A_u F_s (\eta / \eta_0) \Phi_s \qquad (1)$$

Synthetic Procedures (Multiple)*1,3-Distyryl-1,3-dimethyl-1,3-disilacyclobutane (**1a**).* Monomer **1a** was prepared by the Grignard reaction of freshly prepared styrylmagnesium bromide (0.1 mol, 0.5 M) with 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane (0.05 mol, 9.2 g). To prepare styrylmagnesium bromide solution, magnesium powder (0.5 mol, 12 g) was added to THF (150 mL) under nitrogen, and the mixture was refluxed for 30 min to activate the magnesium powder. 4-Bromostyrene solution (0.11 mol, 15 g; in 50 mL of THF) was then added dropwise to the refluxing mixture. After 2 min, the temperature of the mixture was brought down and maintained between 1 and 4 °C with the help of an ice bath. After the addition of 4-bromostyrene solution, stirring was continued at room temperature for 6 h. After analyzing the yield of styrylmagnesium bromide with GC (yield ≈ 95%), 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane solution (0.1 mol in 50 mL of THF) was added slowly to the above Grignard solution at room temperature, and the mixture was stirred for 12 h, which was followed by overnight refluxing. Dry methanol (50 mL) was then added to neutralize the unreacted Grignard reagent. After the separation of the solution from the precipitated magnesium salt, the product was extracted with the hexane (50 mL). Evaporation of hexane at low pressure yielded the product (**1a**) as a viscous liquid (5.04 g). Yield 55%; GC purity ≈ 95%. ^{1}H NMR ($CDCl_3$, ppm): 0.22 (m, $Si-CH_3$, 6H); 0.44 (m, $Si-CH_2-Si$, 4H); 5.18 (m, 2H); 5.72 (m, 2H); 6.66 (m, 2H); 7.17−7.54 (m; aryl CH, 8H). ^{13}C NMR ($CDCl_3$, ppm): −0.15, 2.08, 4.2 (broad), 8.3 (m), 114.29 (d), 125.53 (m), 133.53 (m), 136.65, 138.15, 139.16. ^{29}Si NMR ($CDCl_3$, ppm): −1.52, −1.76.

ADMET Polymerization (Typical Procedure). The ADMET polymerization of the monomers was performed in an inert atmosphere inside a glovebox equipped with a vacuum outlet for removal of the ethylene. Typically, the reaction was carried out on neat monomers in a one-necked RB (equipped with a three-way connector) using the Grubbs second-generation catalyst (catalyst/monomer; 1:100) at 65 °C. After the RB was introduced into an inert atmosphere glovebox, the monomer and second-generation Grubb's catalyst (100:1 monomer:catalyst) were added, and the mixture was stirred under vacuum at 65 °C. After 6 h, an additional aliquot of catalyst was added to the mixture. The catalyst was added periodically (after 6 h) until no further increase in molecular weight was noted. Removal of ethylene was performed periodically using the three-way connector to shift the reaction equilibrium toward the polymer. Once the reaction reaches optimum viscosity, i.e., no more stirring was possible, the reaction was terminated by exposing to air. The polymer was then precipitated by adding methanol (100 mL). The polymer was subsequently washed with methanol (50 mL) three times to remove the catalyst residues. The isolated polymer **2a** (0.2 g) was then purified by dissolution in chloroform (1.0 mL) and then gradually adding methanol (30 mL) to the polymer solution. The precipitated polymer **2b** was isolated and characterized by multinuclear NMR, GPC, and DSC. **S-CLPCS (2a)**: GPC: M_n = 5400, M_w = 9729, PDI = 1.8. ^{1}H NMR ($CDCl_3$, ppm): 0.22 (br, $Si-CH_3$); 0.59 (br, $Si-CH_2-Si$, 4H); 7.17 (br, $-CH{=}CH-$); 7.41−7.62 (br, aryl−*H*). ^{13}C NMR ($CDCl_3$, ppm): 1.1 (br), 4.2 (br), 8.28 (br), 127.21 (br), 125.12 (br), 130.65 (br), 135.32 (br), 139.3 (br). ^{29}Si NMR ($CDCl_3$, ppm): −1.76, −1.52. **S-CLPCS (2b)**: GPC: M_n = 8100, M_w = 12 960, PDI = 1.6. ^{1}H NMR ($CDCl_3$, ppm): 0.18 (br, Si−CH_3); 0.59 (br, Si−CH_2−Si, 4H); 7.1 (br, −C*H*=C*H*−); 7.41−7.62 (br, aryl−*H*). ^{13}C NMR ($CDCl_3$, ppm): 1.1 (br), 4.2 (br), 8.28 (br), 127.21 (br), 125.12 (br), 130.65 (br), 135.32 (br), 139.3 (br). ^{29}Si NMR ($CDCl_3$, ppm): −1.81, −1.58.

Dimer and Tetramer Oligomer Separation by HPLC. Separation of the dimer and tetramer oligomers was performed by using reversed-phase liquid chromatography. A C18-bonded silica column (C18, 100 Å pore, 70 × 22 mm) and a mixture of methylene chloride/acetonitrile (36/64, v/v) were used as the stationary and the mobile phase, respectively. The temperature of the column was controlled by circulating fluid from a programmable bath/circulator (NESLAB, RTE-111) and maintained at 20 °C. The injection sample concentration of polymer **2a** was about 100 mg/mL, and the flow rate of the mobile phase was 1.0 mL/min. The dimer and tetramer were separated from polymer **2a** and were characterized by NMR and MALDI-TOF. **Dimer**: ^{1}H NMR ($CDCl_3$, ppm): 0.12 (Si−CH_3); 0.53 (Si−CH_2−Si); 5.18−6.63 (aryl−C*H*=CH_2); 7.11 (−SiC*H*=C*H*Si−); 7.28−7.43 (aryl−*H*). ^{29}Si NMR ($CDCl_3$, ppm): −1.63. MALDI-TOF: (*m*/*z*) = 719, 721. **Tetramer**: ^{1}H NMR ($CDCl_3$, ppm): 0.16 (Si−CH_3); 0.53 (Si−CH_2−Si); 5.19−6.67 (aryl−C*H*=CH_2); 7.10 (−SiC*H*=C*H*Si−); 7.3−7.48 (aryl−*H*). ^{29}Si NMR ($CDCl_3$, ppm): −1.63, −1.78. MALDI-TOF: (*m*/*z*) = 1285, 1283.

(E)*-1,2-Bis(4-(trimethylsilyl)phenyl)ethene (**A**).* Trimethylchlorosilane (0.1 mol, 10.8 g) solution in THF (50 mL) was added dropwise to a freshly prepared solution of styrylmagnesium bromide (0.1 mol, 0.5 M) in a 250 mL RB flask, and the reaction mixture was stirred at room temperature. Stirring was continued for 12 h followed by overnight reflux. Dry methanol (50 mL) was added dropwise to the vigorously stirred reaction mixture. The solution was removed by slowly decanting the supernatant liquid from the precipitate. The solvents were removed from the mixture under reduced pressure, and pure trimethyl-(4-vinylphenyl)silane (GC purity > 99%) was finally isolated by vacuum distillation (yield 90%). Neat trimethyl(4-vinylphenyl)silane (10 g) was ADMET dimerized by the second-generation Grubbs catalyst in a 100 mL RB under an inert atmosphere in a glovebox. White crystals were observed within 2 h of stirring; no further stirring was possible after 6 h owing to the solidification of the reaction mixture. To isolate the pure **A**, the white crystals were washed with dry methanol three times (20 mL), and the residual solvent was evaporated under reduced pressure. Yield ≈ 99%. Melting point = 155 °C. ^{1}H NMR ($CDCl_3$, ppm): 0.26 {Si(CH_3)$_3$}; 7.11 (2H); 7.24(2H); 7.49 (2H). ^{13}C NMR ($CDCl_3$, ppm): −0.3, 125.67, 127.4, 130, 132.1, 139.21. ^{29}Si NMR ($CDCl_3$, ppm): −9.87, −8.71.

(E)*-1,2-Bis{4-(1,1,3-trimethyl-1,3-disilacyclobutane)phenyl}ethene (**B**).* To prepare **B**, 1 M solution of methylmagnesium bromide (25 mL) was added slowly to the neat 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane (0.025 mol, 4.6 g), and the reaction mixture was stirred for 10 h at ambient temperature. 1,1,3-Trimethyl-3-chloro-1,3-disilacyclobutane was fractionally distilled from a mixture of dichloro- and monochloro-substituted DSCB monomers (yield ≈ 55%). Freshly prepared styrylmagnesium bromide solution (0.05 mol, 0.5 M) in THF (50 mL) was slowly added to the 1,1,3-trimethyl-3-chloro-1,3-disilacyclobutane (0.05 mol) in 50 mL of THF, and the mixture was refluxed overnight. Evaporation of the solvent and the vacuum distillation of the crude mixture furnished 1,1,3-trimethyl-3-styryl-1,3-disilacyclobutane (**1c**) (GC purity ≈ 98%). The ADMET polymerization of the monomer **1c** was performed in the presence of the second-generation Grubbs catalyst under an inert atmosphere as described previously. Around 15% of the monomer remained unreacted even after 48 h stirring and repeated evacuation of the byproduct ethylene gas. The isolation of the pure **B** (GC purity ≈ 99%) was carried out by eluting the reaction mixture through a silica packed column with hexane. Yield ≈ 45%. ^{1}H NMR ($CDCl_3$, ppm): 0.22 (m, Si−CH_3, 18H); 0.44 (m, Si−CH_2−Si, 8H); 7.11 (2H); 7.24 (2H); 7.49 (2H). ^{13}C NMR ($CDCl_3$, ppm): −0.15, 2.08, 4.2 (broad), 8.3 (m), 125.67, 127.4, 130, 132.1, 139.21. ^{29}Si NMR ($CDCl_3$, ppm): −1.61.

*Bis(dimethyl(4-vinylphenyl)silyl)methane (**1d**).* Freshly prepared styrylmagnesium bromide (0.08 mol, 0.5 M) was added slowly to bis(chlorodimethylsilyl)methane (0.034 mol, 5 g) solution in THF (100 mL) and was refluxed for 24 h. After the termination of the residual Grignard reagent with methanol, the supernatant liquid was decanted from the flask. The solvent was evaporated under reduced pressure, and the final product was obtained by stirring the crude product under vacuum for 24 h. Yield ≈ 80%. ^{1}H NMR ($CDCl_3$, ppm): −0.03 (SiCH_3, 12H); 0.14 (SiCH_2Si, 2H); 5.15 (d, 2H); 5.69 (d, 2H); 6.6 (q, 2H); 7.32 (d, 2H); 7.4 (d, 2H). ^{13}C NMR ($CDCl_3$, ppm): −4.08; 6.88; 7.84; 114.91; 125.83; 134.12; 136.76; 138.1; 139.16. ^{29}Si NMR ($CDCl_3$, ppm): −1.36.

*(Methylene-Bridged) Oligomer mixture (**C**).* GPC: M_n = 1900, M_w = 3230, PDI = 1.7. ^{1}H NMR ($CDCl_3$, ppm): −0.03 (br, −SiCH_3), 0.14 (br, −SiCH_2Si−), 7.15, 7.32 (br, aryl−*H*), 7.4 (br, aryl−*H*). ^{13}C NMR ($CDCl_3$, ppm): −4.08, 6.88, 7.71, 125.23, 133.46, 137.69, 138.1, 139.16. ^{29}Si NMR ($CDCl_3$, ppm): −1.35.

*Bis(dimethyl(4-vinylphenyl)silyl)ethane (**1e**).* Bis(chlorodimethylsilyl)ethane was dissolved in 20 mL of dry THF and added slowly to the 2-fold excess of the THF solution of the styrylmagnesium bromide. After the addition was completed and the exothermic reaction had subsided, the mixture was refluxed for 24 h, cooled to room temperature, and added slowly to 100 mL of dry methanol. The supernatant liquid was separated by decanting and dried, and all volatiles were removed under vacuum. Pure compound was isolated by vacuum distillation of the crude mixture. Yield ≈ 65%. GC purity ≈ 98%. ^{1}H NMR ($CDCl_3$, ppm): −0.03 (SiCH_3, 12H); (SiCH_2Si, 4H) 0.14, 5.15 (d, 2H), 5.69 (d, 2H), 6.6 (q, 2H), 7.32 (d, 2H), 7.4 (d, 2H). ^{13}C NMR ($CDCl_3$, ppm): −4.08, 6.88, 7.84. 114.91, 125.83, 134.12, 136.76, 138.1, 139.16. ^{29}Si NMR ($CDCl_3$, ppm): −1.38.

*(Ethylene-Bridged) Oligomer Mixture (**D**).* M_n = 2000, M_w = 3400, PDI = 1.7. ^{1}H NMR ($CDCl_3$, ppm): −0.03 (br, −SiCH_3), 0.14 (br, −SiCH_2CH_2Si−), 7.17, 7.34 (br, aryl−*H*), 7.45 (br, aryl−*H*). ^{13}C NMR ($CDCl_3$, ppm): −4.08, 6.88, 7.71, 125.3, 133.16, 137.79, 138.16, 139.19. ^{29}Si NMR ($CDCl_3$, ppm): −1.36.

Acknowledgment. This work was supported by a grant from the New York State Office of Science, Technology and Academic Research (NYSTAR TTIP grant). We thank Professor E. Fred Schubert and graduate student Qi Dai (Department of Physics, RPI) for their assistance with the measurement of photoluminescence, Dr. Dmitri Zagorevski (Center for Biotechnology and Interdisciplinary Studies, RPI) for obtaining the MALDI-TOFF mass spectra, and Dr. Kungsoek Oh (Department of Chemistry and Chemical Biology, RPI) for his help in running the HPLC experiments. Our thanks are also due to Professor Chang Y. Ryu (Department of Chemistry and Chemical biology, RPI) for the use of his UV chamber, TGA (Mettler-Toledo Thermal Analysis grant), and HPLC instruments.

Supporting Information Available: GPC chromatograms, MALDI TOF spectra, NMR, and FT-IR spectra with assignments. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Kim, H. K.; Ryu, M.-K.; Kim, K.-D.; Lee, S.-M. *Macromolecules* **1998**, *31*, 1114–1123.
(2) Tanaka, K.; Ago, H.; Yamabe, T.; Ishikawa, M.; Ueda, T. *Organometallics* **1994**, *13*, 3496–3501.
(3) Matsumi, N.; Umeyama, T.; Chujo, Y. *Macromolecules* **2001**, *34*, 3510–3511.
(4) Kwak, G.; Masuda, T. *Macromolecules* **2002**, *35*, 4138–4142.
(5) Wang, F.; Kaafarani, B. R.; Neckers, D. C. *Macromolecules* **2003**, *36*, 8225–8230.
(6) Chen, R.-M.; Chien, K.-M.; Wong, K.-T.; Jin, B.-Y.; Luh, T.-Y. *J. Am. Chem. Soc.* **1997**, *119*, 11321–11322.
(7) Mori, A.; Takahisa, E.; Kajiro, H.; Nishihara, Y. *Macromolecules* **2000**, *33*, 1115–1116.
(8) Miao, Y.-J.; Herkstroeter, W. G.; Sun, B. J.; Wong-Foy, A. G.; Bazan, G. C. *J. Am. Chem. Soc.* **1995**, *117*, 11407.
(9) Solaro, R.; Galli, G.; Ledwith, A.; Chiellini, E. In *Polymer Photophysics*; Phillips, D., Ed.; Chapman & Hall: London, **1985**; pp 377−430.
(10) Walree, V. C. A.; Roest, M. R.; Schuddeboom, W.; Jenneskens, L. W.; Verhoeven, J. W.; Warman, J. M.; Kooijman, H.; Spek, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 8395.
(11) Cheng, Y.-J.; Hwu, T.-Y.; Hsu, J.-H.; Luh, T.-Y. *Chem. Commun.* **2002**, 1978–1979.
(12) Ohshita, J.; Kunai, A. *Acta Polym.* **1998**, *49*, 379–403.
(13) Fang, M.-C.; Watanabe, A.; Matsuda, M. *Macromolecules* **1996**, *29*, 6807–6813.
(14) Ohshita, J.; Kanaya, D.; Ishikawa, M.; Koike, T.; Yamanaka, T. *Macromolecules* **1991**, *24*, 2106.
(15) Corriu, R. J. P.; Guerin, C.; Henner, B.; Kuhlmann, T.; Jean, A.; Garnier, F.; Yassar, A. *Chem. Mater.* **1990**, *2*, 351.
(16) Yuan, C.-H.; West, R. *Appl. Organomet. Chem.* **1994**, *8*, 423.
(17) Corriu, R. J. P.; Douglas, W. E.; Yang, Z. X.; Karakus, Y.; Cross, G. H.; Bloor, D. *J. Organomet. Chem.* **1993**, *455*, 69.
(18) Hu, S. S.; Weber, W. P. *Polym. Bull.* **1989**, *21*, 133.
(19) Ohshita, J.; Matsuguchi, A.; Furumori, K.; Hong, R.-F.; Ishikawa, M. *Macromolecules* **1992**, *25*, 2134.
(20) Ohshita, J.; Kanaya, D.; Watanabe, T.; Ishikawa, M. *J. Organomet. Chem.* **1995**, *489*, 165.
(21) Corriu, R. J. P.; Douglas, W. E.; Yang, Z.-X. *J. Polym. Sci., Part C: Polym. Lett.* **1990**, *28*, 431.
(22) Ijadi-Maghsoodi, S.; Barton, T. J. *Macromolecules* **1990**, *23*, 4485.
(23) Corriu, R. J. P.; Douglas, W. D.; Yang, Z.-X. *J. Organomet. Chem.* **1991**, *417*, C50.
(24) Fang, M.-C.; Watanabe, A.; Matsuda, M. *Chem. Lett.* **1994**, *23*, 13–16.
(25) Mao, S. S. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1995**, *117*, 5365.
(26) Mukherjee, N.; Peetz, R. M. *Macromolecules* **2008**, *41*, 6677–6685.
(27) Smith, D. W.; Wagener, K. B. *Macromolecules* **1993**, *26* (7), 1633–1642.
(28) Smith, D. W.; Wagener, K. B. *Macromolecules* **1993**, *26* (14), 3533–3537.
(29) Church, C.; Pawlow, J. H.; Wagener, K. B. *Macromolecules* **2002**, *35* (15), 5746–5751.
(30) Grubbs, R. H., Ed.; *Handbook of Olefin Metathesis*; Wiley-VCH: Weinheim, **2003**; Vols. *1−3*.
(31) Wu, Z.; Papandrea, J. P.; Apple, T.; Interrante, L. V. *Macromolecules* **2004**, *37* (14), 5257–5264.
(32) Hyun, J.; Han, J.; Ryu, C. Y.; Interrante, L. V. *Macromolecules* **2006**, *39* (25), 8684–8691.
(33) Rathore; Jitendra, S.; Interrante, L. V. *PMSE Prepr.* **2007**, *87*, 800–801.
(34) Rathore; Jitendra, S.; Interrante, L. V. *PMSE Prepr.* **2008**, *99*, 241–242.
(35) Wu, H. J.; Interrante, L. V. *Chem. Mater.* **1989**, *1* (5), 564–568.
(36) Sakurai, H. In *Silicon Chemistry*; Corey, J., Y., Corey, E. R., Gaspar, P. P., Eds.; Ellis Horwood: Chichester, **1988**; Chapter 16.
(37) Morisaki, Y.; Fujimura, F.; Chujo, Y. *Organometallics* **2003**, *22*, 3553–3557.
(38) Kwak, G.; Masuda, T. *Macromol. Rapid Commun.* **2002**, *23*, 68–72.
(39) Interrante, L. V.; Liu, Q.; Rushkin, I.; Shen, Q. *J. Organomet. Chem.* **1996**, *521*, 1–10.