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Soluble High-T_g Polymers for Second-Order Nonlinear Optics from an Unusual Mix of Imide and Siloxane Linkages in the Backbone

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ABSTRACT: Covalent linking of imide, dimethylsiloxane, and high-β nonlinear optical (NLO)-active chromophores in the backbone yields polymers that are soluble and that possess high thermal stabilities and glass transition temperatures. Easily fabricated and poled thin films of these polymers exhibit good second-order nonlinear optical susceptibilities with long-term temporal stabilities of the second-harmonic generation signals.

Introduction

Polymer-based materials which exhibit efficient second-order nonlinear optical (NLO) properties have been receiving considerable recent attention in the development of photonics-based technologies for optical signal processing, data storage, and sensors. The major advantages of such systems are their ultrafast optical response time, high laser damage threshold, high mechanical and dimensional stability, flexibility of chemical/structure modification, etc.[1−3] Design strategies for achieving high second-order optical nonlinearities include adequate number density of high-β chromophores in the polymeric backbone, high solubility to effect good optical quality thin films, high thermal stability, effective electric-field poling of the randomly oriented chromophores, and high temporal stability of the resultant NLO signals. In this regard, functionalized polyimides incorporating NLO-active chromophores in the polymeric backbone have been intensely studied in recent years.[4−11] Such polymers offer low optical loss, reasonable number density of chromophores, and high poling efficiency due to their high glass transition temperatures (T_g). Polyimides also exhibit long-term stability of the second-harmonic generation signals, since the poling-induced chromophore dipolar alignment, which is thermodynamically unstable, can be maintained for a long time. However, one of the problems associated with the polyimides is their solubility, which is an important issue to process polymers into thin films. Most of the functionalized polyimides tend to be insoluble, and thus their precursors, poly(amic acids), must be used for processing into thin films that are subsequently imidized at high temperatures.[6−9] The control of optical quality of the resultant thin films is a significant issue in the latter approach. To circumvent these problems, we have developed a new methodology that introduces dimethylsiloxane linkages into the NLO chromophore/imide backbone. The methyl groups at each Si center in the siloxane linkages should lead to higher solubility of the desired polymers,[12,13] and high strength of Si−O bonds in the backbone will impart high thermal stability to these polymers. In addition, transparency of Si−O linkages in the IR−vis region is expected to lead to low optical loss in the desired polymers. We report herein synthesis of a variety of imide−siloxane-linked polymers with variable lengths of siloxane linkages ($-(\mathrm{OSiMe_2})_n-$, $n = 2, 3$), incorporating three different kinds of NLO-active chromophores such as Disperse Red, a pyridinium salt based dye, and 1-amino-4-nitrobenzene. A detailed evaluation of their physical properties, including second-harmonic generation (SHG) characteristics and temporal stabilities of the resultant SHG signals, is also reported. It is inferred from these studies that important physical characteristics of these polymers such as solubility and glass transition temperatures can be tailored by controlling the length of siloxane linkages in the backbone, and the SHG response from these polymers shows long-term stability at room temperature.

Experimental Section

General Procedures. All manipulations were performed using standard Schlenk line techniques. ^{1}H NMR spectra were recorded on a JOEL 270-MHz FT-NMR spectrometer. The UV−Vis absorption spectra were obtained on a Hewlett-Packard 8453 spectrophotometer. The number- and weight-average molecular weights (M_n, M_w) of polymer **10** were measured by gel permeation chromatography (GPC) in chloroform with polystyrene as the standard. Glass transition temperatures (T_g) were obtained using differential scanning calorimetry (DSC) using a Seiko TK/DSC-220 instrument, and thermogravimetric analyses (TGA) of polymers were performed using a Seiko TK/DTA-220 instrument with a heating rate of 20 °C/min. Elemental analyses were carried out by Microanalytical Services Ltd. and Guelph Chemical Laboratories Ltd. The second-order NLO properties of the spin-coated polymeric thin films were obtained using a SHG technique in which a Q-switch Nd:YAG laser beam, operating at 1064 nm with a pulse width of ~10 ns and a 10-Hz repetition rate, was used as the fundamental source.

Materials. *N*-Methylpyrrolidinone (NMP) was purified by vacuum distillation over phosphorus pentoxide. Toluene and tetrahydrofuran (THF) were dried over sodium, and pyridine was dried over potassium hydroxide. All other starting materials purchased from Aldrich were used without purification unless otherwise noted. 1,3-diethylaminotetramethyldisiloxane, 1,5-diethylaminohexamethyltrisiloxane, compound **1b**, 2,2′-[4-[(4-nitrophenyl)azo]phenyl]iminodiethanol (Disperse Red 19, **3a**), and 1-methyl-4-{4′-[*N*,*N*-bis(2-hydroxyethyl)-amino]styryl}pyridinium tetraphenylborate (**3b**) were prepared according to literature procedures.[12−16]

Synthesis. Compound 1a. To a solution of 4-aminophenol (210 mg, 1 mmol) in 25 mL of toluene was added *N*,*N*-diethyl(trimethylsilyl)amine (145 mg, 1 mmol). The resulting mixture was stirred under nitrogen for 24 h. The solvent was removed under vacuum to afford a pale yellow liquid (170 mg,

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95%). ^{1}H NMR (270 MHz, C_6D_6): δ 0.20 (s, 9H, $Si(CH_3)_3$), 2.74 (s, 2H, NH_2), 6.30 (d, 2H, C_6H_4, J_{H-H} = 8.5 Hz), 6.76 (d, 2H, C_6H_4, J_{H-H} = 8.7 Hz). MS (EI): 181. UV−vis ($CHCl_3$): λ_{max} 398 nm. Anal. Calcd for $C_9H_{15}NOSi$ (181): C, 59.67; H, 8.29; N, 7.74. Found: C, 59.32; H, 8.15; N, 7.56.

Compound 2a. To a solution of 4-aminophenol (1.05 g, 5 mmol) in 25 mL of THF was added 1,3-diethylaminotetramethyldisiloxane (875 mg, 2.5 mmol). The resulting mixture was stirred under nitrogen for 24 h at room temperature and then at 70 °C. The solvent was removed under vacuum, and the residue was extracted into 15 mL of benzene. The latter was removed from the filtrate to afford a pale yellow viscous liquid (780 mg, 90%). ^{1}H NMR (270 MHz, DMSO): δ 0.14 (s, 12H, $Si(CH_3)_2$), 4.39 (s, 2H, NH_2), 6.49 (d, 4H, C_6H_4, J_{H-H} = 8.8 Hz), 6.57 (d, 4H, C_6H_4, J_{H-H} = 9.0 Hz). MS (EI): 348. Anal. Calcd for $C_{16}H_{24}N_2O_3Si_2$ (348): C, 55.17; H, 6.90; N, 8.05. Found: C, 54.87; H, 6.78; N, 8.01.

Compound 2b. A mixture of 4-aminophenol (1.05 g, 5 mmol) and 1,5-diethylaminohexamethyltrisiloxane (730 mg, 2.5 mmol) in 25 mL of THF was stirred under nitrogen for 2 days. The solvent was removed under vacuum, and the residue was extracted into 15 mL of benzene. The latter was removed from the filtrate to afford a yellow viscous liquid (840 mg, 84%). ^{1}H NMR (270 MHz, DMSO): δ 0.17 (s, 12H, $Si(CH_3)_2$), 0.11 (s, 6H, $Si(CH_3)_2$), 4.37 (s, 2H, NH_2), 6.50 (d, 4H, C_6H_4, J_{H-H} = 8.7 Hz), 6.60 (d, 4H, C_6H_4, J_{H-H} = 8.7 Hz). MS (EI): 422. Anal. Calcd for $C_{18}H_{30}N_2O_4Si_3$ (422): C, 51.18; H, 7.11; N, 6.64. Found: C, 50.74; H, 7.02; N, 6.13.

Compound 2c. To a solution of 2-amino-5-nitrophenol (1.27 g, 5 mmol) in 40 mL of toluene was added 1,3-diethylaminotetramethyldisiloxane (730 mg, 2.5 mmol) dropwise. The mixture was stirred under nitrogen for 40 h. The solvent was removed under vacuum, and the product was purified by recrystallization from chloroform (0.95 g, 87%). Mp: 274−276 °C. ^{1}H NMR (270 MHz, DMSO): δ 0.31 (s, 12H, $Si(CH_3)_2$), 6.39 (s, 4H, NH_2), 7.60 (d, 2H, C_6H_3, J_{H-H} = 8.6 Hz), 7.71 (d, 2H, C_6H_3, J_{H-H} = 8.5 Hz), 7.76 (d, 2H, C_6H_3, J_{H-H} = 8.6 Hz). MS (EI): 438. UV−vis ($CHCl_3$): λ_{max} 396 nm ($\epsilon = 2.67 \times 10^3$ cm^{-1} M^{-1}). Anal. Calcd for $C_{16}H_{22}N_4O_7Si_2$ (438): C, 43.84; H, 5.02; N, 12.79. Found: C, 43.29; H, 4.92; N, 12.65.

Compounds **4a** and **4b** were prepared by an adaptation of a literature procedure.[8]

Compound 4a: 1.50 g, 73%. Mp: 245−247 °C. ^{1}H NMR (270 MHz, DMSO): δ 4.10 (d, 4H, NCH_2, J_{H-H} = 5.2 Hz), 4.65 (d, 4H, OCH_2, J_{H-H} = 5.2 Hz), 7.20 (d, 2H, C_6H_4, J_{H-H} = 9.2 Hz), 7.85 (d, 2H, C_6H_4, J_{H-H} = 8.9 Hz), 7.95 (d, 2H, C_6H_4, J_{H-H} = 9.0 Hz), 8.18 (d, 2H, C_6H_4, J_{H-H} = 8.5 Hz), 8.43 (m, 6H, C_6H_3). UV−vis (NMP): λ_{max} 468 nm ($\epsilon = 4.55 \times 10^3$ cm^{-1} M^{-1}). MS (EI): 678. Anal. Calcd for $C_{34}H_{22}N_4O_{12}$ (678): C, 60.18; H, 3.25; N, 8.26. Found: C, 59.79; H, 3.21; N, 7.92.

Compound 4b: 1.80 g, 62%. Mp: 125−127 °C. ^{1}H NMR (270 MHz, DMSO): δ 3.94 (s, 3H, $N^+{-}CH_3$), 4.08 (d, 4H, NCH_2, J_{H-H} = 5.2 Hz), 4.61 (d, 4H, OCH_2, J_{H-H} = 5.2 Hz), 7.0−7.3 (m, 23H, C_6H_5, C_6H_4, $=CH$), 7.71 (d, 2H, C_6H_4, J_{H-H} = 8.7 Hz), 8.02 (d, 1H, $=CH$, J_{H-H} = 15.8 Hz), 8.14 (d, 2H, NC_5H_4, J_{H-H} = 6.5 Hz), 8.48 (m, 6H, C_6H_4), 8.67 (d, 2H, NC_5H_4, J_{H-H} = 6.5 Hz). MS (FAB): 966. UV−vis ($CHCl_3$): λ_{max} 459 nm ($\epsilon = 3.68 \times 10^3$ cm^{-1} M^{-1}). Anal. Calcd for $C_{60}H_{47}BN_2O_{10}$ (965.8): C, 74.55; H, 4.87; N, 2.90. Found: C, 74.32; H, 4.67; N, 2.98.

Polymers **5**−**9** were prepared by a general procedure reported below for polymer **5**: A mixture of the diamino monomer **2a** (124 mg, 0.5 mmol) and the dianhydride monomer **4a** (339 mg, 0.5 mmol) in 30 mL of anhydrous NMP was stirred for 4 h at room temperature and then heated to 100 °C for another 4 h. Half of the solvent was removed under vacuum at 70 °C. The mixture was then poured into methanol (100 mL), and the precipitate was collected by filtration. The solid product was washed with methanol and chloroform several times and dried under vacuum at 70 °C for 24 h (340 mg, 70%). ^{1}H NMR (270 MHz, DMSO): δ 0.13 (s, 12H, $Si(CH_3)_2$), 4.15 (br, 4H, NCH_2), 4.73 (br, 4H, OCH_2), 7.21 (br, 2H, C_6H_4), 7.85 (br, 2H, C_6H_4), 7.98 (br, 2H, C_6H_4), 8.16 (br, 2H, C_6H_4), 8.40 (m, 6H, C_6H_3). UV−vis (NMP): λ_{max} 467 nm ($\epsilon = 5.43 \times 10^3$ cm^{-1} M^{-1}). Anal. Calcd for $C_{50}H_{42}N_6O_{13}Si_2$ (990): C, 60.61; H, 4.24; N, 8.49. Found: C, 59.91; H, 4.63; N, 9.07.

Polymer 6: 64%. ^{1}H NMR (270 MHz, DMSO): δ 0.15 (s, 12H, $Si(CH_3)_2$), 0.08 (s, 6H, $Si(CH_3)_2$), 4.15 (br, 4H, NCH_2), 4.73 (br, 4H, OCH_2), 7.19 (br, 2H, C_6H_4), 7.85 (br, 2H, C_6H_4), 7.97 (br, 2H, C_6H_4), 8.19 (br, 2H, C_6H_4), 8.44 (m, 6H, C_6H_3). UV−vis ($CHCl_3$): λ_{max} 466 nm ($\epsilon = 5.10 \times 10^3$ cm^{-1} M^{-1}). Anal. Calcd for $C_{52}H_{48}N_6O_{14}Si_3$ (1064): C, 58.65; H, 4.51; N, 7.90. Found: C, 58.97; H, 4.61; N, 7.68.

Polymer 7: 57%. ^{1}H NMR (270 MHz, DMSO): δ 0.10 (s, 12H, $Si(CH_3)_2$), 4.01 (s, 3H, $N^+{-}CH_3$), 4.18 (br, 4H, NCH_2), 4.69 (br, 4H, OCH_2), 7.0−7.4 (m, 23H, C_6H_5, C_6H_4, $=CH$), 7.81 (br, 2H, C_6H_4), 8.10 (br, 1H, $=CH$), 8.23 (br, 2H, NC_5H_4), 8.49 (m, 6H, C_6H_3), 8.72 (br, 2H, NC_5H_4). UV−vis (NMP): λ_{max} 458 nm ($\epsilon = 4.71 \times 10^3$ cm^{-1} M^{-1}). Anal. Calcd for $C_{76}H_{67}BN_4O_{11}Si_2$ (1277.8): C, 71.37; H, 5.24; N, 4.38. Found: C, 71.76; H, 5.27; N, 4.21.

Polymer 8: 65%. ^{1}H NMR (270 MHz, DMSO): δ 0.12 (s, 12H, $Si(CH_3)_2$), 0.07 (s, 6H, $Si(CH_3)_2$), 3.97 (s, 3H, $N^+{-}CH_3$), 4.16 (br, 4H, NCH_2), 4.66 (br, 4H, OCH_2), 7.0−7.4 (m, 23H, C_6H_5, C_6H_4, $=CH$), 7.81 (br, 2H, C_6H_4), 8.07 (br, 1H, $=CH$), 8.22 (br, 2H, NC_5H_4), 8.46 (m, 6H, C_6H_3), 8.70 (br, 2H, NC_5H_4). UV−vis (NMP): λ_{max} 456 nm ($\epsilon = 4.23 \times 10^3$ cm^{-1} M^{-1}). Anal. Calcd for $C_{78}H_{73}BN_4O_{12}Si_3$ (1351.8): C, 69.24; H, 5.40; N, 4.14. Found: C, 70.43; H, 5.48; N, 4.10.

Polymer 9: 52%. ^{1}H NMR (270 MHz, DMSO): δ 0.25 (s, 12H, $Si(CH_3)_2$), 4.21 (br, 4H, NCH_2), 4.78 (br, 4H, OCH_2), 6.75 (br, 2H, C_6H_3), 7.29 (br, 2H, C_6H_4), 7.63 (br, 2H, C_6H_3), 7.78 (br, 2H, C_6H_3), 7.84 (br, 2H, C_6H_4), 7.98 (br, 2H, C_6H_4), 8.15 (br, 2H, C_6H_4), 8.44 (m, 6H, C_6H_3). UV−vis (NMP): λ_{max} 356, 464 nm ($\epsilon = 1.93 \times 10^3$, 4.94×10^3 cm^{-1} M^{-1}). Anal. Calcd for $C_{50}H_{40}N_8O_{17}Si_2$ (1080): C, 55.56; H, 3.70; N, 10.37. Found: C, 56.21; H, 3.67; N, 10.22.

Polymer 10. To a solution of 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (444 mg, 1 mmol) in 15 mL of anhydrous NMP was added 438 mg (1 mmol) of compound **2c**. The mixture was stirred under nitrogen for 2 h and heated to 100 °C for another 4 h. The solvent was removed under vacuum. The polymer was purified by recrystallization from chloroform/methanol and washed with methanol several times (570 mg, 67%). ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.14 (s, 12H, $Si(CH_3)_2$), 6.67 (br, 2H, C_6H_3), 7.53 (br, 2H, C_6H_3), 7.69 (br, 2H, C_6H_3), 7.92 (br, 6H, C_6H_3). UV−vis ($CHCl_3$): λ_{max} 357 nm ($\epsilon = 2.65 \times 10^3$ cm^{-1} M^{-1}). Anal. Calcd for $C_{35}H_{24}F_6N_4O_{11}Si_2$ (846): C, 49.65; H, 2.84; N, 6.62. Found: C, 50.28; H, 2.93; N, 6.30. M_w = 32 000, M_n = 13 000, M_w/M_n = 2.46.

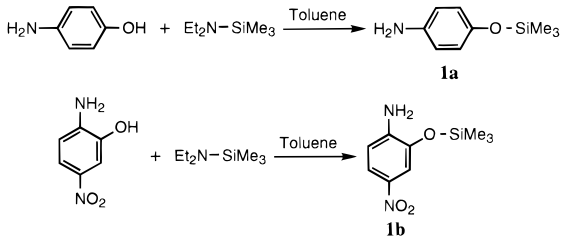
Polymeric Thin Films. The solution of a polymer was prepared by dissolving it into NMP (for polymers **5**−**9**) or chloroform (for polymer **10**), filtering it through 0.2-μm syringe filters, and then spin-coating onto a glass substrate with an indium−tin oxide (ITO) conductive layer. The film was dried under vacuum at 60 °C for 24 h. The thin film was heated to elevated temperatures from 100 to 220 °C over 40 min with the application of dc electric fields from 4.0 to 4.5 kV at corona discharge setup (1.0 cm of a tip-to-plane gap) and then was cooled to room temperature in 30 min.

Results and Discussion

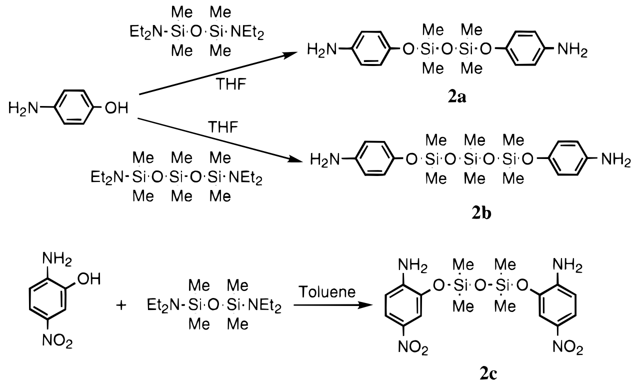
Synthesis. Aminosilanes ($R'_3Si{-}NR_2$, R′ and R = Me, Et), which can be easily prepared from the reaction of the corresponding chlorosilanes with excess amines, react almost quantitatively with organic compounds containing acidic protons via acid−base hydrolysis.[12] For example, (trimethylsilyl)diethylamine, $(CH_3)_3Si{-}N(CH_2CH_3)_2$, reacts with 4-aminophenol to give 4-aminotrimethylsilylphenol (**1a**) or 2-amino-5-nitrophenol to yield 2-amino-5-nitrotrimethylsilylphenol (**1b**) and diethylamine (Scheme 1).

Using a similar acid−base hydrolytic approach, diamino monomers, **2a**−**c**, were prepared from the diaminosiloxane derivatives and the corresponding alcohol (Scheme 2). To determine the effect of the length of the siloxane chain on the properties of the polymers, we

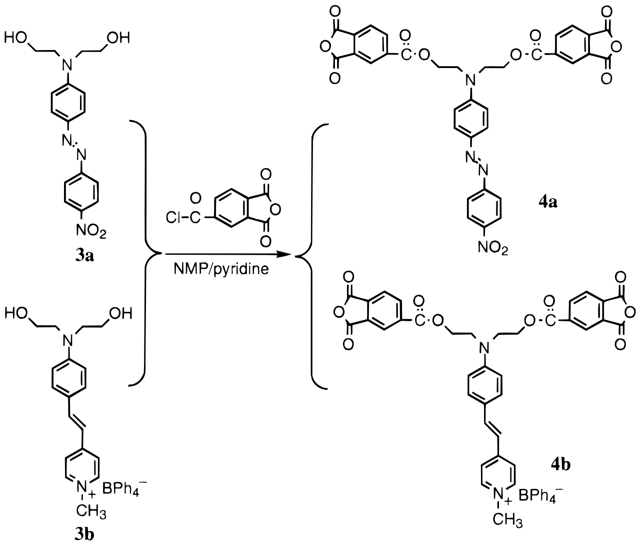
Scheme 1



Scheme 2



Scheme 3

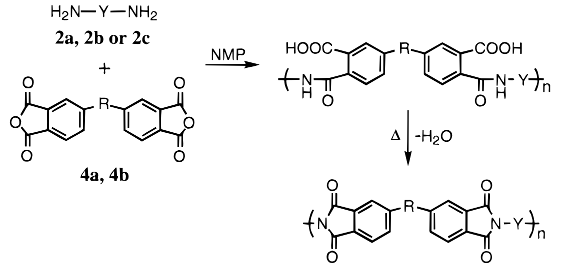


chose two types of Si compounds, namely, 1,3-diethylaminotetramethyldisiloxane and 1,5-diethylaminohexamethyltrisiloxane. Both can be conveniently prepared from the reaction of the corresponding dichlorosiloxanes with excess diethylamine.[13]

Dianhydride monomers employed in this study (**4a** or **4b**) were prepared by reacting 1 equiv of the NLO chromophore **3a** or **3b** with 2 equiv of trimellitic anhydride acid chloride in the presence of pyridine, which neutralizes HCl in the reaction (Scheme 3).

Synthesis of polymers was achieved in two steps: (i) polymerization of the dianhydride monomer **4a** or **4b** with a diamino monomer (**2a**–**2c**) at room temperature to give the corresponding poly(amic acid), and (ii) imidization of the poly(amic acid) by cyclization at 100 °C (Scheme 4). The imidization reaction was monitored by observing the disappearance of the proton NMR peaks of the carboxylic acid (13.2 ppm) and amide (10.5 ppm) groups. NMP was used as a solvent for the polymerization process; however, other polar aprotic solvents, such as *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO), can also be employed for these reactions. Scheme 5 shows the structures of different imide–siloxane-linked polymers reported in this study. These polymers were characterized using standard techniques, and pertinent data are reported in Table 1.

Scheme 4



Polymers **5 -10**

Polymer	Diamine	Anhydride
5	2a	4a
6	2b	4a
7	2a	4b
8	2b	4b
9	2c	4a
10	2c	R: -C(CF$_3$)$_2$-

Polymers **5**–**9** were soluble in polar solvents such as NMP, DMAc, DMF, and DMSO. Through quantitative solubility tests of these polymers in NMP, it was found that polymers **5** and **7** were more soluble than polymers **6** and **8**. The former contain one more dimethysiloxane group in the backbone than the latter, which, as expected, improves the solubility due to an increase in the length of the dimethylsiloxane linkage. Polymer **10** was soluble in common organic solvents. The higher solubility of this polymer is likely due to the backbone containing a $-C(CF_3)_2-$ group and a less polar NLO chromophore. The $-C(CF_3)_2-$ groups are commonly used to improve the solubility of polymers. The less polar NLO group in **10** induces a weaker interaction of chromophores among polymeric chains that enhances solubility.

For polymers **5**–**9**, viscosity measurements were carried out by using a Ubbelohde type viscometer and NMP as the solvent to evaluate the relative molecular weights of these polymers. The viscosity of these polymers in a decreasing order was found to be **5** > **6** > **8** > **7** > **9**, which implies that the estimated molecular weights of the polymers also decrease in the same order. The weight-average molecular weight for polymer **10**, measured in chloroform using GPC (with polystyrene as a standard), was found to be 32 000 with a polydispersity of 2.46.

Thermal Stability. The thermal stabilities of the polymers were determined by thermogravimetric analysis (TGA). T_d (Table 1) is the temperature when 5% weight loss was observed in a nitrogen atmosphere. As seen from Table 1, these polymers display high thermal stability, which can be ascribed to high mechanical strength imparted by stable and strong Si–O bonds in dimethylsiloxane linkages and imide groups in the backbone. Polymers **5**, **6**, **9**, and **10**, which contain either **2a** or **2c** or both NLO chromophores, show decomposition temperatures from 290 to 342 °C. These

Scheme 5

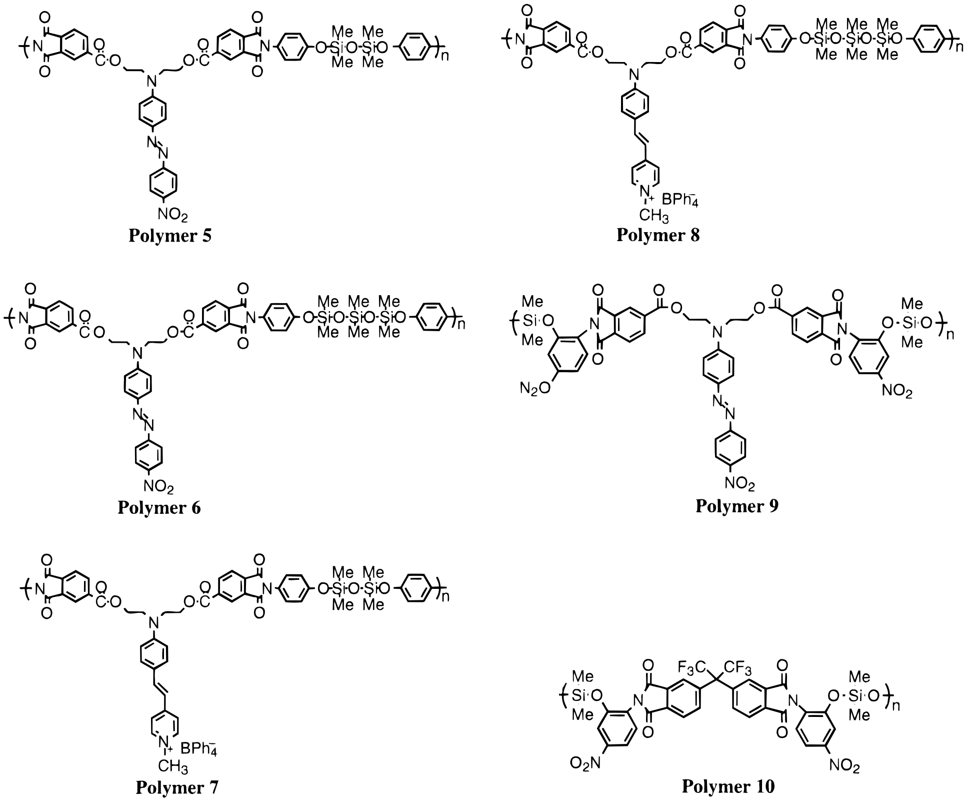


Table 1. Physical Properties of Polymers

polymer	η_{int}, dL/g	λ_{max} (nm)	T_d[a] (°C)	T_g[b] (°C)
5	0.34	467	287	214
6	0.31	466	314	201
7	0.25	458	240	203
8	0.27	456	238	188
9	0.22	356, 464	303	217
10	[c]	357	342	172

[a] T_d = decomposition temperature. [b] T_g = glass transition temperature. [c] For polymer **10**, the molecular weight was measured by GPC (M_w = 32 000 and M_n = 13 000).

values are capable of meeting thermal requirements in constructing optical devices. T_d values of polymers **7** and **8**, which contain pyridinium salt (**2b**) as the NLO chromophore, are 240 and 238 °C, respectively, which are about 50−100 °C lower than those of other polymers. This probably is due to the low thermal stability of the pyridinium salt, which decomposes faster than that of the imide−siloxane backbone.

Glass Transition Temperatures. The glass transition temperatures (T_g) of these polymers were determined by differential scanning calorimetry, and these range from 172 to 217 °C (Table 1). High T_g of these polymers is mainly attributed to the imide linkages in the backbone. As is seen from Table 1, for polymers containing similar NLO chromophores, T_g decreases with an increase in the length of siloxane linkages. For example, T_g of polymer **5** with the disiloxane linkages in the polymer is 13 °C higher than that of polymer **6** containing the trisiloxane linkages. Similarly, there is a 15 °C temperature difference between polymer **7** with disiloxane and polymer **8** with trisiloxane linkages in the backbone. These differences in T_g values arise from the flexibility of the siloxane bond, which may lead to a rotation along the backbone and cause faster relative motion among polymeric main chains.[17] For similar backbones, the type of NLO chromophore in the polymeric structure also showed an effect on the T_g values. For example, polymer **5** or **6** containing Disperse Red had about a 10 °C higher T_g than polymer **7** or **8**, which contains pyridinium salt dye (Table 1). This is likely due to a stronger electrostatic interaction between polar chromophores in polymers **5** and **6** that restricts chromophoric mobility, especially the chain rotation along the backbone, which results in higher T_g. Polymers **5** and **9** were found to possess similar T_g values, around 215 °C. Polymer **9** was expected to offer a higher T_g because it contains two rigid groups (benzene rings from **2c**) that can reduce the relative motion among polymeric main chains. Lower T_g in **9** may be attributed to its lower molecular weight compared with that of polymer **5** (Table 1).

Polymer **10** exhibited a relatively low T_g. The possible reason is that it contains a *p*-aminonitrobenzene type NLO chromophore which is less polar than Disperse Red dye and pyridinium salt (polymers **6**−**9**) and leads to weaker interaction between the chromophores. The presence of $-C(CF_3)_2-$ groups in the backbone also tends to disrupt chain packing and facilitates less chain−chain interaction.

UV−Vis Absorption Spectra. The peak positions in the UV−vis absorption spectra of polymers **5**−**9** (Table 1) were found to be similar to those of the corresponding monomers: 467 nm for **4a**, 458 nm for **4b**, 398 nm for **1c**. These results suggest that polar properties of the chromophores are not affected by the polymerization process. However, for polymer **10** a 40-nm blue shift was observed relative to its monomer (**2c**; λ_{max} = 396 nm). This large blue shift may be attributed to the fact that polymerization of the amino groups leading to amide linkages lowers their electron-donating ability, in comparison to the original donor (NH_2) group in compound **2c**. This will reduce the charge-transfer

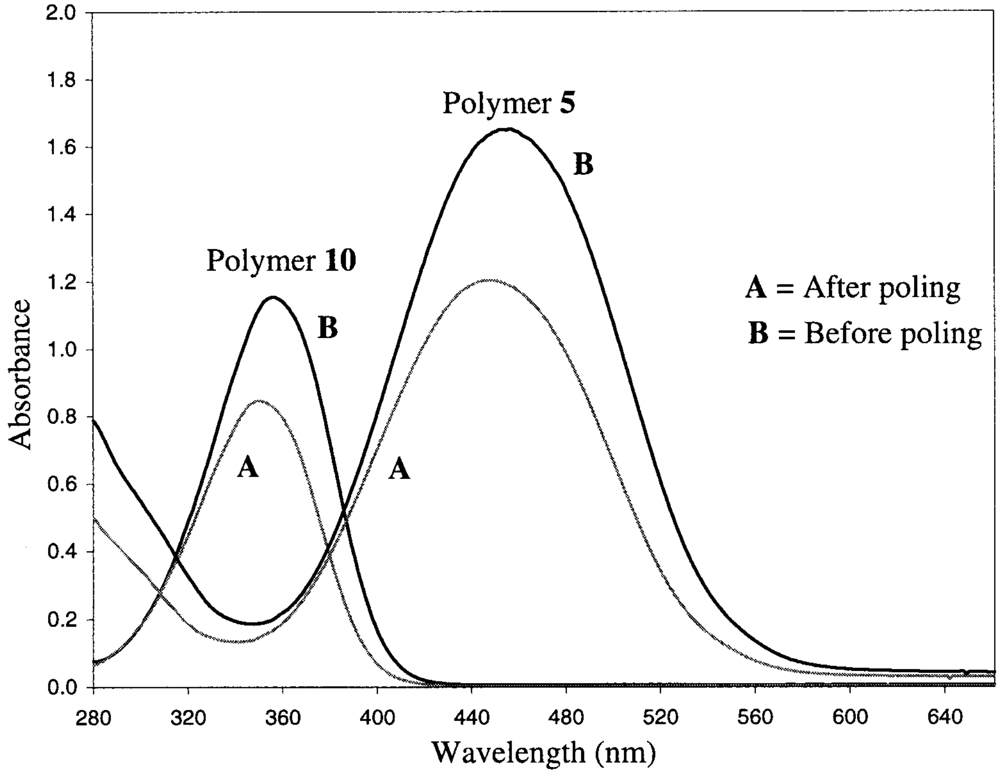


Figure 1. UV−visible absorption spectra of the thin films of polymers **5** and **10** before and after electric field poling.

interaction between the electron acceptor (NO_2) and the resultant donor groups.

The absorption maximum in polymer **10** is around 355 nm, which is out of the absorption region of the second-harmonic generation (SHG) wavelength of 532 nm that is employed in SHG experiments. Thus, in polymer **10** we expect to observe only nonresonant contributions to SHG, while for polymers **5**−**9** which consist of either **2a** or **2b** with absorption maxima in the range of 456−468 nm, the SHG signals should be weakly enhanced since the SHG wavelength falls in the tail of their absorption curves.

It was found that the absorbance of the thin films of the above polymers decreased after electric-field poling. Representative spectra are shown in Figure 1. It suggests that the poling-induced alignment of chromophores is parallel to the incident light. The ordering parameter of a poled polymeric film is defined by ($1 - A/A_0$), where A and A_0 are absorbances before and after poling, respectively, and is commonly used to describe the poling efficiency.[18] The ordering parameters of these polymers were in the range of 0.21−0.28, which suggests that these polymers are efficiently poled.

Second-Harmonic Generation Measurements. All the polymers reported here were found to be soluble in polar solvents. The latter offers ease of processibility in the preparation of good optical quality thin films. The NLO properties of these polymers were examined by measuring second-harmonic generation in transmission from the appropriate thin film spin-coated on an ITO-coated glass slide. A Q-switched Nd:YAG laser, operating at 1064 nm with a pulse width of ~10 ns and a 10-Hz repetition rate, was used as the fundamental source. The thin film was kept rotating at a speed of 2°/min from 0 to 60° during the process of measurements. The SHG signal was recorded and amplified using a photomultiplier tube and then averaged in a boxcar integrator. A quartz crystal was used as the reference sample. The poling conditions and SHG characteristics of polymers are listed in Table 2.

Table 2. Second-Order NLO Related Properties of Polymers and Their Thin Films

polymer	sample thickness (μm)	chromophore density wt (%)	$\chi^2 \times 10^{-8}$ esu	poling temp (°C)	electric field (kV)
5	0.62	33	20	220	4.0
6	0.75	31	23	210	4.0
7	0.54	49	14	210	4.5
8	0.65	46	13	200	4.5
9	0.50	30, 28	9.8	220	4.5
10	0.58	36	1.7	200	4.5

As expected, no signal was observed without the application of an external electric field, which suggests that the dipoles in these polymers are randomly oriented. Poling temperatures were set around T_g of poled polymers, and a 4.0 kV dc electric field was applied to polymers **5** and **6** and a 4.5 kV dc electric field to polymers **7**−**10** which contain either pyridinium salt (**7**, **8**) or *p*-nitroaminobenzene type (**9**, **10**) NLO chromophores in the backbone. The latter usually require higher poling electric fields.[2,3] The χ^2 values for polymers **5** and **6** were found to be $\sim 20 \times 10^{-8}$ esu, for polymers **7** and **8** $\sim 14 \times 10^{-8}$ esu, for polymer **9** 9.8×10^{-8} esu, and for polymer **10** $\sim 2 \times 10^{-8}$ esu. These values are comparable with those for polyimides with various Disperse Red dyes[4−11] and for polyurethanes with hemicyanine dyes.[15] The difference in χ^2 values among polymers **5**−**10** can be attributed to different molecular hyperpolarizabilities (β) of the chromophores. In general, a polymer which contains higher β chromophores is expected to give a larger χ^2 value. For example, β of Disperse Red dye, 59.4×10^{-30} esu, is about 6 times that of *p*-nitroaminobenzene, 10.3×10^{-30} esu.[19] As is seen from Table 2, χ^2 values of polymers **5** and **6** are ~10 times that of polymer **10**. Although polymer **9** contains two types of NLO-active chro-

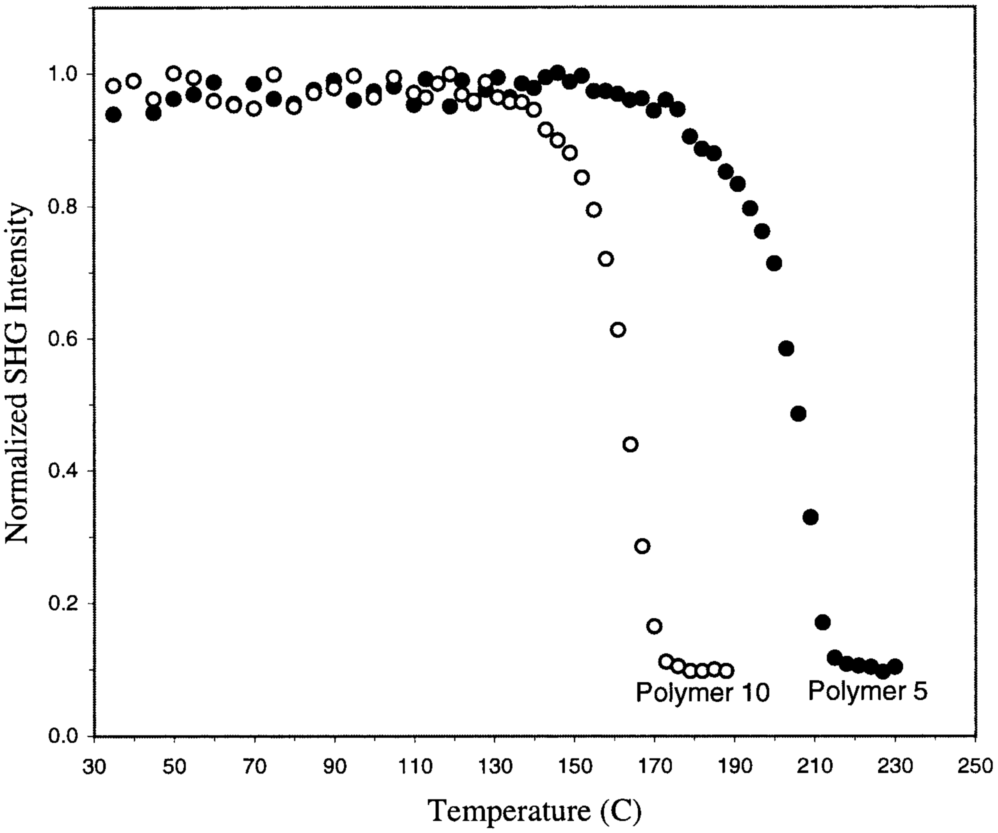


Figure 2. SHG intensity as a function of temperature for the poled polymeric thin films of polymers **5** and **10** after the electric field was removed.

mophores, Disperse Red dye and *p*-nitroaminobenzene, in the backbone, its χ^2 value was found to be lower than those of polymers **5** and **6**, which only contain Disperse Red dye. This may be attributed to (i) lower number density of Disperse Red chromophores in polymer **9**; (ii) 1 magnitude order lower NLO response by *p*-nitroaminobenzene type chromophores, and (iii) the addition of *p*-nitroaminobenzene type chromophores next to Disperse Red dye which produces lower resultant local factors.

The temporal stability of chromophore dipole orientation after the removal of the external electric field was examined at room temperature by measuring the change of SHG intensity with time. At room temperature, there was no decay in the intensity of the SHG signal for all the polymers measured for 1800 h. No decay was observed when a similar study was carried out for polymers **5** and **7** at 80 °C with measurements made up to 200 h. These studies indicate that the dipole orientations in these polymers are quite stable which can be attributed to high T_g of these polymers.

The dependence of SHG stability on temperature was also explored. The samples were heated to 100 °C quickly, then the heating rate was reduced, and the samples finally were kept at 3 °C/min after 130 °C. Figure 2 shows temperature-dependent SHG data for polymers **5** and **10**. It was found that the SHG signal of the thin films of these polymers remained very stable before ~30−40 °C from their T_g, after which they started to decay. When the samples were heated to 10−15 °C before their T_g, the SHG signals decreased very fast and then completely disappeared at T_g. A similar temperature dependence of SHG signals has been observed for functionalized polyimides.[7]

Conclusions

Polymers containing NLO-active chromophores and imide−siloxane linkages in the backbone are easily accessible using a new polymerization methodology. Introduction of dimethylsiloxane linkages in the backbone leads to enhanced solubilities and thermal stabilities of the functionalized polyimides while retaining their useful physical characteristics such as high glass transition temperatures. These polymers show second-harmonic generation efficiencies comparable to those for functionalized polyimides or polyurethanes and exhibit high temporal stabilities of the resultant SHG signals.

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References and Notes

(1) Marks, T. J.; Ratner, M. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34* (2), 155 and references therein.

(2) Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem. Rev.* **1994**, *94*, 31.

(3) Nalwa, H. S.; Watanabe, T.; Miyata, S. In *Nonlinear Optics of Organic Molecules and Polymers*; Nalwa, H. S., Miyata, S., Eds.; CRC Press: Boca Raton, FL, 1997; p 89.

(4) Lin, J. T.; Hubbard, M. A.; Marks, T. J. *Chem. Mater.* **1992**, *4*, 1148.

(5) Weder, C.; Neuenschwander, P.; Suter, U. W.; Prêtre, P.; Kuatz, P.; Günter, P. *Macromolecules* **1994**, *27*, 2181.

(6) Verbiest, T.; Burland, D. M.; Jurich, M. C.; Lee, V. Y.; Miller, R. D.; Volksen, W. *Macromolecules* **1995**, *28*, 3005.

(7) Yu, D.; Gharavi, A.; Yu, L. *J. Am. Chem. Soc.* **1995**, *117*, 11680.

(8) Becker, M. W.; Sapochak, L. S.; Ghosen, R.; Xu, C.; Dalton, L. R.; Shi, Y.; Steier, W. H.; Jen, A. K.-Y. *Chem. Mater.* **1994**, *6*, 104.

(9) Dalton, L. R.; Wu, B.; Harper, A. W.; Ghosn, R.; Ra, Y.; Liang, Z.; Montgomerg, R.; Kalluri, S.; Shi, Y.; Steier, W. H.; Jen, A. K.-Y. In *Polymers for second-order nonlinear optics*; Lindsay, G. A., Singer, K. D., Eds.; ACS Symposium Series 601; American Chemical Society: Washington, DC, 1995; p 159.

(10) Chen, T.-A.; Jen, A. K.-Y.; Cai, Y. *Macromolecules* **1996**, *29*, 535.

(11) Lee, H.-J.; Lee, M.-H.; Han, S. G.; Kim, H.-Y.; Ahn, J.-H.; Lee, E.-M.; Won, Y. H. *Polymer Chem.* **1998**, *36*, 301.

(12) Jiang, H.; Kakkar, A. K.; Lebuis, A.-M.; Zhou, H.; Wong, G. K. *J. Mater. Chem.* **1996**, *6* (6), 1075.

(13) Jiang, H.; Kakkar, A. K. *Macromolecules* **1998**, *31* (8), 2501.

(14) Chen, M.; Yu, L.; Dalton, L. R.; Shi, Y.; Steier, W. H. *Macromolecules* **1991**, *24* (19), 5421.

(15) Wang, N. P.; Leslie, T. M.; Wang, S.; Kowel, S. T. *Chem. Mater.* **1995**, *7*, 185.

(16) Moon, K.-J.; Shim, H.-K.; Lee, K.-S.; Zieba, J.; Prasad, P. N. *Macromolecules* **1996**, *29*, 861.

(17) Voronkov, M. G.; Mileshkevich, V. P.; Yuzheleskii, Yu. A. *The siloxane bond: Physical Properties and Chemical Transformations*; Consultants Bureau: New York, 1978.

(18) Page, R. H.; Jurich, M. C.; Reck, B.; Sen, A.; Twieg, R. J.; Swalen, J. D.; Bjorlund, G. C.; Wilson, C. G. *J. Opt. Soc. Am. B* **1990**, *7*, 1239.

(19) Ulman, A.; Willand, C. S.; Kohler, W.; Robello, D. R.; Willams, D. J.; Handley, L. In *Materials for Nonlinear optics: Chemical perspective*; Marder, S. R., Sohn, J. E., Stucky, G. D., Eds.; ACS Symposium Series 455; American Chemical Society: Washington, DC, 1991; p 170.

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