

Synthesis of *o*-Xylene-Organosilicon Hybrid Polymer and Its Optical Properties

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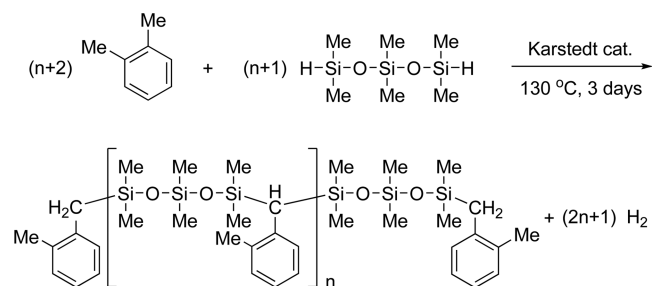
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We present synthesis of a new kind of organic-inorganic hybrid polymer, poly xylene-hexamethyltrisiloxane hybrid (PXS) by a new synthetic way from *o*-xylene and 1,1,3,3,5,5-hexamethyltrisiloxane. The merged molecular structure of the two monomeric components for the PXS polymer was confirmed by ¹³C- and ¹H-NMR, and FT-IR. Its optical absorption and emission properties were investigated by UV-vis absorption and photoluminescence (PL) spectroscopy. The PXS exhibits absorption at 265 nm which is the same with the *o*-xylene but tailing up to nearly 400 nm, which is maybe related the polymeric structure of the PXS. For the PL investigation, the PXS shows red-shift of the peak from 288 nm (*o*-xylene) to 372 nm in the case of excitation at 265 nm, at which both PXS and *o*-xylene have sufficiently high absorption for excitation. When 325-nm laser is used for excitation, the PXS shows a broader peak at 395 nm compared to the excitation at 265 nm and the *o*-xylene shows no luminescence probably due to the lack of absorption at 325 nm.

Key Words : Organic-inorganic hybrid materials, Polyorganosiloxanes, *o*-Xylene, 1,1,3,3,5,5-Hexamethyltrisiloxane, Photoluminescence

Introduction

Organic-inorganic hybrid materials which contain both components mixed at a molecular level have been widely used for various applications due to their superior mechanical, thermal, optical, and electrical properties.¹⁻³ Polyorganosiloxane (R_nSiO_{2-0.5n}) is one of the most representative organic-inorganic hybrid materials where R is any of alkyl, alkylene, aryl, arylene, and so on.^{4,5} Its electrical and optical stabilities from the inorganic -Si-O-Si- backbone structure as well as additional functionalities from the organic moiety has made it diversely applicable for electronic and optoelectronic fields such as gate insulator in transistor,⁶ insulating matrix,⁷ charge trap material in memory device,⁸ encapsulant in light-emitting diode (LED),⁹ and so on. Such polyorganosiloxane is usually known to be easily synthesized by hydrolysis/condensation polymerization (so-called sol-gel polymerization) of alkoxy-containing organosilicone monomer or hydrosilylation between vinyl-containing and H-terminated silicone monomers usually in a presence of Pt catalyst.



Scheme 1. Synthesis of poly xylene-hexamethyltrisiloxane hybrid (PXS).

Herein, we report a new kind of organic-inorganic hybrid polymer, poly xylene-hexamethyltrisiloxane hybrid (PXS), synthesized by a new synthetic way and its optical absorption and luminescence properties (Scheme 1). Solution of 1,1,3,3,5,5-hexamethyltrisiloxane in *o*-xylene was heated at 130 °C in the presence of Karstedt's catalyst (Pt-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex) in Ar atmosphere for 3 days, in which the *o*-xylene was used as solvent and reactant as well.

Experimental

Chemicals. All chemicals were used as received without further purification. *o*-Xylene (anhydrous, 97%), and tetrahydrofuran (THF, anhydrous, ≥ 99.9%) were purchased from Sigma-Aldrich Co. Inc. (St. Louis, MO, USA). 1,1,3,3,5,5-Hexamethyltrisiloxane (> 95%) and Karstedt catalyst, platinum-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (2 wt % solution in toluene) were purchased from Gelest Inc. (Morrisville, PA, USA) and JSI Silicone Co. (Seongnam-si, South Korea), respectively.

Synthesis of Poly Xylene-hexamethyltrisiloxane Hybrid (PXS). The synthesis was carried out using conventional Schlenk line technique. Two solutions were prepared in a glove box filled with Ar gas; platinum-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (2 wt % in toluene 40 mg) solution in *o*-xylene (2 mL), and 1,1,3,3,5,5-hexamethyltrisiloxane (300 mg) solution in *o*-xylene (2 mL). The Pt catalyst solution was added to the *o*-xylene (75 mL) connected to a condenser in Schlenk line under Ar atmosphere. Then, the 1,1,3,3,5,5-hexamethyltrisiloxane solution was dropped wisely into the solution. The solution was heated at 130 °C and kept for 3 days under Ar condition. After drying the solution from the remaining *o*-xylene, only THF-soluble

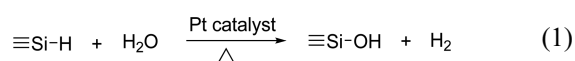
one was obtained by dissolving and filtering (PTFE, 0.2 μm). Finally, the PXS was obtained after drying at 110 $^{\circ}\text{C}$ under reduced pressure of approximately 1×10^{-2} torr overnight.

Characterization. All NMR data were collected on a superconducting FT-NMR 300 MHz (Varian Inc, Palo Alto, California, U.S.A.). Chemical shifts are reported in parts per million (ppm) and THF- d_8 was used as the solvent. The FT-IR measurements were conducted on a Nicolet 380 spectrometer (Waltham, MA, USA) operated in the mid-IR range of 4000-400 cm^{-1} , with all spectra obtained at a spectral resolution of 7.7 cm^{-1} in transmittance mode. Molecular weights were measured by gel permeation chromatography (GPC) using a Waters Breeze HPLC system with THF as the eluent. Molecular weights were calibrated using polystyrene as the standard. UV-vis absorbance spectroscopy was performed in the 200-1000 nm range with a SCINCO S-3150 spectrophotometer. Photoluminescence (PL) spectroscopy was carried out using a Fluorometer (Cary Eclipse, Agilent) with a Xenon pulse lamp at 265 nm and 325 nm of 15 W power.

Results and Discussion

The chemical structure of the synthesized PXS is investigated by NMR (Figure 1) and FT-IR (Figure 2). In ^{13}C -NMR spectrum (Figure 1(a)), nearly six peaks from the aromatic ring are detected at 139.63, 135.99, 130.51, 127.75, 127.56, and 126.44 ppm (**a-f**), while pure *o*-xylene shows different chemical shifts at 136.98, 130.23, and 126.55 ppm (Supporting Figure S1), implying changes in chemical environment of the xylene molecule due to functionalization. In addition, four characteristic peaks were detected at 63.22 (**g**), 30.68 (**h**), 18.74 (**i**), and near 1.42 (**j**) ppm. The peaks at 30.68 (**h**) and 63.22 (**g**) ppm are attributed to benzylic carbons of the *o*-xylene which are bi- and mono-functionalized with methylsilane (H-SiMe) of the 1,1,3,3,5,5-hexamethyltrisiloxane^{10,11} and methylsilanol (HO-SiMe),^{12,13} respectively, by transition metal (Pt) catalyzed dehydrogenative coupling reaction, as drawn in Figure 1(c) *fragment I*¹⁴⁻¹⁶ and *II*.^{17,18}

The *fragment II* would be resulted from hydrolyzed 1,1,3,3,5,5-hexamethyltrisiloxane monomer reacting with *o*-xylene by following catalytic reaction:^{19,20} the silane (Si-H) group in the 1,1,3,3,5,5-hexamethyltrisiloxane undergoes the catalyzed-hydrolysis with water which was probably residual in the *o*-xylene solvent:



In addition to the direct reaction with the *o*-xylene, giving rise to the *fragment II*, the newly-formed silanol group (Si-OH) can further react with another silane group to form siloxane (Si-O-Si) by following dehydrogenative coupling reaction:

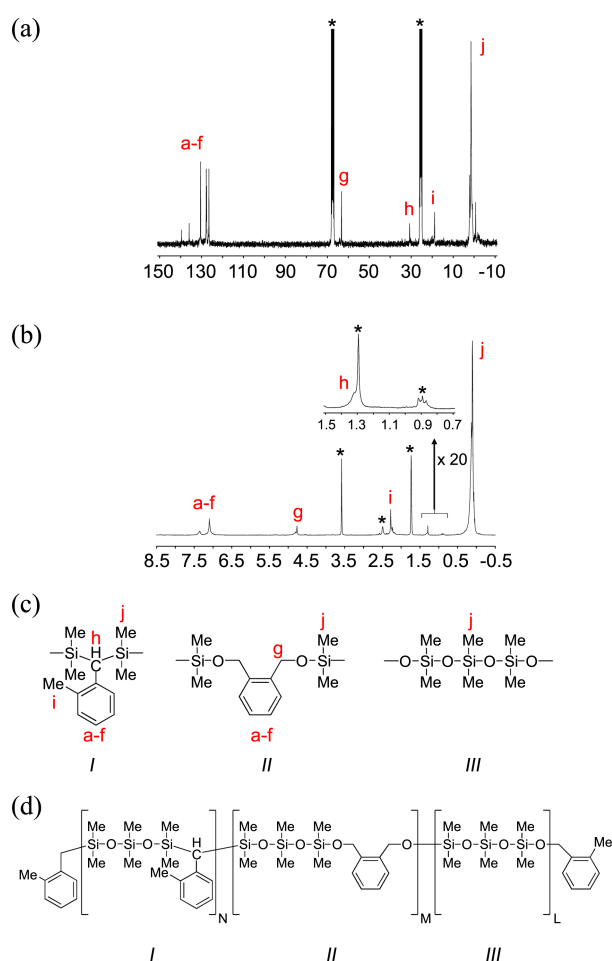
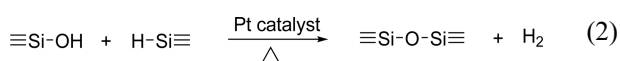
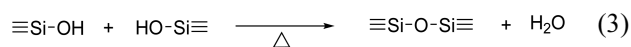


Figure 1. (a) ^{13}C - (75 MHz; THF- d_8), (b) ^1H -NMR spectra (300 MHz; THF- d_8) of the PXS, (c) its fragmentary molecular structures, and (d) polymeric molecular structure. The fragments I, II, and III could be alternatively repeated in the PXS polymer. *THF, residual H_2O , and *n*-hexane.

The siloxane also can be formed by self-condensation between the silanol groups, releasing a water molecule:



The resultant siloxanes from Eqs. (2) and (3) can react with the *o*-xylene to give the *fragment III* in Figure 1(c). The mechanistic consideration for these Pt-catalyzed reactions is under investigation.

The corresponding protons were found at 7.37-7.08 (**a-f**), 4.81 (**g**),^{12,13} and 1.33 ppm (**h**)^{10,11} in ^1H -NMR spectrum (Figure 1(b)). The asterisks indicate peaks coming from THF NMR solvent (3.59 and 1.73 ppm), residual water (~ 2.6 ppm), and *n*-hexane (1.29 and 0.89 ppm). Note that the proton in methine group (-CH-) of the *fragment I* is observable at 1.33 ppm although it is not distinct due to neighboring with that from *n*-hexane. By combining the NMR results, the polymeric molecular structure of the PXS is drawn in Figure 1(d). In the ^1H -NMR spectrum (Figure 1(b)), the integral ratio of **g**:**i**:**j** is around 1:2.3:32. Because the ratio of **g**:**i** is 1:2.3, the repeating number N for the

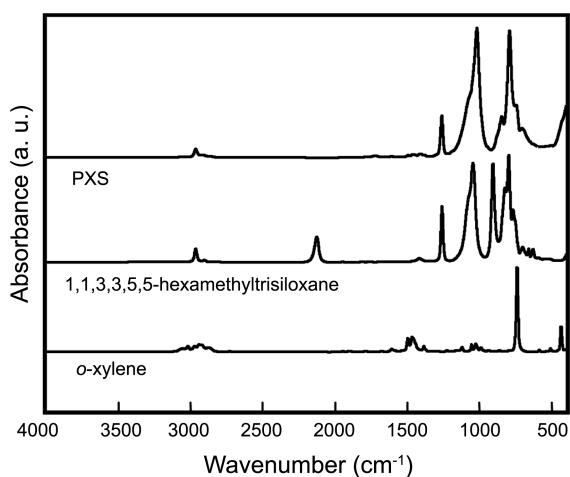


Figure 2. FT-IR spectra of the synthesized poly xylene-hexamethyltrisiloxane hybrid (PXS) and two reagents: 1,1,3,3,5,5-hexamethyltrisiloxane and *o*-xylene.

fragment I is approximately three times higher than *M* for the *fragment II* ($N = 3M$). Based on this relation, the excess number of protons (*j*) from methyl groups in the siloxane chain can be calculated so that the repeating number *L* for the *fragment III* is deduced to be approximately 3 ($N:M:L = 3:1:3$). Note that the *fragments I, II, and III* could be repeated not only sequentially but also alternatively in the PXS polymer.

The molecular structure of the PXS was also confirmed by FT-IR (Figure 2). While 1,1,3,3,5,5-hexamethyltrisiloxane shows its characteristic peaks at 2960 cm^{-1} (sp^3 C-H stretching in methyl groups), 2130 cm^{-1} (Si-H stretching), 1260 cm^{-1} (Si-CH₃ bending), $1100\text{--}1000\text{ cm}^{-1}$ (Si-O-Si asymmetric stretching), 910 cm^{-1} (Si-H bending), and 800 cm^{-1} (Si-C vibration),²¹⁻²³ those of *o*-xylene are detected at $3110\text{--}3070\text{ cm}^{-1}$ (sp^2 C-H stretching in aromatic group), $2970\text{--}2880\text{ cm}^{-1}$ (sp^3 C-H stretching in methyl groups), $1600\text{--}1400\text{ cm}^{-1}$ (aromatic C=C stretching), and 740 cm^{-1} (out-of-plane C-H wag in *ortho*-position substituted benzene ring) which is a unique peak of *o*-xylene.^{21,24} Basically, the synthesized PXS shows most of the peaks from both reagents, indicating merged molecular structure of both, except for the disappearance of the peaks from the Si-H groups at 2130 and 910 cm^{-1} due to the polymerization reaction on them, of which the molecular structure is consistent with that expected from the NMR results. The weight-averaged molecular weight (*M_w*) of the PXS polymer was determined by gel permeation chromatography (GPC) to be approximately 7160 with a polydispersity of 5.6 (Supporting Figure S2).

The optical absorption and emission properties of the synthesized PXS were investigated by UV-vis absorption and photoluminescence (PL) spectroscopy (Figure 3). Both spectra were measured for the solutions dissolved in tetrahydrofuran (THF) with a concentration of 0.01 wt %. While the *o*-xylene shows a sharp peak at 265 nm (λ_{max}) which is attributed to $\pi\text{-}\pi^*$ transitions in the aromatic group,²⁵ the PXS exhibits absorption at the same λ_{max} but tailing up to nearly 400 nm, which is maybe related the polymeric

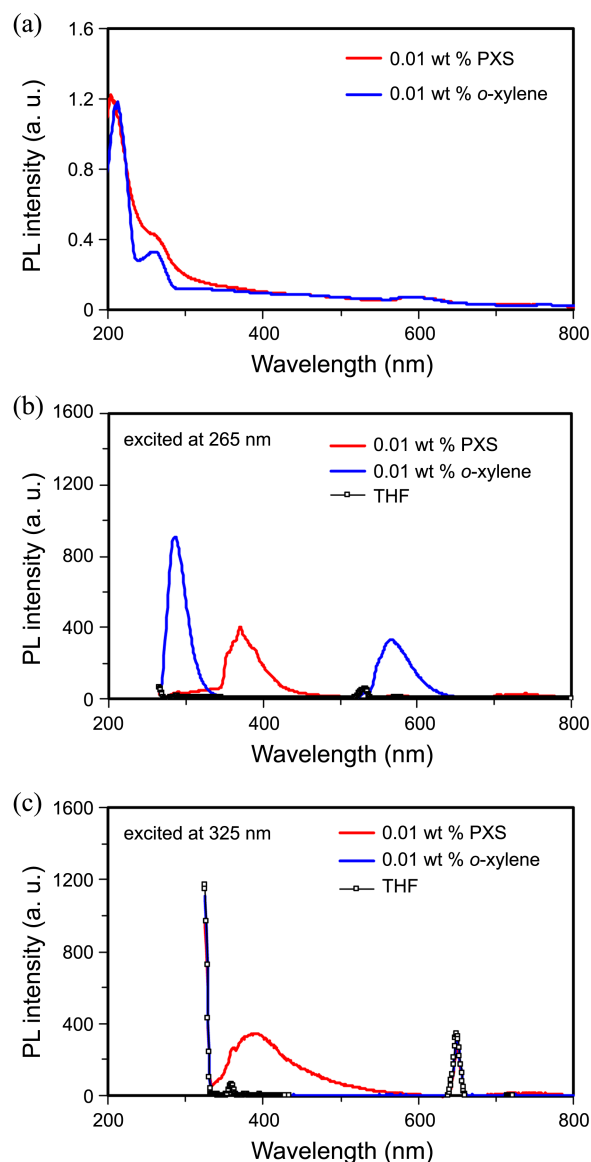


Figure 3. (a) UV-vis absorption and PL spectra by excitation at (b) 265 nm and (c) 325 nm of PXS and *o*-xylene in solution states dissolved in THF with concentration of 0.01 wt %.

structure of the PXS (Figure 3(a)). The PL spectra were measured using two different excitation wavelengths; 265 nm and 325 nm (Figure 3(b) and (c)). In the case of excitation at 265 nm, at which both PXS and *o*-xylene have sufficiently high absorption for the excitation, the PXS shows red-shift of the peak from 265 nm (*o*-xylene) to 372 nm. One another peak at 570 nm from the *o*-xylene is thought to be an emission from *o*-methylbenzyl radical which is generated by photodissociation of *o*-xylene.²⁶ When 325-nm light is used for excitation, the *o*-xylene shows no luminescence probably due to the lack of absorption at 325 nm. The PXS shows a broader peak at 395 nm (λ_{max}), compared to when excited at 265 nm. In the both PL spectra (Figure 3(b) and (c)), peaks at the wavelength of exactly two times longer than excitation light source are observed; 530 nm for 265-nm excitation (Figure 3(b)) and

650 nm for 325-nm excitation (Figure 3(c)). This is from the multiple-order diffraction of excitation light in the fluorometer equipped with a diffraction-grating type monochromator, not from the samples.²⁷

Such optical properties of the PXS polymer would be related to its electronic structure and/or excitation (by absorption) and decay processes. The details of the photo-physical origins are under investigation.

Conclusion

A new kind of organic-inorganic hybrid polymer, poly xylene-hexamethyltrisiloxane hybrid (PXS) was synthesized by a new synthetic way. The molecular structure of the polymer was analyzed by ¹³C- and ¹H-NMR, and FT-IR. Its optical properties were investigated by UV-vis absorption and PL spectroscopy. Compared to its monomeric optically-active component, *o*-xylene, the PXS shows extension of absorption peak in UV-vis spectrum to the longer wavelength and red-shift in PL spectrum, which is probably related to its polymeric molecular structure and still under the investigation.

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Supporting Information. Supporting Figure S1 (¹³C-NMR result of *o*-xylene), Supporting Figure S2 (GPC results), and Supporting Figure S3 (UV-vis results according to the solution concentration).

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