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Optical Properties of Silicon Network Polymers

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ABSTRACT: The optical properties of silicon network polymers with isobutyl, hexyl, cyclohexyl, β-phenethyl, and 2-phenylpropyl side chains are investigated. In complete contrast to linear polysilanes, the observed photoluminescence is in the visible region and it has a broad bandwidth. This photoluminescence is shown to originate from the high dimensionality of the silicon network structures of these polymers.

Introduction

Polysilanes are well-known as one-dimensional (1D) silicon-based materials that have alkyl or aryl groups in their side chains. Many kinds of polysilanes have been synthesized[1] for application as silicon–carbide precursors[1] or as photoresists.[1] Polysilanes also have other attractive physical properties such as photoluminescence,[2] photoconductivity,[3,4] nonlinear susceptibility,[5] and high mobility,[6] indicating that they are semiconducting polymers. However, the band-gap energies observed to date are undesirably high at 3–4 eV.

Keeping the band-gap energy (E_g) at values below 3–4 eV is one of the most important steps in developing the semiconducting properties of silicon-based materials. E_g can be estimated from the band structure formed by the delocalized σ electrons of silicon bonding along the silicon backbone.[7,8] Silicon-based materials with E_g between 1 and 4 eV could be created by controlling this electronic band structure.

Strong electron delocalization in the trans conformation[9] or a decrease of the ionization potential by electronic interaction between the backbone and the side chains[7] is very important for reducing the E_g of polysilane. However, even in bis(*p*-hexylphenyl)polysilane, which has both trans conformation and the σ–π mixing effect that occurs between the σ orbitals along the backbone and the π orbitals localized at phenyl rings, the value of E_g is never less than 3 eV.[10]

This research is aimed at reducing E_g by increasing the dimensionality of the silicon network backbone based on the conjecture that a high-dimensional structure would result in a smaller band gap close to the 1.1 eV of crystalline silicon (c-Si).[11] Recently, high-dimensional silicon network polymers have been synthesized from trichlorosilanes by a Wurtz type reaction while using ultrasound during polymerization.[12,13] However, the optical properties of the resulting silicon network polymers are not clearly understood.

In this study, several types of polymers with different side chains were prepared for optical measurements to investigate the distinct characteristics of their silicon backbones, which are independent of their side chains. Five different silicon network polymers were synthesized, and their optical properties were measured: their side chains were isobutyl, hexyl, cyclohexyl, β-phenethyl, and 2-phenylpropyl. All of these polymers exhibited visible photoluminescence with a broad bandwidth. This suggests that the photoluminescence originates from high-dimensional silicon network structures with an E_g of 2–3 eV. We will discuss the optical properties of these polymers on the basis of the dimensional structure of the silicon backbone.

Experimental Section

The silicon network polymers were synthesized by a Wurtz type reaction from organotrichlorosilanes, using molten sodium as the catalyst and a crown ether as cocatalyst, in an argon atmosphere, without using ultrasound. All the reagents, except sodium metal, were purified prior to use.

The molecular weight distributions of the polymers synthesized in this work were measured by a Toyosoda HLC-837 gel permeation chromatograph using a tetrahydrofuran solution. All molecular weights were reported versus polystyrene standard. Solution ^{1}H, ^{13}C, and ^{29}Si NMR spectra were observed by a Varian XL-200 spectrometer. All chemical shifts were referenced to tetramethylsilane standard in $CDCl_3$. IR absorption spectra were obtained by a Hitachi 260-50 infrared spectrophotometer using KBr disk. Absorption spectra in a range from 200 to 850 nm were measured using a Hitachi 340L recording spectrophotometer. Photoluminescence spectra were measured in a cryostat, in vacuo, using a Hitachi 850 fluorescence spectrophotometer. Thin polymer films spin-coated on SiO_2 substrates from toluene solution were used for measuring these spectra.

Synthesis of the hexyl–silicon network polymer was carried out as follows.[14] Dry toluene (50 mL) containing sodium metal (1.9 g) and 12-crown-4 (0.41 g) was refluxed while being stirred in an argon atmosphere. Hexyltrichlorosilane (5 g) was added dropwise into this mixture. After the addition was complete, the reaction mixture was stirred for 1 h. It was cooled down to room temperature, and ethanol (30 mL) was added to remove the sodium metal and to terminate the end groups. After an additional 1 h of stirring, the mixture was poured into ethanol (600 mL) and the precipitate was separated from the solution by filtration. The filtrate was washed with water, and a yellow powder was obtained. This powder was reprecipitated using a toluene–methanol system. The final result was 440 mg (17%) of yellow powder that was soluble in an ordinary organic solvent such as toluene, tetrahydrofuran, or chloroform.

The other silicon network polymers were synthesized by the same procedure but using different monomers. This resulted in another four polymers with isobutyl, cyclohexyl, β-phenethyl, or 2-phenylpropyl side chains. These polymers were all soluble in ordinary organic solvents such as toluene, tetrahydrofuran, or chloroform. Their yields and color are listed in Table I. All polymers are yellow or orange powders with yields of 15–80%.

The molecular weight distributions of the synthesized polymers are shown in Figure 1. They all have similar shapes and their weight average molecular weights are 3000–12 000, except that the hexyl–silicon network polymer also exhibited a higher molecular weight fraction ranging from 100 000 to 1 000 000.

^{29}Si NMR spectra of the polymers were observed in order to clarify how the silicon atoms in the polymers connect with each other. In the case of the hexyl–silicon network polymer, it exhibited a very broad resonance peak at δ_{Si} = −61 as shown in Figure 2. However, there were no other peaks, such as ones due to Si–O–Si or 1D silicon bonding. This value of −61 ppm compares with other silicon materials as follows: Dihexylpolysilane and methylhexylpolysilane have δ = −24.8 and −32.0, respectively.[15] These two materials consist of silicon atoms with

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Table I
Yields and the Colors of the Synthesized Polymers[a]

side chain	yield, %	color
isobutyl	41.1	orange
hexyl	17.0	yellow
cyclohexyl	14.8	yellow
β-phenethyl	81.9	pale yellow
2-phenylpropyl	30.7	pale yellow

[a] Polymerization time for isobutyl-silicon network polymer was only 30 min.

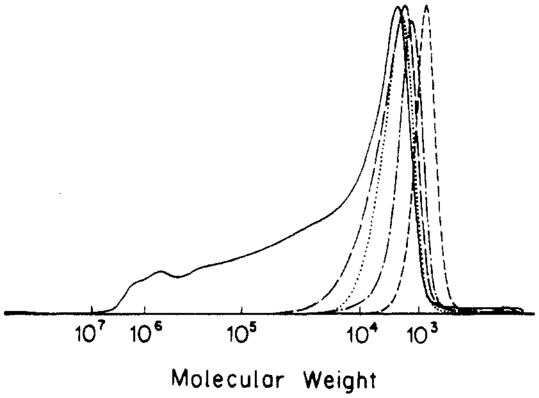

Figure 1. Molecular weight distribution measured by gel permeation chromatography: (···) isobutyl, (—) hexyl, (- - -) cyclohexyl, (– –) β-phenethyl, (– · · –) 2-phenylpropyl.

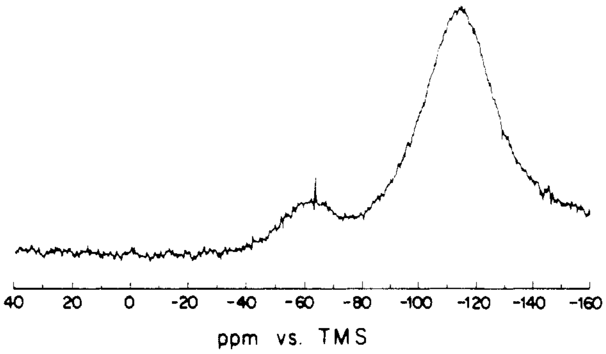

Figure 2. ^{29}Si NMR spectrum of the hexyl-silicon network polymer. The large peak around 110 ppm arises from the glass test tube.

two silyl substituents. On the other hand, $CH_3(CH_2)_5Si(SiMe_3)_3$ and $PhSi(SiMe_3)_3$, which have silicon atoms with three silyl substituents, have peaks at −74.8 and −74.2, respectively.[12] Therefore, the chemical shift observed in the hexyl-silicon network polymer is similar to the latter values, suggesting the presence of silicon atoms having three silyl substituents. The other silicon network polymers with different side chains also showed chemical shifts of around −60 ppm, so they are considered to consist of silicon atoms with three silyl substituents.

IR spectra of the polymers were also observed. The hexyl-silicon network polymer had peak wavelengths that were basically the same as the polymer synthesized in previous experiments using ultrasound.[13] In addition to these peaks, weak broad absorbances between 1100 and 1000 cm^{-1} were also observed in all the polymers. These spectra indicate that the polymers contain small amounts of Si–O–Si or Si–O–R (R = alkyl or aryl group), even though these resonance peaks were not observed by ^{29}Si NMR.

The NMR peaks and the IR absorbance peaks of each polymer are listed below. **Isobutyl**: ^{1}H NMR δ 1.01 (br), 1.85 (br); ^{13}C NMR δ 23.80, 26.40, 28.32; ^{29}Si NMR δ −60; IR 2950 (vs), 2920 (s), 2860 (s), 2350 (w), 1456 (s), 1393 (m), 1376 (s), 1359 (s), 1322 (m), 1223 (s), 1156 (s), 1081 (m), 1023 (m), 952 (w), 822 (m), 718 (s), 680 (w). **Hexyl**: ^{1}H NMR δ 0.89 (br), 1.29 (br); ^{13}C NMR 14.15, 22.83, 30.38, 31.76, 34.40; ^{29}Si NMR δ −61; IR 2977 (vs), 2936 (vs), 2885 (vs), 2870 (vs), 2086 (w), 1475 (s), 1465 (s), 1417 (w), 1386 (m), 1348 (w), 1301 (w), 1260 (w), 1172 (w), 1108 (m), 1083 (w), 1051 (w), 1009 (m), 959 (m), 900 (w), 849 (w), 767 (w), 680 (s). **Cyclohexyl**: IR 2920 (vs), 2845 (vs), 2670 (w), 2080 (w), 1705 (w), 1619 (w), 1460 (m), 1445 (s), 1353 (w), 1292 (w), 1267 (w), 1169 (s), 1083 (m), 1037 (m), 993 (s), 911 (w), 887 (s), 845 (s), 812 (m), 700 (m), 521 (m). **β-Phenethyl**: ^{1}H NMR δ 1.645 (br), 2.76 (br), 7.04 (br); ^{13}C NMR δ 18.32, 35.95, 125.7, 126.7, 128.3, 143.1; ^{29}Si NMR δ −60; IR 3060 (m), 3024 (s), 2920 (s), 2330 (w), 1600 (s), 1491 (s), 1447 (s), 1065 (m), 1025 (m), 881 (w), 729 (s), 693 (vs). **2-Phenylpropyl**: ^{1}H NMR δ 1.31 (br), 2.96 (br), 7.18 (br); ^{13}C NMR δ 26.6, 39.1, 126.2, 128.3, 149.2; ^{29}Si NMR δ −60; IR 3065 (m), 3030 (s), 2960 (s), 2925 (s), 2870 (s), 2360 (w), 1603 (m), 1491 (s), 1451 (s), 1400 (w), 1370 (m), 1277 (w), 1220 (w), 1184 (w), 1156 (w), 1095 (m), 1072 (m), 1030 (m), 1008 (w), 910 (m), 761 (s), 699 (vs), 532 (m).

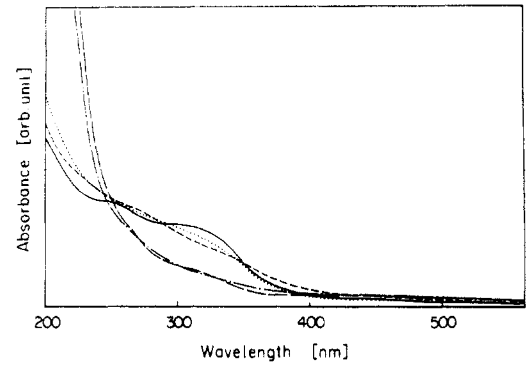

Figure 3. Optical absorption spectra of silicon network polymers: (···) isobutyl, (—) hexyl, (- - -) cyclohexyl, (– –) β-phenethyl, (– · · –) 2-phenylpropyl.

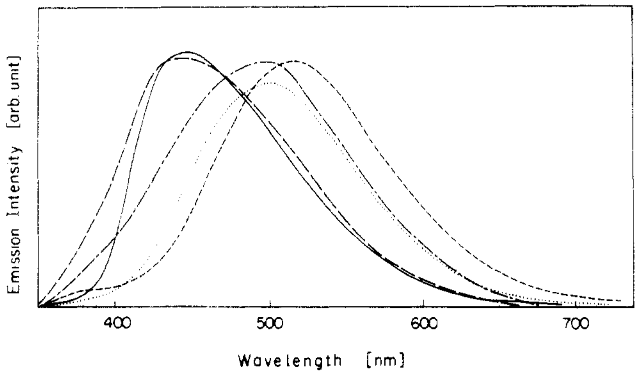

Figure 4. Emission spectra of silicon network polymers (excitation 300 nm): (···) isobutyl, (—) hexyl, (- - -) cyclohexyl, (– –) β-phenethyl, (– · · –) 2-phenylpropyl.

Results and Discussion

UV Absorption. UV absorption spectra of the synthesized polymers are shown in Figure 3. Polymers with alkyl groups as side chains exhibited a strong absorption in the shorter wavelength region of less than 250 nm, an absorption shoulder at about 350 nm, and a long tail that extended to 800 nm. For the polymers with phenyl groups as side chains, the shoulder absorption could not be observed clearly, but, in all cases, the absorbance decreased monotonically as the wavelength increased. These spectrum features are quite different from those of 1D silicon polymers, such as dihexylpolysilane, which has two sharp absorption peaks at 315 and 365 nm, with the half-widths of 30 and 18 nm, respectively.[16]

Photoluminescence. The photoluminescence spectra of these polymers are shown in Figure 4. Each polymer has a broad photoluminescence spectrum in the visible light region, irrespective of its side-chain group. They all show a long tail stretching from below 400 nm to over 700 nm. This is also quite different from linear polysilanes, such as dihexylpolysilane, which has a sharp emission spectrum peak at 380 nm with a half-width of 13 nm at room temperature.

The first possibilities we considered for the origin of the photoluminescence in silicon network polymers were the contributions of impurities, side chains, and degradation products.

Polysilanes are usually synthesized in the same manner as silicon network polymers. The only difference is the use of dichlorosilane, instead of trichlorosilane, as the monomer. Although many optical investigations have been carried out using polysilanes synthesized in this way,[17] photoluminescence arising from impurities has never been observed. Furthermore, trichlorosilane, which is used as the monomer, does not in itself exhibit photoluminescence. Therefore, the photoluminescence observed in these polymers does not arise from impurities or from the monomers.

Next, we considered effects arising from the side chains. Photoluminescence arising from these effects was only observed in special cases: from the formation of excimer sites in methylnaphthylpolysilane[18] and from the interaction between the silicon backbone and the side chains in methylphenylpolysilane[19] at low temperature. The photoluminescence in these two cases depended strongly on their side-chain features: stacking effects or $\sigma-\pi$ conjugation, respectively. Silicon network polymers, however, exhibited no marked differences in photoluminescence spectra, regardless of their side chains. This suggests that photoluminescence is not caused by side-chain effects.

The contribution of degradation products such as the siloxane compounds accompanying Si–O–Si bonding was also considered. Photoluminescence spectra of a sample were measured before and after exposure to sunlight. After exposure, the photoluminescence in the longer wavelength region lost its intensity and the photoluminescence peak shifted to a lower wavelength, and the peak intensity was less than half of that in the original sample. If photoluminerscence arises from the degradation products, its intensity should increase as the polymer degrades during exposure. However, no such increase in photoluminescence intensity was observed. Therefore, the photoluminescence does not result from the Si–O–Si network initially present in the as-grown polymers nor from that subsequently produced by photodegradation.

In conclusion, the photoluminescence originates from the silicon backbone itself. The next section discusses how the silicon backbone can emit visible light.

Network Structure. If the polymers had a 1D silicon backbone structure, the absorption spectra would have to have sharp absorption peaks. However, the absorption spectra obtained from our polymers do not show any sharp peaks. This suggests that the polymers form silicon network structures that have higher network dimensions.

Photoluminescence observations for various silicon-based materials are shown in Figure 5. The peak energy values of the photoluminescence spectra for amorphous silicon (a-Si:H),[20] polysilane alloy,[20] hexyl–silicon network polymer, and dihexylpolysilane are 0.8, 1.2, 2.8, and 3.3 eV, respectively. The photoluminescence spectrum for the hexyl–silicon network polymer is between the dihexylpolysilane and the polysilane alloy. The photoluminescence of a-Si:H originates from its 3D silicon network structure, that of the polysilane alloy from the mixed structure of 1D polysilane and 3D silicon microclusters, and that of dihexylpolysilane from the 1D silicon backbone structure. Thus, it is conjectured that, in hexyl-silicon network polymer, the photoluminescence arises from silicon network structures that have a silicon backbone with a dimension between 1D and 3D. Next, these spectra will be discussed using E_g calculated on the basis of the dimensionality of the silicon backbone.

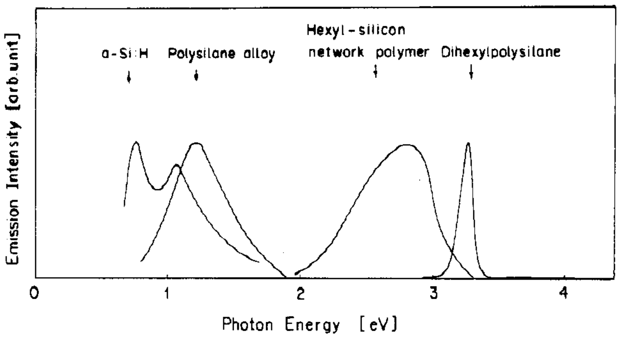

Figure 5. Schematic diagram of the emission spectra for silicon network materials with various dimensionalities: dihexylpolysilane, polysilane alloy,[20] a-Si:H,[20] and hexyl–silicon network polymer.

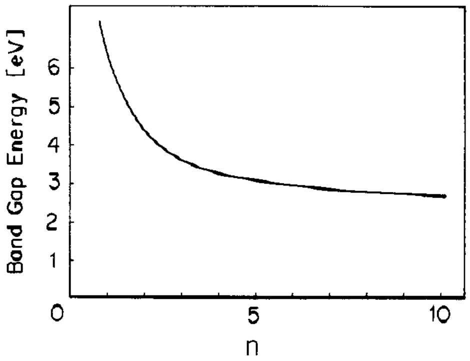

Figure 6. Theoretical calculations of band-gap energy for ideal planar polymers: n denotes the size of a planar polymer consisting of $n \times n$ unit cells.

E_g can be estimated using a simple quantum well model.[11] Disilane, a zero-dimensional (0D) silicon material, is treated as a unit cell in this method. Silicon-based materials are classified according to the connection of these disilane unit cells. For example, polysilane has a 1D silicon structure containing a linear connection of disilane. Similarly, planar polymers and crystalline silicon have 2D and 3D silicon network structures composed of connections of chains and planes, respectively. In this method, E_g is estimated for every size and different dimensional silicon backbone material by using the known values of E_g for disilane (6.5 eV), polysilane (4.0 eV), siloxene (2.5 eV), and c-Si (1.1 eV). These values show that E_g decreases as the dimensionality of the silicon network increases.

The E_g of an ideal, square silicon network structure, such as the square part of one plane cut from c-Si, is estimated using this method. The E_g calculated for this ideal square plane, consisting of $n \times n$ unit cells is shown in Figure 6 against n. A small E_g of less than 3 eV can be achieved when n, the polymer size, is over 5 (molecular weight >5000).

Silicon network polymers, however, consist of silicon network structures with various sizes and dimensionalities. Each of them has a different E_g due to delocalization of the σ electrons along the silicon backbone. In such a mixed system, photoluminescence generally arises from the narrow band gap region, which corresponds to polymers with large sizes or high-dimensional structures. The photoluminescence experiments show broad spectra with E_g of between 2 and 3 eV, with peaks around 2.5 eV. The calculation above showed that an E_g of less than 3 eV is possible in the polymers that have a molecular weight of over 5000. Therefore, this is consistent with the observation of visible photoluminescence in these polymers. The broadness of the spectra are suggested to come from the variety of polymer sizes and dimensionality.

Conclusion

Silicon network polymers exhibit quite different optical properties from linear polysilanes. Their absorption spectra have completely different profiles, and they have broad photoluminescence spectra in the visible light region. These optical properties are attributed to a silicon network structure with a high dimensionality close to that of a 2D structure. These new materials provide important clues in bridging the gap between 1D and 3D silicon structures.

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Characterization of the Chain Dynamics of PEEK by CPMAS ^{13}C NMR

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ABSTRACT: Dipolar rotational spin-echo, T_1(C), $T_{1\rho}$(C), and both direct and indirect $T_{1\rho}$(H) relaxation experiments have been performed on partially crystalline poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene), commonly known as PEEK. The results of these experiments demonstrate that main-chain aromatic rings are dynamically active in only a relatively small part of the amorphous fraction. Most of the rings in both amorphous and crystalline regions are immobile. On average, the ether-ether rings in the amorphous regions of PEEK are slightly less mobile than the ether--ketone rings, presumably the result of interchain packing in the lattice.

Introduction

Poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene), commonly known as PEEK,[1] has only ether oxygens and carbonyl carbons linking main-chain aromatic rings. PEEK is hydrophobic and resists all common organic solvents. Because PEEK can be heated above the melting point of its crystalline phase without chemical degradation, the fabrication of tough PEEK composites is practical. Gaining some understanding of the mechanical properties of these composites may be helped by a characterization of the microscopic chain dynamics of the PEEK matrix.

Magic-angle spinning, natural-abundance ^{13}C NMR experiments can be performed on samples of PEEK to be used in engineering applications. Special preparations of labeled materials are not required. Many of the natural-abundance ^{13}C NMR methods developed to characterize PEEK as a homopolymer can also be applied to PEEK as one component of an engineering composite. In this paper, we report the results of a variety of ^{13}C NMR dynamics experiments performed on partially crystalline samples of PEEK homopolymer. We interpret these results in terms of motions of the two kinds of main-chain aromatic rings of PEEK, in either the amorphous or crystalline regions of the polymer.

Experiments

Magic-Angle Spinning. Cross-polarization magic-angle spinning ^{13}C NMR spectra were obtained at room temperature on

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