Functionalized Siloxane-Linked Polymers for Second-Order Nonlinear Optics

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ABSTRACT: A variety of polymers containing NLO-active chromophores covalently bound in the siloxane-linked backbones, $[-R_2Si(OSiR_2)_nO(\text{NLO-chromophore})O-]_n$ ($R = CH_3$ or CH_3/C_6H_4) and $[-R_2Si(OSiR_2)_n\text{-}OR'O(\text{NLO-chromophore})O-]_n$ ($R' = C_6H_4$, $C_6H_4C_6H_4$), has been prepared. Their solubility in common organic solvents and high thermal stability impart ease of thin film preparation and poling at high temperatures. These polymers exhibit good second-harmonic generation susceptibilities, and the temporal stabilities of the SHG signals are dependent on the polymer backbone and the molecular structures of the NLO chromophores. A detailed analysis of their physical properties is reported.

Introduction

The design of new materials which exhibit high second-order nonlinear optical (NLO) efficiencies continues to attract much interest due to their potential applications in the photonics based industries. Several design strategies[1,2] have been employed to achieve adequate number density of acentrically aligned high-β chromophores for a large bulk second-order NLO response ($\chi^{(2)}$). Poled polymers, in which a thin film of the desired polymer is fabricated and subjected to an external electric field at elevated temperatures, followed by slow cooling under an applied voltage, offer promise in the design of materials with sustainable net chromophore alignment of the macrostructure. The inherent practical requirements for device manufacture based on poled polymers include ultrafast optical response time, high laser damage threshold, high mechanical and dimensional stability, etc.[3−5] High thermal stability and solubility in common organic solvents are also important performance issues in the construction of polymer based NLO devices. We have developed a synthetic approach based on simple acid−base hydrolytic chemistry to siloxane-linked polymers containing NLO-active chromophores in the backbone. The advantages of these polymers include (i) good solubility in common organic solvents due to the presence of methyl groups at each Si center, (ii) improved thermal stability due to strong Si−O−Si linkages in the polymer main chain, and (iii) low optical loss since Si−O bonds are transparent in the IR−vis region. We report herein synthesis of a variety of these polymers with variable lengths of siloxane linkages incorporating numerous high-β chromophores and a detailed evaluation of their physical properties, including their second-harmonic generation (SHG) characteristics and the temporal stabilities of the resultant SHG signals. As expected, the physical properties of these polymers that are of interest depend on the structure of the siloxane−chromophore backbone. To evaluate such effects, we decided to study the following variables: (a) the structure of the bifunctional NLO chromophore, (b) the length of dimethylsiloxane linkages in the backbone, $[-Me_2SiO-]_m$ ($m = 1, 2, 3$), (c) the effect of changing substituents on Si, $SiMe_2$ to SiMePh, and (d) the introduction of rigid spacers between siloxane units, C_6H_4, $C_6H_4C_6H_4$. Polymers containing dimethylsiloxane linkages exclusively are generally associated with very low glass transition temperatures (T_g). It is inferred from a detailed study of the above-mentioned relationships that one can achieve high T_g and simultaneously tailor useful properties such as solubility, thermal stability, and temporal alignment stability of the desired polymers by introducing a combination of simple variables in the polymer backbone.

Experimental Section

General. All manipulations were performed using standard Schlenk line techniques. ^1H 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 molecular weights of the polymers were measured by gel permeation chromatography (GPC) in chloroform with polystyrene as the standard. Glass transition temperatures (T_g) were obtained by using differential scanning calorimetry (DSC) using a Seiko TK/DSC-220 instrument, and thermogravimetric analysis (TGA) of polymers was performed on a Seiko TK/DTA-220 instrument with a heating rate of 20 °C/min. Elemental analyses were carried out by Microanalytical Services Ltd. The second-order NLO efficiencies of the spin-coated polymeric thin films were measured by using the second harmonic generation 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. Dioxane was dried by distillation over calcium hydride and then stored under a nitrogen atmosphere. Triethylamine and cyclohexanone were distilled over K_2CO_3, THF over sodium, and diethylamine over potassium hydroxide. All other starting materials, purchased from Aldrich, were used without purification unless otherwise noted. Polymer precursors, 1-bis(3-hydroxypropyl)amino-4-nitrobenzene (**1a**), 2,2′-[4-[(4-nitrophenyl)azo]phenyl]iminobisethanol (Disperse Red 19) (**1b**), and 1-methyl-4-(4′-[*N,N*-bis(2-hydroxyethyl)amino]styryl)-pyridinium tetraphenylborate (**1c**) were prepared according to the literature procedures.[6−9]

Synthesis. Compound 2a. To a solution of 1-bis(3-hydroxypropyl)amino-4-nitrobenzene (**1a)** (127 mg, 0.5 mmol) in 5 mL of THF was added *N,N*-diethyltrimethylsilylamine (145 mg, 1 mmol). The mixture was stirred under a nitrogen atmosphere for 5 h. The solvent was then removed under vacuum to afford a yellow solid product. The compound was further purified by recrystallization from a diethyl ether/hexane mixture (120 mg, 75%). ^1H NMR (270 MHz, $CDCl_3$) δ

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0.12 (s, 18 H, $Si(CH_3)_3$), 1.74 (m, 4 H, CH_2), 3.51 (t, 4 H, $O-CH_2$, $J_{H-H} = 6.0$ Hz), 3.62 (t, 4 H, $N-CH_2$, $J_{H-H} = 6.0$ Hz), 6.80 (d, 2 H, C_6H_4, $J_{H-H} = 9.0$ Hz), 8.03 (d, 2 H, C_6H_4, $J_{H-H} = 9.0$ Hz). MS(EI) 398. UV−vis ($CHCl_3$) λ_{max}/nm 398 ($\epsilon = 19\ 800$ cm^{-1} M^{-1}). Mp 172−174 °C. Anal. Calcd for $C_{18}H_{34}N_2O_4Si_2$ (398): C, 54.27%; H, 8.54%; N, 7.04%. Found: C, 54.12%; H, 8.28%; N, 6.73%.

Compound 2b. To a solution of Disperse Red 19 (**1b**) (165 mg, 0.5 mmol) in 5 mL of THF was added *N*,*N*-diethyltrimethylsilylamine (145 mg, 1 mmol). The resulting mixture was stirred under nitrogen overnight. The solvent and diethylamine were removed under vacuum to give a red solid product. The compound was further purified by recrystallization from a dichloromethane/hexane mixture (220 mg, 90%). ^1H NMR (270 MHz, DMSO) δ 0.07 (s, 18 H, $Si(CH_3)_3$), 3.65 (t, 4 H, $O-CH_2$, $J_{H-H} = 5.8$ Hz), 3.76 (t, 4 H, $N-CH_2$, $J_{H-H} = 5.8$ Hz), 6.91 (d, 2 H, C_6H_4, $J_{H-H} = 9.0$ Hz), 7.83 (d, 2 H, C_6H_4, $J_{H-H} = 8.8$ Hz), 7.93 (d, 2 H, C_6H_4, $J_{H-H} = 8.8$ Hz), 8.36 (d, 2 H, C_6H_4, $J_{H-H} = 8.8$ Hz). MS(EI) 474. UV−vis ($CHCl_3$) λ_{max}/nm 482 ($\epsilon = 46\ 300$ cm^{-1} M^{-1}). Mp 193−195 °C. Anal. Calcd for $C_{22}H_{34}N_4O_4Si_2$ (474): C, 55.70%; H, 7.17%; N, 11.81%. Found: C, 55.27%; H, 7.02%; N, 11.23%.

Compound 2c. A mixture of *N*,*N*-diethyltrimethylsilylamine (58 mg, 0.4 mmol) and 1-methyl-4-(4′-[*N*,*N*-bis(2-hydroxyethyl)amino]styryl)pyridinium tetraphenylborate (**1c**) (120 mg, 0.2 mmol) in 3 mL of dry cyclohaxanone was stirred under N_2 overnight. The solvent was then removed under vacuum at 60 °C. The residue was dissolved in 3 mL of dichloromethane and then poured into 10 mL of hexane. The red-orange precipitate was collected by filtration (140 mg, 88%). ^1H NMR (270 MHz, DMSO) δ 0.06 (s, 18 H, $Si(CH_3)_3$), 3.58 (t, 4 H, $O-CH_2$, $J_{H-H} = 5.6$ Hz), 3.74 (t, 4 H, $N-CH_2$, $J_{H-H} = 5.6$ Hz), 4.17 (s, 3 H, N^+-CH_3), 6.8−7.2 (m, 23 H, C_6H_4, $B-C_6H_5$ and $=$CH), 7.57 (d, 2 H, C_6H_4, $J_{H-H} = 8.8$ Hz), 7.89 (d, 1 H, $=$CH, $J_{H-H} = 16.1$ Hz), 8.03 (d, 2 H, C_6H_4, $J_{H-H} = 6.8$ Hz), 8.67 (d, 2 H, C_6H_4, $J_{H-H} = 6.7$ Hz). MS(EI) 762. UV−vis ($CHCl_3$) λ_{max}/nm 472 ($\epsilon = 69\ 400$ cm^{-1} M^{-1}). Mp 136−138 °C. Anal. Calcd for $C_{48}H_{59}BN_2O_2Si_2$ (762): C, 80.36%; H, 8.23%; N, 3.91%. Found: C, 81.28%; H, 7.93%; N, 3.49%.

Compound 3a. To a solution of 1,3-dichlorotetramethyldisiloxane (2.03 g, 10 mmol) in 40 mL of dry diethyl ether was added dropwise 4 mL of diethylamine. A white pricipitate was formed immediately. The resulting mixture was further stirred for 3 h. The precipitate was filtered off under a nitrogen atmosphere. The solvent was removed from the filtrate under vacuum, and the product was purified by distillation at 60 °C under vacuum to afford a colorless liquid (2.60 g, 90%). ^1H NMR (270 MHz, C_6D_6) δ 0.20 (s, 12 H, $Si(CH_3)_2$), 1.03 (t, 12 H, CH_3, $J_{H-H} = 6.9$ Hz), 2.87 (q, 8 H, CH_2, $J_{H-H} = 6.9$ Hz).

Compound 3b. A similar procedure to that given for compound **3a**. 92%. ^1H NMR (270 MHz, C_6D_6) δ 0.22 (s, 6 H, $Si(CH_3)_2$), 0.24 (s, 12 H, $Si(CH_3)_2$), 1.04 (t, 12 H, CH_3, $J_{H-H} = 7.0$ Hz), 2.88 (q, 8 H, CH_2, $J_{H-H} = 7.0$ Hz).

Compound 4. A similar procedure to that given for compound **3a**. 90%. ^1H NMR (270 MHz, C_6D_6) δ 0.56 (s, 6 H, $Si(CH_3)_3$), 1.07 (t, 12 H, CH_3, $J_{H-H} = 6.5$ Hz), 2.91 (q, 8 H, CH_2, $J_{H-H} = 6.5$ Hz), 7.11 (m, 6 H, C_6H_5), 7.65 (m, 4 H, C_6H_5).

Compound 5. A mixture of Disperse Red 1 (314 mg, 1 mmol) and bis(dimethylamino)dimethylsilane (74 mg, 0.5 mmol) in 15 mL of THF was stirred under nitrogen at room temperature for 2 h and then at 60 °C for 14 h. The solvent was removed under vacuum to afford a red solid product that was further purified by recrystallization from a chloroform/hexane mixture (290 mg, 75%). ^1H NMR (270 MHz, DMSO) δ 0.06 (s, 6 H, $Si(CH_3)_2$), 1.15 (t, 6 H, $J_{H-H} = 6.6$ Hz, CH_3), 3.55 (m, 8 H, NCH_2), 3.83 (t, 4 H, $J_{H-H} = 6.6$ Hz, OCH_2), 6.86 (d, 4 H, $J_{H-H} = 9.2$ Hz, C_6H_4), 7.94 (d, 4 H, $J_{H-H} = 9.2$ Hz, C_6H_4), 8.38 (d, 4 H, $J_{H-H} = 9.1$ Hz, C_6H_4). MS (EI) 684. UV−vis ($CHCl_3$) λ_{max}/nm 483 ($\epsilon = 52\ 100$ cm^{-1} M^{-1}). Mp 241−243 °C.

Compound 6. To a solution of Disperse Red 1 (157 mg, 0.5 mmol) in 10 mL of THF was added dropwise 1,3-bis(diethyamino)tetramethyldisiloxane (73 mg, 0.25 mmol) in 5 mL of THF. The resulting mixture was stirred under nitrogen for 24 h. The solvent was removed under vacuum to afford a red solid product, and the latter was purified by recrystallization from a methanol/pentane mixture (140 mg, 75%). ^1H NMR (270 MHz, C_6D_6) δ 0.11 (s, 12 H, $Si(CH_3)_2$), 0.77 (t, 6 H, CH_3, $J_{H-H} = 5.8$ Hz), 2.92 (m, 8 H, $N-CH_2$ and CH_2-O), 3.18 (m, 4 H, $N-CH_2$), 6.45 (d, 4 H, C_6H_4, $J_{H-H} = 8.8$ Hz), 7.76 (d, 4 H, C_6D_6, $J_{H-H} = 8.7$ Hz), 7.95 (d, 4 H, C_6H_4, $J_{H-H} = 8.8$ Hz), 8.15 (d, 4 H, C_6H_4, $J_{H-H} = 8.8$ Hz). MS(FAB) 758. UV−vis ($CHCl_3$) λ_{max}/nm 480 ($\epsilon = 50\ 700$ cm^{-1} M^{-1}). Mp 265−267 °C. Anal. Calcd for $C_{36}H_{46}N_8O_7Si_2$ (758): C, 56.99%; H, 6.09%; N, 14.78%. Found: C, 56.25%; H, 5.87%; N, 14.42%.

Compound 7. To a solution of 1-bis(3-hydroxypropyl)-amino-4-nitrobenzene (**1a**) (127 mg, 0.5 mmol) in 10 mL of THF was added dropwise a solution of dimethylsilylbis-(dimethylamine) (74 mg, 0.5 mmol) in 5 mL of THF. The resulting mixture was stirred under nitrogen for 24 h. The solvent was removed under vacuum to afford a yellow solid product. The compound was further purified by recrystallization from a dichloromethane/hexane mixture (110 mg, 71%). ^1H NMR (270 MHz, $CDCl_3$) δ 0.07 (s, 6 H, $Si(CH_3)_2$), 1.88 (m, 4 H, CH_2), 3.59 (t, 4 H, $O-CH_2$, $J_{H-H} = 5.9$ Hz), 3.75 (t, 4 H, $N-CH_2$, $J_{H-H} = 5.9$ Hz), 6.70 (d, 2 H, C_6H_4, $J_{H-H} = 8.4$ Hz), 8.12 (d, 2 H, C_6H_4, $J_{H-H} = 8.4$ Hz). MS(EI) 310. UV−vis ($CHCl_3$) λ_{max}/nm 396 ($\epsilon = 22\ 200$ cm^{-1} M^{-1}). Mp 202−204 °C. Anal. Calcd for $C_{14}H_{22}N_2O_4Si$ (310): C, 54.19%; H, 7.10%; N, 9.03%. Found: C, 53.78%; H, 6.73%; N, 8.72%.

Compound 8. To a solution of 2,2′-(4-[(4-nitrophenyl)azo]-phenyl)iminobisethanol (Disperse Red 19) (**1b**) (165 mg, 0.5 mmol) in 10 mL of dioxane was added dropwise a solution of dimethylsilylbis(dimethylamine) (74 mg, 0.5 mmol) in 5 mL of dioxane. The resulting mixture was stirred under N_2 overnight. The solvent was removed under vacuum to afford a red solid product. The compound was further purified by recrystallization from a chloroform/hexane mixture (160 mg, 83%). ^1H NMR (270 MHz, DMSO) δ 0.13 (s, 6 H, $Si(CH_3)_2$), 3.62 (t, 4 H, $O-CH_2$, $J_{H-H} = 5.6$ Hz), 3.73 (t, 4 H, $N-CH_2$, $J_{H-H} = 5.6$ Hz), 6.91 (d, 2 H, C_6H_4, $J_{H-H} = 8.8$ Hz), 7.83 (d, 2 H, C_6H_4, $J_{H-H} = 8.7$ Hz), 7.93 (d, 2 H, C_6H_4, $J_{H-H} = 8.7$ Hz), 8.36 (d, 2 H, C_6H_4, $J_{H-H} = 8.8$ Hz). MS(EI) 386. UV−vis ($CHCl_3$) λ_{max}/nm 480 ($\epsilon = 54\ 700$ cm^{-1} M^{-1}). Mp 237−239 °C. Anal. Calcd for $C_{18}H_{22}N_4O_4Si$ (386): C, 55.96%; H, 5.70%; N, 14.51%. Found: C, 55.01%; H, 5.87%; N, 14.01%.

Polymer 9. The polymers **9** and **10** were prepared by a general procedure reported below for polymer **9**. To a solution of 1-bis(3-hydroxypropyl)amino-4-nitrobenzene (**1a**) (508 mg, 2 mmol) in 3 mL of THF was added with stirring 1,3-bis-(diethyamino)tetramethyldisiloxane (**3a**) (584 mg, 2 mmol). The resulting mixture was left to stir under N_2 for 24 h and then refluxed for 5 h. The reaction flask was cooled to room temperature, and the solvent was removed under vacuum. The residue was washed several times with methanol to afford a yellow viscous product (210 mg, 66%). ^1H NMR (270 MHz, $CDCl_3$) δ 0.13 (s, 12 H, $Si(CH_3)_2$), 1.82 (br, 4 H, CH_2), 3.50 (br, 4 H, $O-CH_2$), 3.71 (br, 4 H, $N-CH_2$), 6.68 (br, 2 H, C_6H_4), 8.04 (br, 2 H, C_6H_4). λ_{max}/nm 398 ($\epsilon = 21\ 600$ cm^{-1} M^{-1}). Anal. Calcd for $C_{16}H_{28}N_2O_5Si_2$ (384): C, 50.00%; H, 7.29%; N, 7.29%. Found: C, 49.13%; H, 7.35%; N, 6.69%. $M_w = 30\ 000$; $M_n = 13\ 200$; $M_w/M_n = 2.27$.

Polymer 10. 57%. ^1H NMR (270 MHz, $CDCl_3$) δ 0.06 (s, 12 H, $Si(CH_3)_2$, 0.14 (s, 12 H, $Si(CH_3)_2$), 1.83 (m, 4 H, CH_2), 3.51(br, 4 H, $O-CH_2$), 3.76 (br, 4 H, $N-CH_2$), 6.59 (br, 2 H, C_6H_4), 8.10 (br, 2 H, C_6H_4). λ_{max}/nm 398 ($\epsilon = 19\ 300$ cm^{-1} M^{-1}). Anal. Calcd for $C_{18}H_{34}N_2O_6Si_3$ (458): C, 47.16%; H, 7.42%; N, 6.11%. Found: C, 46.26%; H, 7.37%; N, 5.73%. $M_w = 16\ 000$; $M_n = 5200$; $M_w/M_n = 3.08$.

Polymer 11. To a mixture of 1-bis(3-hydroxypropyl)amino-4-nitrobenzene (**1a**) (254 mg, 1 mmol) and hydroquinone (110 mg, 1 mmol) in 4 mL of THF was added with stirring 1,3-bis-(diethyamino)tetramethyldisiloxane (**3a**) (584 mg, 2 mmol). The resulting mixture was left to stir under nitrogen for 24 h and then refluxed for 8 h. The reaction flask was cooled and the solvent was then removed under vacuum. The residue was washed several times with methanol to afford a yellow viscous product (320 mg, 51%). ^1H NMR (270 MHz, $CDCl_3$) δ 0.09 (s, 12 H, $Si(CH_3)_2$), 0.12 (s, 12 H, $Si(CH_3)_2$), 1.81 (br, 4 H, CH_2), 3.52 (br, 4 H, O−CH_2), 3.68 (br, 4 H, N−CH_2), 6.67 (br, 2 H, C_6H_4), 6.74 (s, 4 H, C_6H_4), 8.05 (br, 2 H, C_6H_4). λ_{max}/nm 401 (ϵ = 18 500 cm^{-1} M^{-1}). Anal. Calcd for $C_{26}H_{44}N_2O_8Si_4$ (624): C, 50.00%; H, 7.05%; N, 4.49%. Found: C, 48.76%; H, 6.98%; N, 4.04%. M_w = 6700; M_n = 4200; M_w/M_n = 1.59.

Polymer 12. The polymers **12**−**14** were prepared by a general procedure reported below for polymer **12**. To a solution of 2,2′-(4-[(4-nitrophenyl)azo]phenyl)iminobis(ethanol) (**1b**, Disperse Red 19) (330 mg, 1 mmol) in 3 mL of dioxane was added with stirring 1,3-bis(diethyamino)tetramethyldisiloxane (**3a**) (292 mg, 1 mmol). The resulting mixture was stirred under nitrogen for 24 h and then refluxed for 10 h. The reaction flask was cooled to room temperature, and the solvent was then removed under vacuum. The residue was washed several times with ethanol to afford a red polymer. The polymer was further purified by recrystallization from a chloroform/methanol mixture (220 mg, 49%). ^1H NMR (270 MHz, DMSO) δ 0.09 (s, 12 H, $Si(CH_3)_2$), 3.62 (br, O−CH_2), 3.79 (br, N−CH_2), 6.79 (br, 2 H, C_6H_4), 7.88 (br, 4 H, C_6H_4), 8.28 (br, 2 H, C_6H_4). λ_{max}/nm 482 (ϵ = 45 700 cm^{-1} M^{-1}). Anal. Calcd for $C_{20}H_{28}N_4O_5Si_2$ (460): C, 52.17%; H, 6.09%; N, 12.17%. Found: C, 52.44%; H, 5.63%; N, 11.79%. M_w = 10 000; M_n = 4000; M_w/M_n = 2.50.

Polymer 13. 50%. ^1H NMR (270 MHz, DMSO) δ 0.07 (s, 12 H, $Si(CH_3)_2$), 0.13 (s, 6 H, $Si(CH_3)_2$), 3.60 (br, 4 H, O−CH_2), 3.84 (br, 4 H, N−CH_2), 6.80 (br, 2 H, C_6H_4), 7.92 (br, 4 H, C_6H_4), 8.30 (br, 2 H, C_6H_4). λ_{max}/nm 484 (ϵ = 41 100 cm^{-1} M^{-1}). Anal. Calcd for $C_{22}H_{34}N_4O_6Si_3$ (534): C, 49.44%; H, 6.37%; N, 10.49%. Found: C, 50.63%; H, 6.07%; N, 9.87%. M_w = 12 000; M_n = 4600; M_w/M_n = 2.61.

Polymer 14. 50%. ^1H NMR (270 MHz, DMSO) δ 0.15 (s, 6 H, $Si(CH_3)$), 3.60 (br, 4 H, O−CH_2), 3.72 (br, 4 H, N−CH_2), 6.5−7.4 (14 H, C_6H_4), 7.84 (br, 4 H, C_6H_4), 8.25 (br, 2 H, C_6H_4). λ_{max}/nm 481 (ϵ = 42 700 cm^{-1} M^{-1}). Anal. Calcd for $C_{30}H_{32}N_4O_5Si_2$ (584): C, 61.64%; H, 5.48%; N, 9.59%. Found: C, 61.96%; H, 5.44%; N, 9.05%. M_w = 9800; M_n = 4700; M_w/M_n = 2.08.

Polymer 15. The polymers **15** and **16** were prepared by a general procedure reported below for polymer **15**. To a mixture of 2,2′-(4-[(4-nitrophenyl)azo]phenyl)iminobis(ethanol) (**1b**, Disperse Red 19) (330 mg, 1 mmol) and hydroquinone (110 mg, 1 mmol) in 5 mL of dioxane was added with stirring 1,3-bis(diethyamine)tetramethyldisiloxane (**3a**) (584 mg, 2 mmol). The resulting mixture was further stirred under N_2 for 24 h and then refluxed for 15 h. The reaction flask was cooled and the solvent was then removed under vacuum. The residue was washed several times with ethanol to afford a red polymer. The latter was further purified by recrystallization from a chloroform/methanol mixture (310 mg, 45%). ^1H NMR (270 MHz, DMSO) δ 0.01 (s, 12 H, $Si(CH_3)_2$), 0.14 (s, 12 H, $Si(CH_3)_2$), 3.61 (br, 4 H, O−CH_2), 3.78 (br, 4 H, N−CH_2), 6.76 (br, 4 H, C_6H_4), 6.84 (br, 2 H, C_6H_4), 7.84 (br, 4 H, C_6H_4), 8.30 (br, 2 H, C_6H_4). λ_{max}/nm 482 (ϵ = 38 500 cm^{-1} M^{-1}). Anal. Calcd for $C_{30}H_{44}N_4O_8Si_4$ (700): C, 51.43%; H, 6.29%; N, 8.00%. Found: C, 52.49%; H, 6.01%; N, 7.14%. M_w = 8700; M_n = 4800; M_w/M_n = 1.81.

Polymer 16. 42%. ^1H NMR (270 MHz, DMSO) δ 0.05 (s, 12 H, $Si(CH_3)_2$), 0.12 (s, 12 H, $Si(CH_3)_2$), 3.63 (br, 4 H, O−CH_2), 3.76 (br, 4 H, N−CH_2), 6.24 (s, 4 H, C_6H_4), 6.71 (br, 4 H, C_6H_4), 6.81 (br, 2 H, C_6H_4), 7.82 (br, 4 H, C_6H_4), 8.27 (br, 2 H, C_6H_4). λ_{max}/nm 480 (ϵ = 39 000 cm^{-1} M^{-1}). Anal. Calcd for $C_{36}H_{48}N_4O_8Si_4$ (776): C, 55.67%; H, 6.19%; N, 7.22%. Found: C, 56.72%; H, 6.47%; N, 6.78%. M_w = 14 000; M_n = 5600; M_w/M_n = 2.50.

Polymer 17. (A general procedure for the synthesis of polymers **17** and **18**.) To a solution of 1-methyl-4-(4′-[*N*,*N*-bis(2-hydroxyethyl)amino]styryl)pyridium tetraphenylborate (**1c**) (618 mg, 1 mmol) in 5 mL of cyclohaxanone was added with stirring 1,3-bis(diethyamino)tetramethyldisiloxane (**3a**) (292 mg, 1 mmol). The resulting mixture was left to stir at room temperature for 24 h and then heated to 80 °C for 12 h. The solvent was removed under vacuum at 60 °C. The residue was dissolved in 10 mL of chloroform and poured into methanol. The red-orange precipitate was collected by filtration (450 mg, 60%). ^1H NMR (270 MHz, DMSO) δ 0.10 (s, 12 H, $Si(CH_3)_2$), 3.60 (br, 4 H, O−CH_2,), 3.72 (br, 4 H, N−CH_2), 4.19 (s, 3 H, N^+−CH_3), 6.4−7.3 (br, 23 H, C_6H_4, B−C_6H_5 and =CH), 7.60 (br, 2 H, C_6H_4), 7.90 (br, 1 H, =CH), 8.06 (br, 2 H, C_6H_4), 8.70 (d, 2 H, C_6H_4). λ_{max}/nm 471 (ϵ = 71 020 cm^{-1} M^{-1}). Anal. Calcd for $C_{46}H_{53}BN_2O_3Si_2$ (747.8): C, 73.82%; H, 7.09%; N, 3.74%. Found: C, 74.70%; H, 6.73%; N, 3.28%. M_w = 8900; M_n = 4000; M_w/M_n = 2.22.

Polymer 18. 57%. ^1H NMR (270 MHz, DMSO) δ 0.06 (s, 12 H, $Si(CH_3)_2$), 0.12 (s, 6 H, $Si(CH_3)_2$), 3.62 (br, 4 H, O−CH_2,), 3.74 (br, 4 H, N−CH_2), 4.20 (s, 3 H, N^+−CH_3), 6.4−7.4 (br, 23 H, C_6H_4, B−C_6H_5 and =CH), 7.63 (br, 2 H, C_6H_4), 7.92 (br, 1 H, =CH), 8.08 (br, 2 H, C_6H_4), 8.70 (d, 2 H, C_6H_4). λ_{max}/nm 470 (ϵ = 67 900 cm^{-1} M^{-1}). Anal. Calcd for $C_{48}H_{59}BN_2O_4Si_3$ (821.8): C, 70.09%; H, 7.18%; N, 3.41%. Found: C, 71.24%; H, 6.84%; N, 3.28%. M_w = 11 000; M_n = 5200; M_w/M_n = 2.11.

Polymer 19. (A general procedure for the synthesis of polymers **19** and **20**.) To a mixture of 1-methyl-4-(4′-[*N*,*N*-bis(2-hydroxyethyl)amino]styryl)pyridium tetraphenylborate (**1c**) (618 mg, 1 mmol) and hydroquinone (110 mg, 1 mmol) in 5 mL of cyclohaxanone was added with stirring 1,3-bis(diethyamino)tetramethyldisiloxane (**3a**) (584 mg, 2 mmol). The resulting mixture was left to stir at room temperature for 24 h and then heated to 80 °C for 20 h. The solvent was removed under vacuum at 60 °C. The residue was dissolved in 10 mL of chloroform and poured into methanol. The red-orange precipitate was collected by filtration (490 mg, 50%). ^1H NMR (270 MHz, DMSO) δ 0.10 (s, 12 H, $Si(CH_3)_2$), 0.14 (s, 12 H, $Si(CH_3)_2$), 3.61 (br, 4 H, O−CH_2,), 3.72 (br, 4 H, N−CH_2), 4.18 (s, 3 H, N^+−CH_3), 6.4−7.0.4 (br, 27 H, C_6H_4, B−C_6H_5 and =CH), 7.60 (br, 2 H, C_6H_4), 7.90 (br, 1 H, =CH), 8.06 (br, 2 H, C_6H_4), 8.72 (d, 2 H, C_6H_4). λ_{max}/nm 472 (ϵ = 62 200 cm^{-1} M^{-1}). Anal. Calcd for $C_{56}H_{69}BN_2O_6Si_4$ (987.8): C, 68.03%; H, 6.99%; N, 2.83%. Found: C, 69.25%; H, 6.71%; N, 2.07%. M_w = 22 000; M_n = 7800; M_w/M_n = 2.82.

Polymer 20. 55%. ^1H NMR (270 MHz, DMSO) δ 0.09 (s, 12 H, $Si(CH_3)_2$), 0.14 (s, 12 H, $Si(CH_3)_2$), 3.59 (br, 4 H, O−CH_2,), 3.70 (br, 4 H, N−CH_2), 4.15 (s, 3 H, N^+−CH_3), 6.4−7.0.4 (br, 31 H, C_6H_4, B−C_6H_5 and =CH), 7.60 (br, 2 H, C_6H_4), 7.88 (br, 1 H, =CH), 8.03 (br, 2 H, C_6H_4), 8.69 (d, 2 H, C_6H_4). λ_{max}/nm 474 (ϵ = 63 100 cm^{-1} M^{-1}). Anal. Calcd for $C_{62}H_{73}BN_2O_6Si_4$ (1063.8): C, 69.98%; H, 6.86%; N, 2.63%. Found: C, 71.18%; H, 6.44%; N, 2.16%. M_w = 16 000; M_n = 8400; M_w/M_n = 1.90.

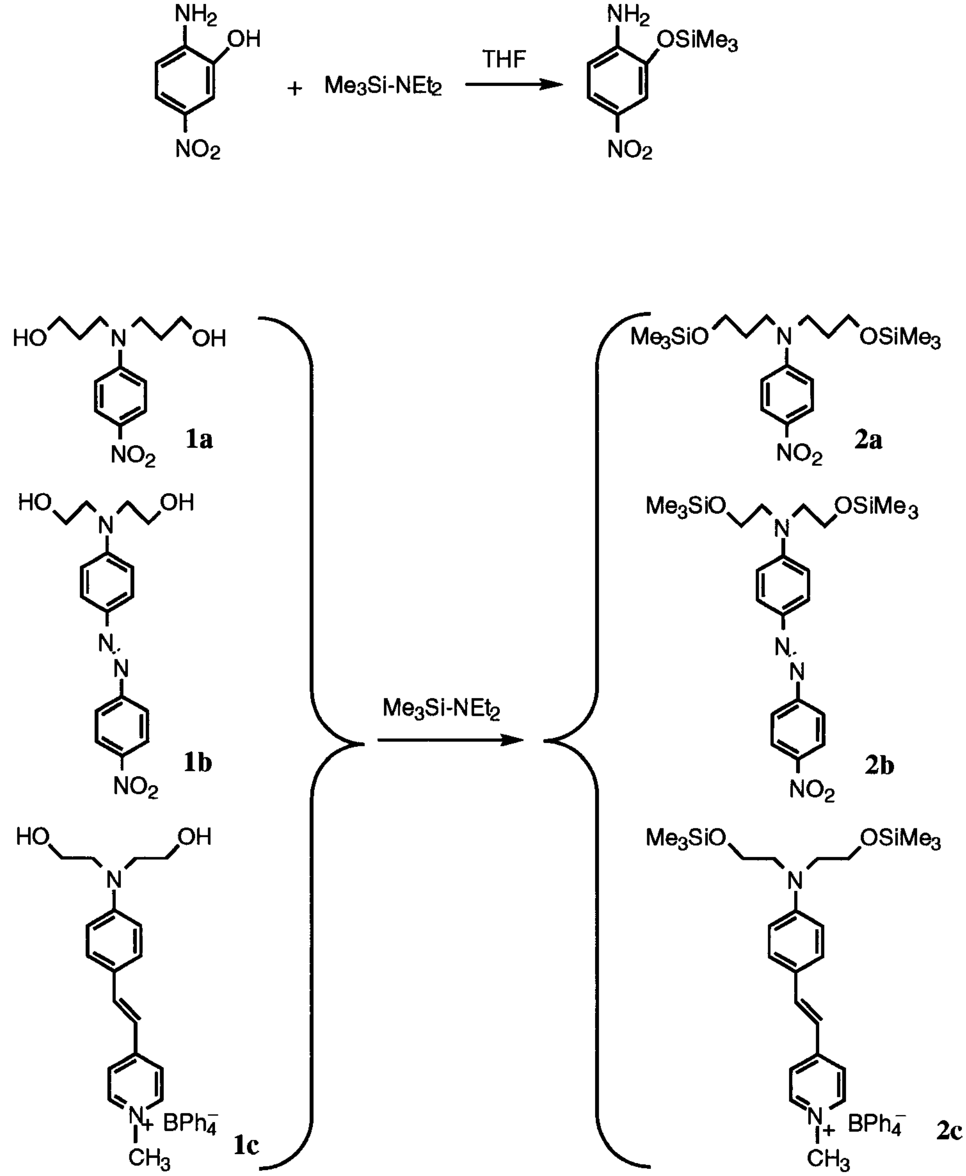
Polymeric Thin Films. The solution of a polymer was prepared by dissolving it (~40 mg) in ~2 mL of chloroform (15% weight concentration), filtered through 0.2-μm syringe filters, which was then spin-coated onto a glass substrate with an indium−tin oxide (ITO) conductive layer. The films were dried under vacuum for 24 h before the poling experiments. Thickness of polymeric thin films was obtained by profilometry measurements using a Dektak III profilometer (Sloan Technology). For poling experiments, the thin films were heated to elevated temperatures (140−190 °C) over a period of 40 min with the application of dc electric fields from 3.5 to 5 KV, using a corona discharge setup (1.0 cm tip-to-plane gap), and then cooled to room temperature over a period of 30 min.

Results and Discussion

Synthesis. It is well-known that aminosilanes (R'_3SiNR_2, R′, R = Me, Et), which can be easily prepared from the reaction of the corresponding chlorosilanes with excess amines, react quantitatively with organic compounds containing acidic protons via acid−base hydrolysis. For example, 2-amino-5-nitrophenol reacts with trimethylsilyldiethylamine, Me_3SiNEt_2 to yield 2-amino-5-nitrotrimethylsilylphenol and diethylamine (Scheme 1).[10] Similarly, 1-bis(3-hydroxypropyl)amino-4-nitrobenzene (**1a**), 2,2′-(4-[(4-nitrophenyl)azo]phenyl)-iminobis(ethanol) (**1b**, Disperse Red 19), and 1-methyl-4-(4′-[*N*,*N*-bis(2-hydroxyethyl)amino]styryl)pyridinium tetraphenylborate (**1c**) react with 2 equiv of Me_3SiNEt_2 to give the corresponding silylated alcohols **2a**, **2b**, and **2c** (Scheme 1).

To determine the effect of the structure and length of the siloxane chain on the properties of the polymers, we chose to study four different types of Si compounds,

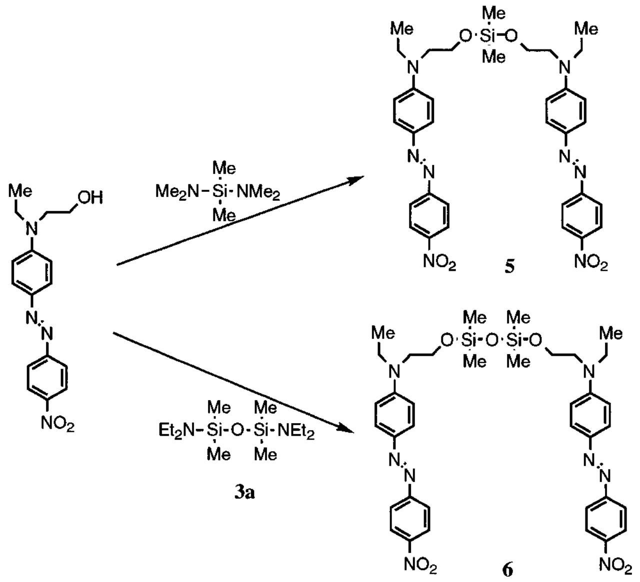
Scheme 1



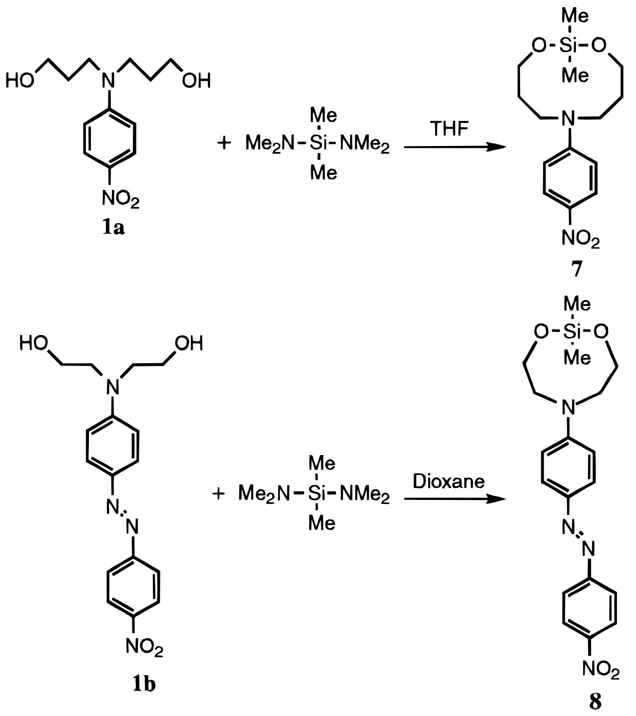
namely, bis(dimethylamino)dimethylsilane ($Me_2Si(NMe_2)_2$), 1,3-bis(diethylamino)tetramethyldisiloxane (**3a**), 1,5-bis(diethylamino)hexamethyltrisiloxane (**3b**), and 1,3-bis(diethylamino)di(methylphenyl)disiloxane (**4**). Bis(dimethylamino)dimethylsilane is commerically available, and the latter three were conveniently prepared from the reaction of their corresponding dichlorosiloxanes with excess dry diethylamine. By use of the acid–base hydrolytic chemistry described above for compounds **2a**–**c**, the reaction of 1 equiv of bis(dimethylamino)dimethylsilane or 1,3-bis(diethylamino)tetramethyldisiloxane with 2 equiv of Disperse Red 1 (Scheme 2) gave dimers **5** and **6**. The latter could be considered as model compounds to the polymers reported here. Based on a similar approach, it is expected that the reaction of equimolar quantities of diaminosilyl compounds and bifunctional chromophores should yield the desired polymers. We first attempted this chemistry by reacting bis(dimethylamino)dimethylsilane with 1-bis(3-hydroxypropyl)amino-4-nitrobenzene (**1a**) or Disperse Red 19 (**1b**). It is interesting to note that these reactions did not lead to the formation of the polymers, but produced stable monomeric compounds **7** and **8** by a possible ring closure process (Scheme 3). This may be due to the close proximity of the two hydroxide groups on the chromophore to the $SiNMe_2$ groups, which facilitates ring formation before any polymerization can proceed. This ring formation should be inhibited when longer aminosiloxanes (**3a**, **3b**, **4**) are used as bases.

Scheme 4 shows the structures of different siloxane-linked polymers that were synthesized in this study. These polymers were prepared by using two methodologies based on a similar acid–base hydrolytic approach. In the first approach used for polymers **9**, **10**, **12**, **13**, **14**, **17**, and **18**, equimolar quantities of the desired bifunctional chromophore and diaminosiloxane are reacted together. For example, 1-bis(3-hydroxypropyl)amino-4-nitrobenzene (**1a**) chromophore was added to a concentrated THF solution of 1,3-bis(diethyamino)tetramethyldisiloxane (**3a**), stirred at room temperature for 1 day, and then refluxed for a few hours to produce polymer **9**. The polymers **11**, **15**, **16**, **19**, and **20** were synthesized by reacting equimolar quantities of the chromophore and a rigid spacer with 2 equiv of the desired diaminosiloxane. For example, one equivalent each of Disperse Red 19 (**1b**) and hydroquinone were added to 2 equiv of 1,3-bis(diethyamino)tetramethyldisiloxane (**3a**) in a concentrated dioxane solution,

Scheme 2



Scheme 3



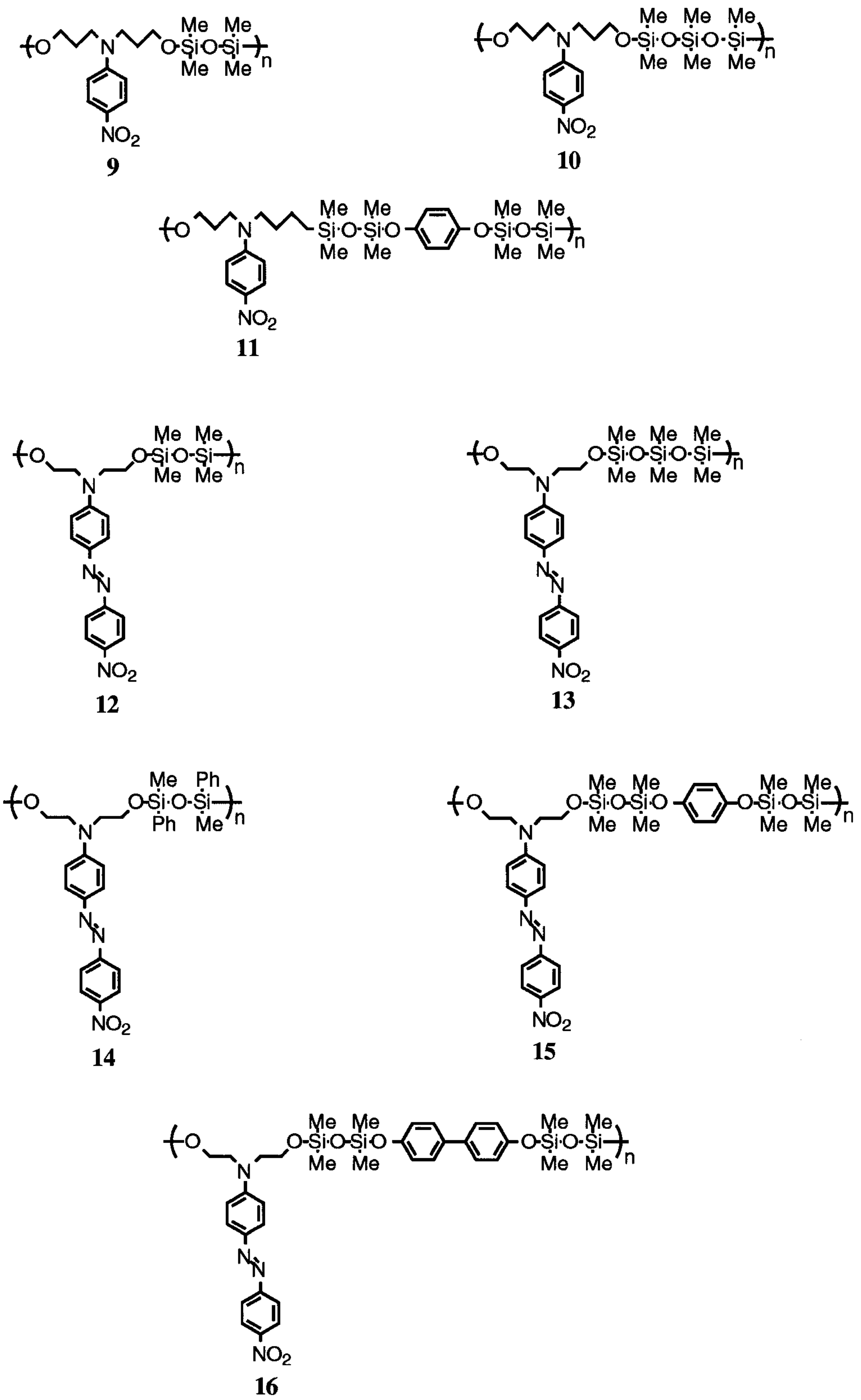
stirred for 1 day at room temperature, and then refluxed for a few hours to yield polymer **15**. The above-mentioned polymers were characterized by using standard techniques, and the pertinent data are reported in Table 1.

Thermal Stability. The thermal stabilities of the polymers were determined by thermogravimetric analysis (TGA) under a nitrogen atmosphere. T_d (Table 1) is the temperature at which a 5% weight loss of the polymer was observed. As seen from Table 1, these polymers display high thermal stabilities, which can be ascribed to high mechanical strength imparted by stable and strong Si−O bonds in the backbone. The polymers **9**−**16**, which contain either **1a** or **1b** as NLO chromophores, show decomposition temperatures from 300 to 330 °C. These values are capable of meeting thermal requirements for constructing optical devices. The T_d of polymers **17**−**20**, which contain pyridinium salt (**1c**) as the NLO chromophore, are about 100 °C lower than those of the others. This is probably due to low thermal stability of the ionic salt, which decomposes much faster than the siloxane backbone.

Glass Transition Temperatures. The glass transition temperatures (T_g) of the polymers empolyed in this study were determined by differential scanning calorimetry. Polymers **9**−**11** were found to be viscous products, and it is expected that their glass transition temperatures are very low. The T_g of polymers **12**−**16** are in the range 96−127 °C, and for polymers **17**−**20**, these ranged from 50 to 90 °C. It is known that the diorganosiloxane polymers usually possess low T_g due to the flexibility of the Si−O backbone.[11] As can be seen from the data presented in Table 1, the glass transition temperatures for the polymers reported here are influenced by a number of factors: (i) *The first factor is the size of the NLO chromophores.* The larger the NLO substituents, more difficult it is for the chains to move or rotate.[11] The glass transition temperatures of copolymers of dimethylsiloxane and NLO chromophore **1a** (polymers **9**−**11)** are low due to the flexible Si−O bond and a fast rotation of the small NLO groups around the backbone. However, T_g is greatly increased by incorporating longer and heavier NLO chromophores (polymers **12**−**20**). This enhancement probably also arises from a strong electrostatic interaction between highly polar chromophores, which restricts chromophoric mobility, especially rotation along the backbone. The chromophores locked in particular configurations limit flexibility of the siloxane linkages and make the backbone more rigid, which leads to higher T_g. Compared with the hemicyanine dye contained in polymers **17**−**20**, Disperse Red 19 (polymers **12**−**16**), seems to be more effective in reducing the flexibility of the siloxanes. The latter leads to a more rigid conformation of the polymer main chain and hence higher T_g. (ii) *Another factor is the length of the siloxane linkages.* As seen from Table 1, T_g decreases with increasing length of the siloxane linkages. For example, T_g of polymer **12** with disiloxane [$-OSi(Me_2)OSi(Me_2)-$] links in the polymeric main chain is about 10 °C higher than that of polymer **13** containing trisiloxane [$-OSi(Me_2)OSi(Me_2)OSi(Me_2)-$] linkages. A similar trend is observed upon comparing polymers **17** and **18**. Reduction of the length of the siloxane linkage to below that of disiloxane, which is expected to lead to higher T_g, is prohibited due to the formation of a ring, as seen in the reaction of the bifunctional NLO chromophores with $Me_2Si(NMe_2)_2$ (Scheme 3). (iii) *The substituents at each Si center*: T_g of polymer **12** is ~7 °C higher than that of polymer **14**. The latter bears one methyl group and one phenyl group attached to each Si atom instead of two methyl groups. (iv) *Introduction of a rigid spacer is another influence.* T_g is also increased by inserting a rigid spacer such as phenol or biphenol between siloxane linkages. The spacer reduces the flexibility of siloxane chains in the polymeric backbone. For example, T_g for polymer **12** without any spacer is 108 °C, and it increases to 120 °C for the polymer containing a phenol linkage (**15**) and to 127 °C for the polymer containing the bisphenol spacer linkage (**16**). A similar trend is observed upon comparing polymers **17**, **19**, and **20**.

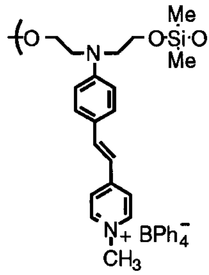
UV−Vis Spectra. The peak positions in the UV−vis spectra of these polymers were found to be similar to those of the corresponding monomers, 398 nm for **1a**, 482 nm for **1b**, and 472 nm for **1c**. This suggests that

Scheme 4



the absorption characteristics of the chromophores are not affected by the polymerization process. For polymers **9**−**11** containing **1a** as the NLO chromophore in the backbone, the absorption maxima are around 400 nm. The second harmonic generation (SHG) wavelength of 532 nm employed in this study is beyond the absorption regions of the latter polymers. Thus, there should be only nonresonant contributions to the SHG signal in these polymers. However, for polymers **12**−**20**, which contain either **1b** or **1c** chromophore (absorption maxima 470−484 nm) in the backbone, the SHG wavelength falls within the tail of the absorption curves, and the signals are expected to be weakly resonance enhanced.

Second-Harmonic Generation Measurements. All polymers reported here were found to be soluble in common organic solvents. As mentioned earlier, this high solubility is imparted by the organosilyl groups in



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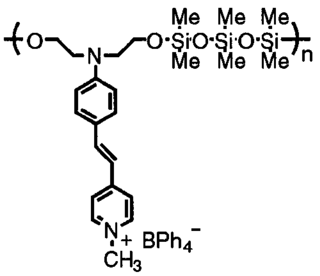

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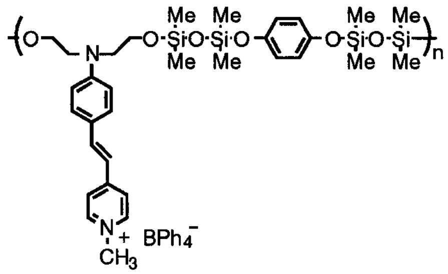

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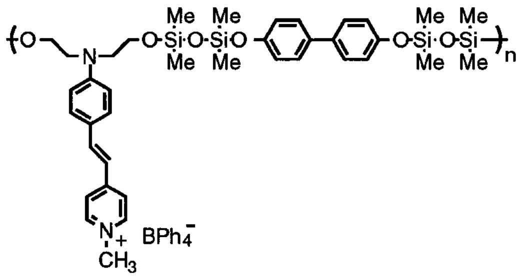

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Table 1. Physical Properties of Polymers[a]

polymer	mol. weight, M_w, M_n	λ_{max}, nm	T_d, °C	T_g, °C
9	30000, 13200	398	339	
10	16000, 5200	398	335	
11	6700, 4200	401	303	
12	10000, 4000	482	330	108
13	12000, 4600	484	316	96
14	9800, 4700	481	302	101
15	8700, 4800	482	301	120
16	14000, 5600	480	335	127
17	8900, 4000	471	230	65
18	11000, 5200	470	228	52
19	22000, 7800	472	203	84
20	16000, 8400	474	218	91

[a] T_d = decomposition temperature; T_g = glass transition temperature.

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
9	0.70	66	3.4	170	5.0
10	0.92	55	2.7	180	5.0
11	0.75	40	2.4	190	5.0
12	0.20	71	52	150	4.0
13	0.12	61	40	150	4.0
14	0.15	42	29	150	4.0
15	0.20	56	37	150	4.0
16	0.18	47	42	150	4.0
17	0.23	82	21	140	3.5
18	0.30	75	15	140	3.5
19	0.20	62	30	140	3.5
20	0.25	58	12	140	3.5

the main chain, and it offers ease of processibility in the preparation of good optical quality thin films. The NLO properties of the above-mentioned polymers were examined by measuring second-harmonic generation in transmission from the appropriate thin film, spin-coated onto an ITO-coated glass slide. 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. The thin film was kept rotating with the speed of 2°/min from 0 to 60° during the process of measurements. The SHG signal was recorded and amplified by using a photomultiplier tube and then averaged in a boxcar integrator. A quartz crystal was used as the reference sample.

As expected, without the application of an external electric field, no signal was observed, suggesting that the dipoles in these polymers are randomly oriented. The poling conditions and SHG characteristics of polymers are listed in Table 2. For the viscous polymers **9**–**11**, a poling temperature of 170–190 °C and dc electric field of 5 KV were applied. The latter are 30–40 °C in temperature and 1–1.5 kV in electric field, higher than for the solid polymers **12**–**20**. The $\chi^{(2)}$ values for polymers **9**–**11** are in the range (2.2–3.5) × 10^{-8} esu. These are much lower than those for polymers **12**–**16** [(30–50) × 10^{-8} esu] and polymers **17**–**20** [(15–30) × 10^{-8} esu]. The higher values of $\chi^{(2)}$ for polymers **12**–**20** than **9**–**11** can be explained by comparing the magnitudes of β, the second-order molecular NLO coefficient. The value of β for Disperse Red 19 (610 × 10^{-30} esu) is about 8 times higher than that of *p*-nitro-*N*,*N*-dimethylaminobenzene (73 × 10^{-30} esu).[15] The β values for the pyridinium salt type chromophores (**1c**) with halides as the counterions [(170–304) × 10^{-30} esu] are also 2–4 times higher than that for *p*-nitro-*N*,*N*-dimethylaminobenzene.[2] The $\chi^{(2)}$ values for the polymers reported here are comparable to the values for other recently reported poled polymers which are soluble in high boiling solvents, e.g., polyurethane with hemicyanine dye (3 × 10^{-8} esu)[9] and polyimides with the Disperse Red dye [(50–170) × 10^{-8} esu].[12–14]

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. As expected, the viscous polymers **9**–**11** showed significant (~70%) SHG signal decay in 2–3 days. However, polymers **12**–**20** showed much higher temporal stabilities of their SHG signals. Approximately 50% of SHG signal decay occurred in the range 240–580 h for polymers **12**–**16** and 408–840 h for polymers **17**–**20**. Alignment stability of chromophore dipoles is expected to be affected by a number of factors including the size of the chromophore relative to the amount of local free volume available in the polymer.[5] Small chromophores such as *p*-nitroaminobenzene are more easily fitted into free volume voids

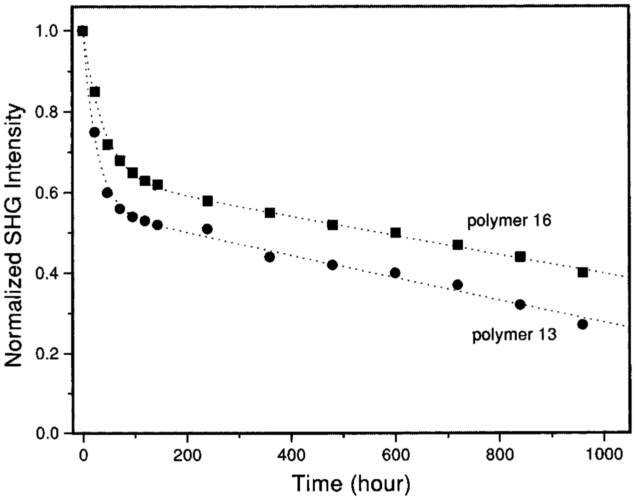

Figure 1. SHG intensity as a function of time for poled films of polymers **13** and **16** at room temperature.

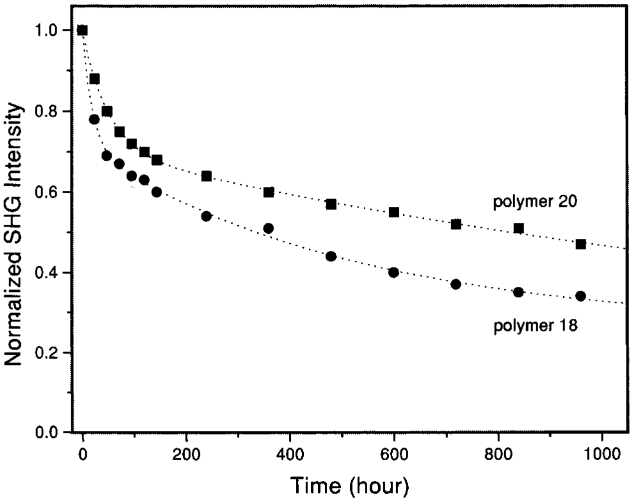

Figure 2. SHG intensity as a function of time for poled films of polymers **18** and **20** at room temperature.

in polymers **9**−**11** and then redistributed without a change in free energy. Polymers **12**−**20** contain larger NLO chromophores, which makes chromophore rotation in polymeric matrixes more difficult and thus imparts higher SHG signal stability.

For polymers containing a *p*-nitroaminobenzene NLO chromophore in the backbone, introduction of a rigid spacer (polymer **11**) did not affect the stability of chromophore alignment, since the performance is above T_g for these polymers. However, for polymers **15, 16, 19**, and **20**, insertion of a rigid spacer into the polymeric main chain led to enhanced temporal stabilities of the chromophore dipole alignment. For example, for polymer **16** with a biphenol rigid spacer in the backbone, the time duration to 50% decay of the SHG signal was ∼340 h longer than without the spacer (**13**) (Figure 1). Similarly, the SHG signal for polymer **20** lasts ∼430 h longer than that for polymer **18** (Figure 2). The temporal alignment stability of the SHG signal is also affected by the nature and size of the NLO chromophore. For example, it is interesting to note that the stability of the SHG signal for the polymer containing the pyridinium salt chromophore **1c** with a bulky counterion BPh_4^- was found to be higher than for that containing the azo dye, **1b** (Figures 1 and 2).

Conclusions

Functionalized siloxane-linked polymers for second-order NLO materials are easily accessible by using the simple acid−base hydrolytic chemistry route. These polymers exhibit good solubility in common organic solvents, high thermal stability, and efficient second harmonic generation characteristics with moderate temporal stabilities of the SHG alignment. We are currently working on (i) chain−chain cross-linked disiloxane polymers with high β chromophores in the backbone, which are expected to improve alignment stability of the chromophoric side groups, and (ii) copolymers containing imide/urethane and siloxane linkages, which are expected to lead to high T_g soluble polymers.

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