Synthesis of Novel Polysiloxanes Containing Charge Transporting and Second-Order Nonlinear Optical Functionalities with Atom Economical Constructs

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ABSTRACT: Novel, highly functionalized polysiloxanes were prepared in which each repeat unit bears, on average, one charge transporting and one to two second-order nonlinear optical chromophores. Covalent attachment of charge-transporting carbazole or diphenylamine derivatives was realized through efficient Pt-catalyzed hydrosilylation. Poly(hydrogen methylsiloxane) was reacted with 9-(2-propenyl)carbazole or (*N*-phenyl-*N*-2-propenylamino)benzene, affording poly[methyl-3-(9-carbazolyl)propylsiloxane] and poly-[methyl-3-(*N*,*N*-diphenylamino)propylsiloxane], respectively. Rather remarkable regiospecific bromination of the two arylamine-containing siloxane polymers was achieved using benzyltrimethylammonium chlorobromate, resulting in the formation of poly[methyl-3-(*N*−(3,6-dibromocarbazolyl))propylsiloxane] and poly[methyl-3-(*N*,*N*-bis(4-bromophenyl)amino)propylsiloxane]. Pd-catalyzed Heck-type coupling of the arylbromide-bearing polysiloxanes with either vinylbenzenephosphonic acid diethyl ester or 4-nitrostyrene afforded stilbene-containing polymers bearing phosphonate ester or nitro moieties as electron-withdrawing functionalities, respectively. These fully functionalized polymers were readily soluble in several common organic solvents.

Introduction

The photorefractive effect, found in materials that are both photoconductive and have nonlinear optical properties, is avidly being pursued for optical processing applications. Photorefractivity holds great potential in holographic optical data storage, beam steering, optical computing and switching, and integrated optics.[1] Photorefractive materials can, in principle, execute such integrated optoelectronic operations as switching, modulation, thresholding, and parallel processing for image processing and display. Until 1990, only inorganic materials were found to be photorefractive. Since then, organic crystals and, more recently, polymers have been synthesized that are photorefractive.[1]

Polymeric photorefractive materials promise many of the traditional advantages associated with polymers, such as good thermal stability, low dielectric constants, and ease of processing. To manifest the photorefractive effect, it is thought that these polymeric materials must contain photocharge generating (CG) and transporting (CT) functionality, charge-trapping sites, and nonlinear optical (NLO) chromophores. Among the major challenges in the field of organic photorefractive materials are to increase stability from phase separation, increase temporal stability, increase thermal stability, increase diffraction efficiency, improve charge transport efficiency, improve tunable wavelength sensitivity, improve electrooptic coefficients, create efficient synthetic methods, and develop reproducible processing methods.

A number of composites systems have been reported where a polymer possessing one of the requisite functionalities (e.g., covalently attached NLO chromophores) is doped with the others (CG and CT dopants) or a photoconductive polymer (e.g., poly(*N*-vinylcarbazole)) is doped with the sensitizer and NLO dopants.[2−22] The high small molecule dopant loading levels necessary (up to 50 wt %) result in some major disadvantages, including diffusion, volatilization, and/or phase separation (crystallization) of the dopants. In addition, plasticizers and compatibilizers are often used to lower the glass-transition temperature (T_g) of the polymer and/or increase solubility of the dopants in the host polymer, respectively. This, in turn, dilutes the effective concentration of the CT, CG, and NLO moieties, potentially diminishing the efficiency and sensitivity of the photorefractive polymer composite.

It naturally followed that polymers were developed in which all the necessary moieties were covalently attached. Several "fully functionalized" polymeric systems have been reported although not all have unambiguously demonstrated photorefractivity.[23−38] Some shortcomings of the majority of single-component systems reported to date include the random orientation and spacing of charge transport moieties and synthetic difficulties.

Herein, we report the synthesis of single-component siloxane polymers in which charge-transporting and NLO functionalities are covalently attached to each polymer repeat unit.[39] In fact, these multifunctional systems contain two NLO chromophores per repeat unit, thereby doubling the NLO chromophore density over conventional NLO polymers. In these polymers, the charge-transporting moiety is integrated into the NLO functionalities, an atom economical approach to designing multifunctional materials. It was recently demonstrated in low molar mass compounds that such multifunctional chromophores exhibited large photorefractive optical net gain and high photorefractive diffraction efficiency.[40] Thus, integrating the NLO chromophores into the CT moiety within the same molecule did not adversely affect the photoconductivity of the carbazole charge transport functionality.

A phosphonate ester was selected as the electron-withdrawing functionality for our NLO component for several reasons. First, the phosphonate ester group has been shown to be nearly as effective as a nitro group for enhancing the electrooptic properties in aniline

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derivatives.[41] Second, the phosphonate ester is a strong hydrogen acceptor for hydrogen bonding. It has been used effectively in forming miscible polymer blends[42] and is expected to aid in the formation of hydrogen bond stabilized composites through favorable enthalpic gains effected by hydrogen bonding. Finally, it imparts excellent solubility to polymers.[39] The synthetic methodology we have developed is versatile (i.e., the charge transport and/or the NLO functionality can be easily changed or modified). To demonstrate the utility of our synthetic methodology, an analogous polysiloxane derivative bearing the electron-withdrawing nitro group was prepared. These polymers, when doped with CG dopants, are expected to exhibit photorefractive behavior, a prospect that is currently under investigation.

Experimental Section

Materials. CH_2Cl_2, methanol, hexanes, Et_2O, EtOAc, triethyl phosphite, allylbromide, Et_3N, DMF, and THF were distilled before use. 4-Bromoacetophenone, $NaBH_4$, poly(hydrogen methylsiloxane) (United Chemical Technologies, NM203, Mn ca. 2000), EtOH, benzyltrimethylammonium chloride, bromine, carbazole, dichloro(dicyclopentadiene)platinum(II), tri-*o*-tolylphosphine, palladium(II) diacetate, $NiCl_2$, fused $KHSO_4$, NaH, CH_3CN, and picric acid were used as received from commercial suppliers. 4-Vinylbenzenephosphonic acid diethyl ester[43,44] (**3**), 9-(2-propenyl)carbazole[45] (**4**), (*N*-phenyl-*N*-2-propenylamino)benzene[46] (**5**), benzyltrimethylammonium chlorobromate[47] ($BTMABr_2Cl$), and 4-nitrostyrene[48] (**10**) were prepared according to previously reported procedures. All reactions were conducted under a dry nitrogen atmosphere unless otherwise indicated.

Measurements. ^{1}H NMR spectra were recorded on Bruker AM-300 or AC-200 spectrometers. FT-IR spectra were recorded on Nicolet Impact 400 or Perkin-Elmer Spectrum 2000 spectrometers. UV−visible spectroscopic measurements were recorded using a Hewlett-Packard diode array spectrophotometer (model 8452A). DSC analyses were secured with a DuPont model 2100 DSC instrument using a scan rate of 20 °C/min (under N_2). Glass-transition temperatures (T_g) were reported from the scan after which no appreciable change was observed. Mass spectra were recorded with a Hewlett-Packard GC/MS model 5972A MSD. Molecular-weight distributions were determined by size exclusion chromatography (SEC, Waters 510 RI, 40 °C, 1 mL/min) in THF solutions using a series of Waters Styragel columns (HR 1, HR 3, and HR 4) calibrated with polystyrene standards. Number-average (M_n) and weight-average (M_w) molecular weights were calculated. Elemental analyses (CHN) were obtained from the University of Toledo Instrumentation Center.

Synthesis of Poly[methyl-3-(9-carbazolyl)propylsiloxane] (6). Poly(hydrogen methylsiloxane) (7.2 g, 0.12 mol equiv) was added to a solution of 9-(2-propenyl)carbazole (30 g, 0.14 mol) in a dry single-necked flask containing 100 mL of distilled toluene under nitrogen. After the addition of dichloro(dicyclopentadiene)platinum (5 mg, 0.015 mmol), the mixture was heated to 60 °C for 12 h under nitrogen. The disappearance of the polymer Si−H peak (2150 cm^{-1}) was monitored by FT-IR. The mixture was then poured into 3 L of cold hexane and reprecipitated twice from THF into hexane. The dark brown polymer was dissolved in THF and passed through a Florisil column (68% yield). ^{1}H NMR (300 MHz, DMF-d_7): δ −0.55 to −0.15 (bs, 3H, Si−CH_3), 0.00−0.45 (bm, 2H, Si−CH_2−), 1.43−1.75 (bm, 2H, N−CR_2−CH_2−), 3.80−4.30 (bm, 2H, N−CH_2−), 7.10−7.65 (bm, 6H, ArH), 8.05−8.35 (bm, 2H, C4 and C5 ArH). T_g = 55 °C. M_n = 6500. M_w = 11700. Anal. Calcd for $C_{16}H_{17}NO$: C, 71.87; H, 6.41; N, 5.24. Found: C, 70.37; H, 6.41; N, 4.94.

Synthesis of Poly[methyl-3-(*N*-(3,6-dibromocarbazolyl))propylsiloxane] (7). Poly[methyl 3-(9-carbazolyl)propylsiloxane] (2.0 g, 7.5 mmol) was dissolved in 100 mL of THF and 40 mL of methanol at room temperature, and to this was added $BTMABr_2Cl$ (7.7 g, 22.5 mmol) with constant stirring. After 5 h, the reaction was stopped and solvents were removed in vacuo. The resulting polymer was washed with water, dissolved in THF, and reprecipitated twice in methanol, affording a white solid polymer (65% yield). ^{1}H NMR (300 MHz, DMF-d_7): δ −0.55 to −0.15 (bs, 3H, Si−CH_3), 0.00−0.45 (bm, 2H, Si−CH_2−) 1.43−1.75 (bm, 2H, N−CR_2−CH_2−), 3.80−4.35 (bm, 2H, N−CH_2-), 7.00−7.30 (bm, 2H, C1, C8 ArH), 7.30−7.60 (bm, 2H, C2, C7 ArH), 8.25−8.60 (bm, 2H, C4, C5 ArH); T_g = 89 °C; M_n = 6800; M_w = 10600. Anal. Calcd for $C_{16}H_{15}Br_2NOSi$: C, 45.20; H, 3.56; N, 3.29. Found: C, 45.09; H, 3.63; N, 3.12.

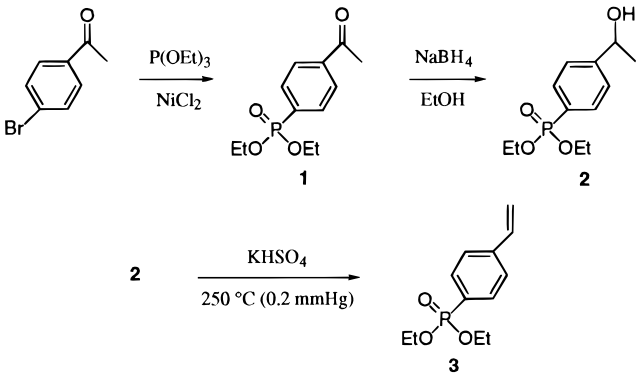
Synthesis of Poly[methyl-3-(3,6-bis(diethyl 4-phosphonatestyryl)carbazolyl)propylsiloxane] (8). To a solution of poly[methyl-3-(*N*−(3,6-dibromocarbazolyl))propylsiloxane] (75 mg, 0.18 mmol) in 5 mL of DMF, palladium(II) diacetate (2.4 mg, 0.01 mmol), tri-*o*-tolylphosphine (6.0 mg, 0.02 mmol), triethylamine (5 mL, 36 mmol), and **3** (136 mg, 0.53 mmol) were added. The yellow reaction mixture was stirred at 90 °C for 12 h. The mixture was poured into 300 mL of methanol to precipitate the polymer. The polymer was filtered, washed with hot methanol twice, and dried *in vacuo*. ^{1}H NMR (300 MHz, DMF-d_7): δ −0.60 to −0.05 (bs, 3H, Si−CH_3), 0.00−0.55 (bm, 2H, Si−CH_2−), 1.10−1.35 (bm, 12H, OCR_2CH_3), 1.40−1.90 (bm, 2H, N−CR_2−CH_2−), 3.45−3.55 (bm, 2H, NCR_2−CH_2−), 3.80−4.40 (bm, 8H, −OCH_2CR_3), 6.90−8.30 (bm, 18H, =CH and ArH). UV−vis λ_{max}: 324 nm (270−440 nm). IR (neat, cm^{-1}): 1595 ($\nu_{stilbene\ C=C}$), 1235 ($\nu_{P=O}$). M_n = 9800. M_w = 11800. Anal. Calcd for $C_{40}H_{47}NO_7P_2Si$: C, 64.59; H, 6.37; N, 1.88. Found: C, 62.39; H, 6.25; N, 2.13.

Synthesis of Poly[methyl-3-(3,6-bis(4-nitrostyryl)carbazolyl)propylsiloxane] (11). To a solution of poly[methyl-3-(*N*−(3,6-dibromocarbazolyl))propylsiloxane] (0.44 g, 1.0 mmol) in 10 mL of DMF, palladium(II) diacetate (3.5 mg, 0.015 mmol), tri-*o*-tolylphosphine (9.4 g, 0.031 mmol), triethylamine (10 mL, 71 mmol), and 4-nitrostyrene (0.46 g, 3.1 mmol) were added. The yellow reaction mixture was stirred at 90 °C for 48 h, cooled to room temperature, passed through a Florisil plug, and concentrated. The orange−red polymer was then dissolved in CH_2Cl_2, washed with water, solvent removed in vacuo, and dried. ^{1}H NMR (300 MHz, DMF-d_7): δ −0.50 to −0.05 (bs, 3H, Si−CH_3), 0.15−0.60 (bm, 2H, Si−CH_2−), 1.40−1.80 (bm, 2H, N−CR_2−CH_2−), 3.55−4.20 (bm, 2H, N−CH_2−), 6.40−6.80, 6.85−7.50, 7.90−8.25 (bm, 18H, =CH and ArH). T_g = 90 °C. M_n = 10200. M_w = 12900. UV−vis λ_{max}: 310 nm (270−500 nm). IR (neat, cm^{-1}): 1605 ($\nu_{stilbene\ C=C}$), 1515 and 1344 (ν_{nitro}). Anal. Calcd for $C_{32}H_{27}N_3O_5Si$: C, 68.43; H, 4.85; N, 7.48. Found: C, 67.91; H, 6.00; N, 6.02.

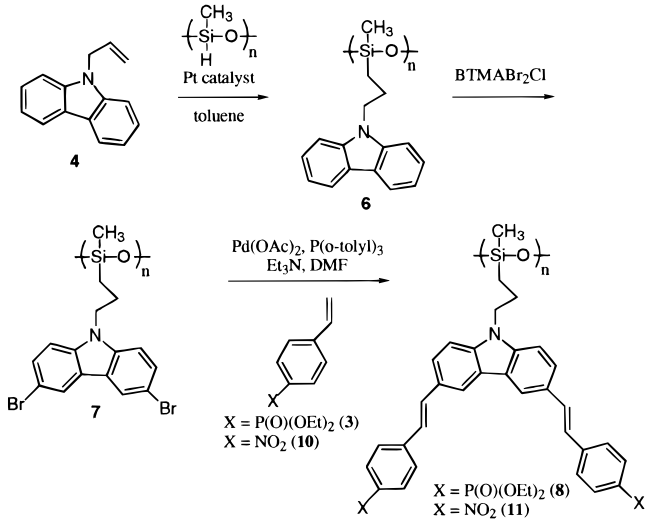
Synthesis of Poly[methyl-3-(*N*,*N*-diphenylamino)propylsiloxane] (12). Poly(hydrogen methylsiloxane) (1.8 g, 30 mmol) was added to a solution of (*N*-phenyl-*N*-2-propenylamino)benzene (8.1 g, 39 mmol) in 70 mL of toluene. After the addition of dichloro(dicyclopentadiene)platinum (1.2 mg, 0.003 mmol), the mixture was heated to 60 °C for 3 days. The disappearance of the polymer Si−H peak (2150 cm^{-1}) was monitored by FT-IR. The mixture was then poured into 700 mL of cold hexane. A solid was obtained, dissolved in THF, and reprecipitated twice into hexane (79% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ −0.40−0.10 (bs, 3H, Si−CH_3), 0.25−0.50 (bm, 2H, Si−CH_2−), 1.46−1.72 (bm, 2H, N−CR_2−CH_2−), 3.40−3.65 (bm, 2H, N−CH_2−), 6.80−7.05 (bm, 6H, ArH), 7.10−7.25 (bm, 4H, ArH). M_n = 5800, M_w = 9400. Anal. Calcd for $C_{16}H_{19}NOSi$: C, 71.33; H, 7.11; N, 5.20. Found: C, 69.54; H, 7.08; N, 4.90.

Synthesis of Poly[methyl-3-(*N*,*N*-bis(4-bromophenyl)amino)propylsiloxane] (13). Poly[methyl 3-(*N*,*N*-diphenylamino)propylsiloxane] (**12**, 4.0 g, 16.3 mmol) was dissolved in 400 mL of THF and 150 mL of methanol at room temperature. To the polymer solution was added $BTMABr_2Cl$ (11.8 g, 34.3 mmol) with constant stirring. After 2 h the reaction was stopped and solvents were removed under reduced pressure. The polymer was dissolved in THF and reprecipitated into methanol twice, affording a white solid product in 95% yield. ^{1}H NMR (300 MHz, DMF-d_7): δ −0.15−0.10 (bs, 3H, Si−CH_3), 0.40−0.52 (bm, 2H, Si−CH_2−), 1.50−1.75 (bm, 2H,

Scheme 1



Scheme 2



N−CR_2−CH_2−), 3.50−3.75 (bm, 2H, N−CH_2−), 6.75−7.10 (bm, 4H, ArH), 7.25−7.51 (bm, 4H, ArH). M_n = 6800. M_w = 9500. Anal. Calcd for $C_{16}H_{17}Br_2NOSi$: C, 44.98; H, 4.01; N, 3.28. Found: C, 44.55; H, 4.12; N, 3.14.

Synthesis of Poly[methyl-3-(*N*,*N*-(4,4′-bis(diethyl 4-phosphonatestyryl)diphenylamino))propylsiloxane] (14). To a solution of poly[methyl-3-(*N*,*N*-bis(4-bromophenyl)amino)-propylsiloxane] (**13**, 0.72 g, 1.8 mmol) in 6.4 mL of DMF, palladium(II) diacetate (4 mg, 0.18 mmol), tri-*o*-tolylphosphine (200 mg, 0.7 mmol), triethylamine (0.5 mL, 4 mmol), and **3** (1.4 g, 5 mmol) were added. The dark reaction mixture was stirred at 90 °C for 12 h and poured in 400 mL of methanol. The polymer was dissolved in CH_2Cl_2 and washed with H_2O. The polymer was reprecipitated into methanol twice and dried in vacuo, affording a bright yellow−green solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ −0.20−0.20 (bs, 3H, Si−CH_3), 0.25−0.75 (bm, 2H, Si−CH_2−), 1.05−1.35 (bm, 12H, P−O−CR_2CH_3), 1.50−1.75 (bm, 2H, N−CR_2−CH_2−), 3.40−3.75 (bm, 2H, N−CH_2−), 3.80−4.25 (bm, 8H, O−CH_2−CR_3), 6.70−7.90 (bm, 20H, =CH and ArH). UV−vis λ_{max}: 390 nm (240−460 nm). IR (neat, cm^{-1}): 1594 ($\nu_{stilbene\ C=C}$), 1240 ($\nu_{P=O}$). M_n = 8900. M_w = 13400. Anal. Calcd for $C_{40}H_{49}NO_7P_2Si$: C, 64.41; H, 6.62; N, 1.88. Found: C, 59.64; H, 6.12; N, 1.77.

Results and Discussion

Styrene phosphonate **3** was prepared in three steps[43,44] (Scheme 1), starting with a $NiCl_2$-mediated Arbuzov-type phosphorylation of 4-bromoacetophenone with triethyl phosphite. The resulting phosphorylated acetophenone derivative **1**, obtained in 66% yield, was then reduced with $NaBH_4$, providing the phosphorylated alcohol **2** in nearly quantitative yield. Elimination of alcohol **2** was accomplished by the slow addition of **2** to molten $KHSO_4$, in a flask fitted with a short path distillation head, under vacuum at 250 °C in the presence of picric acid. 4-Vinylbenzenephosphonic acid diethyl ester (**3**) was collected in 48% yield and purified by column chromatography using basic alumina (bp = 128−130 °C/0.6 mmHg; lit. 132−134 °C/0.8 mmHg[43]). Although other hindered phenolic antioxidants were used to inhibit free radical polymerization of the resulting styrene phosphonate **3**, picric acid was found to be the most effective.

Poly(hydrogen methylsiloxane) (PHMS, M_n ca. 2000) was used to prepare charge transporter/NLO chromophore-bearing polysiloxanes in a three-step sequence of reactions (Scheme 2). Hydrosilylation of PHMS was achieved with 9-(2-propenyl)carbazole[45] (**4**) and dichloro(dicyclopentadiene)platinum(II) in toluene at 60 °C for 12 h, as previously reported.[21] Progress of the reaction was readily monitored by FT-IR analysis; disappearance of the Si−H absorption at 2150 cm^{-1} was observed. IR and ^{1}H NMR spectra confirmed the near-complete hydrosilylation as evidenced in Figures 1a and 2a by the absence of Si−H stretch at 2150 cm^{-1} in the IR and Si−H resonance at 4.7 ppm in the NMR spectra, respectively. Carbazole aromatic protons were clearly observed in the ^{1}H NMR spectrum as broad multiplets at 7.10−7.65 for those in the C1, C2, C3, C6, C7, and C8 aromatic ring positions and at 8.05−8.35 for those in the C4 and C5 hydrogens (Figure 1a). The methyl and methylene functionalities adjacent to Si appeared at −0.55 to −0.15 and 0.00−0.45 ppm, respectively. Methylene hydrogens α and β to nitrogen were observed at 3.80−4.30 and 1.43−1.75 ppm, respectively. The sharp peaks in the spectrum are due to residual hydrogens in DMF-d_7, H_2O, and TMS, all from the NMR solvent employed. The T_g of poly[methyl-3-(9-carbazolyl)propylsiloxane] (**6**) was found to be 55 °C, while the M_n and M_w were 6500 and 11 700, respectively. From the elemental analysis, it was calculated that the hydrosilylation reaction occurred in 93% yield, supporting the relatively high efficiency of the reaction. Thus, the charge-transporting carbazole moieties reside on 93% of every repeat unit of polysiloxane **6**.

It should be mentioned that the hydrosilylation reaction between PHMS and 3,6-dibromo-9-(2-propenyl)-carbazole, prepared from 3,6-dibromocarbazole and allyl bromide, was unsuccessful. A small amount of the debrominated carbazole derivative and starting materials were recovered. It is likely that the Pt catalyst underwent insertion into the aryl bromide bond followed by reductive elimination to deactivate the catalyst. Hence, it was necessary to conduct the bromination after hydrosilylation.

Regiospecific dibromination of **6** was achieved using benzyltrimethylammonium chlorobromate ($BTMABr_2Cl$)[47] in a THF/CH_3OH mixture at room temperature, affording poly[methyl-3-(*N*−(3,6-dibromocarbazolyl))-propylsiloxane] (**7**) as a white solid. The IR and ^{1}H NMR spectra are displayed in Figures 1b and 2b, respectively. The aromatic proton signals in the NMR spectrum correlate well with those of authentic 3,6-dibromocarbazole, with the C4, C5 proton resonances appearing at 8.25−8.60, the C2, C7 signals appearing at 7.30−7.60, and the C1, C8 protons observed at 7.00−7.30 ppm. The methyl and methylene proton resonances were relatively unchanged, occurring in similar positions to those in starting material **6**. The T_g for poly[methyl-3-(N-(3,6-dibromocarbazolyl))propylsiloxane] (**7**) was found to be 89 °C, while the M_n and M_w

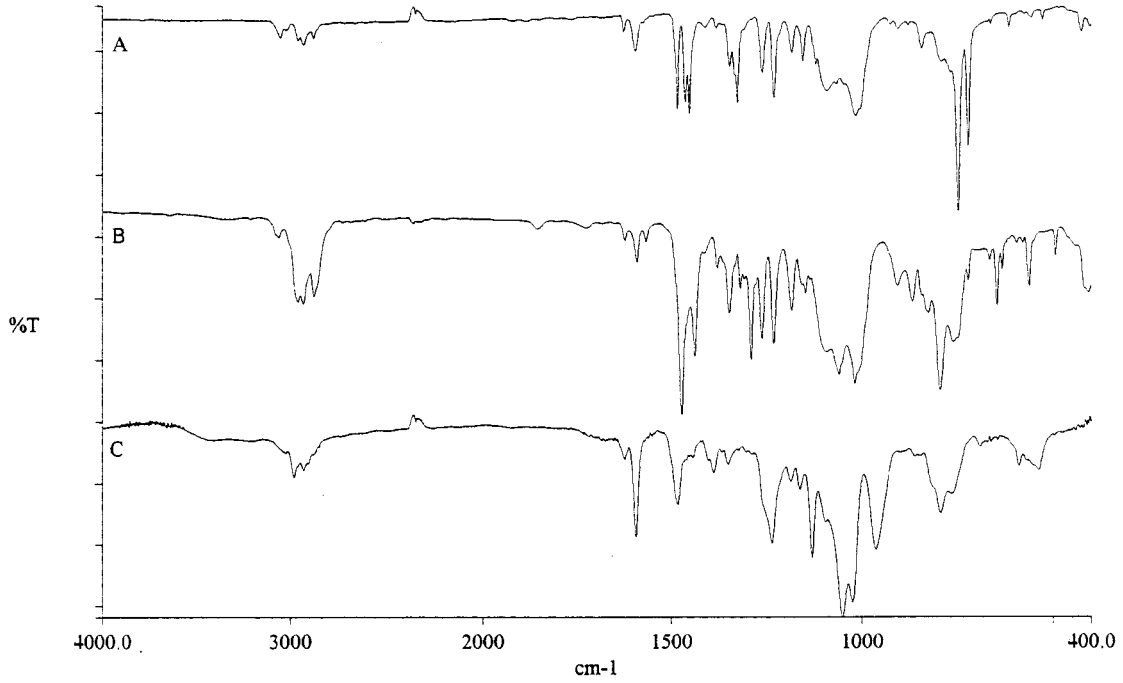


Figure 1. FT-IR spectra (films cast on KBr) of (a) poly[methyl-3-(9-carbazolyl)propylsiloxane] (**6**), (b) poly[methyl-3-(*N*−(3,6-dibromocarbazolyl))propylsiloxane] (**7**), and (c) poly[methyl 3-(3,6-bis(diethyl 4-phosphonatestyryl)carbazolyl)propylsiloxane] (**8**).

were 6800 and 10 600, respectively. From the elemental analysis, it was calculated that the bromination occurred in 97% yield, affording a polymer that was 90% brominated overall, a confirmation of the high fidelity of the bromination reaction. The regiospecificity of the bromination was demonstrated on carbazole itself. When treated with $BTMABr_2Cl$, carbazole was transformed cleanly into 3,6-dibromocarbazole, which was identical to authentic, commercially available 3,6-dibromocarbazole. Thus, the $BTMABr_2Cl$ reagent was, indeed, effective for the regiospecific *p*-bromination of aromatic amines.

Construction of stilbene NLO chromophore units was accomplished under Heck reaction conditions[49,50] using the Pd-catalyzed reaction of poly[methyl-3-(*N*-(3,6-dibromocarbazolyl))propylsiloxane] (**7**) and vinylbenzenephosphonic acid diethyl ester (**3**). $Pd(OAc)_2$, tri-*o*-tolylphosphine, and Et_3N in DMF were used, and the reaction mixture was heated at 90 °C for 12 h. IR and ^1H NMR spectra were secured for the resulting bright fluorescent yellow polymer, poly[methyl-3-(3,6-bis(diethyl 4-phosphonatestyryl)carbazolyl)propylsiloxane] (**8**), and are illustrated in Figures 1c and 2c, respectively. A characteristic phosphonate P═O stretching band was observed in the IR spectrum at 1235 cm^{-1}.

Absent in the ^1H NMR spectrum of **8** (Figure 2c) were resonances due to styrene olefinic protons, whereas phosphonate ethyl ester CH_3 and CH_2 signals were clearly observable at 1.23 and 3.50 ppm, respectively. The methyl and methylene proton resonances were relatively unchanged, occurring in similar positions to those in starting material **7**. The aromatic and stilbene olefinic hydrogens appeared in the region of 6.90−8.30 ppm. The sharp peaks in the spectrum are again due to residual hydrogens in $CDCl_3$ and TMS, both from the NMR solvent employed. No T_g was observable by DSC; however, the polymer appeared to become tacky at ca. 125 °C. Polymer **8** absorbed from 270 to 440 nm with λ_{max} = 324 nm and possessed M_n and M_w of 9800 and 11 800, respectively. The elemental analysis data indicated the Heck reaction took place in 84% yield, affording **8** with an estimated 59% of the repeat units bearing two phosphorylated stilbenoid units while 34% bear one stilbenoid group, taking into account the degree of incomplete reaction from the previous two steps. Noteworthy, is the ready solubility of **8** in several common organic solvents (e.g., CH_2Cl_2, $CHCl_3$, CH_3CN, THF, and DMF). This is a particularly important attribute of this polymer for processing considerations, both thick and thin films have been formed via solvent casting and spin coating, respectively.

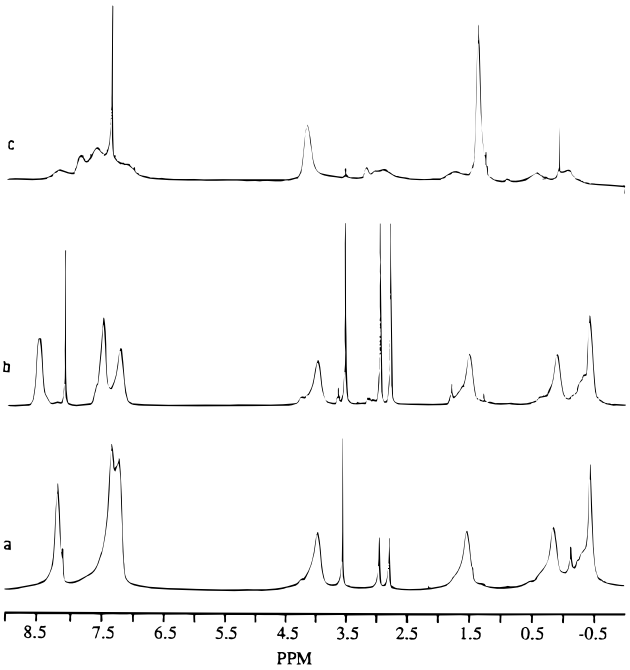


Figure 2. 300 MHz ^1H NMR spectra of (a) poly[methyl-3-(9-carbazolyl)propylsiloxane] (**6**) in DMF-d_7, (b) poly[methyl 3-(*N*−(3,6-dibromocarbazolyl))propylsiloxane] (**7**) in DMF-d_7, and (c) poly[methyl-3-(3,6-bis(diethyl 4-phosphonatestyryl)-carbazolyl)propylsiloxane] (**8**) in $CDCl_3$.

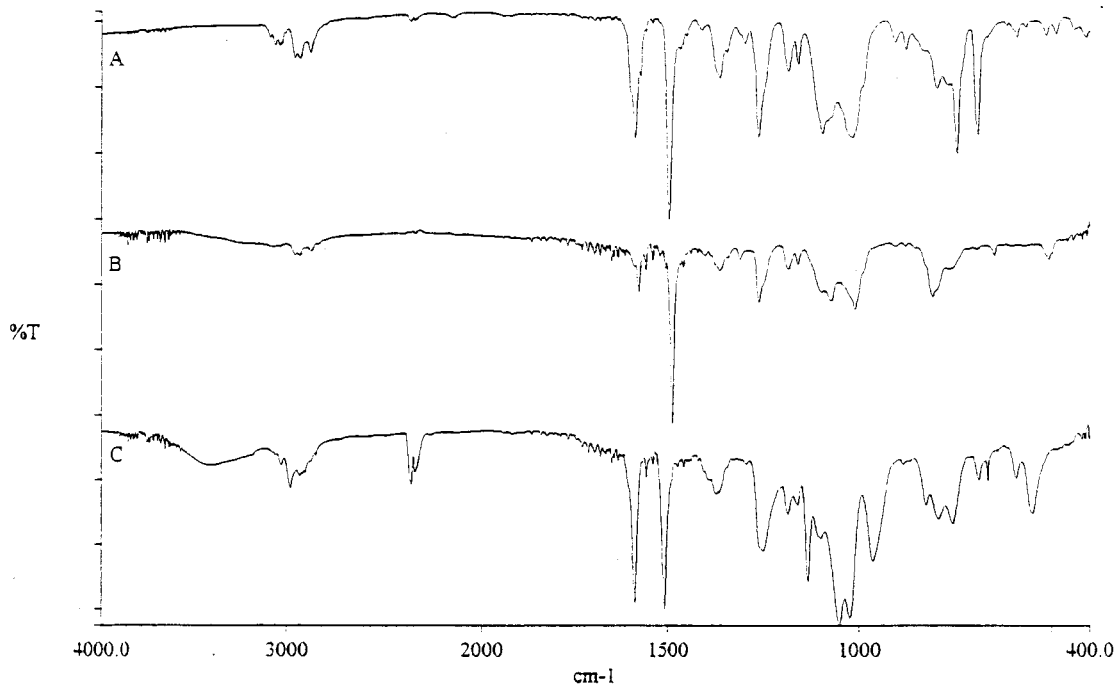


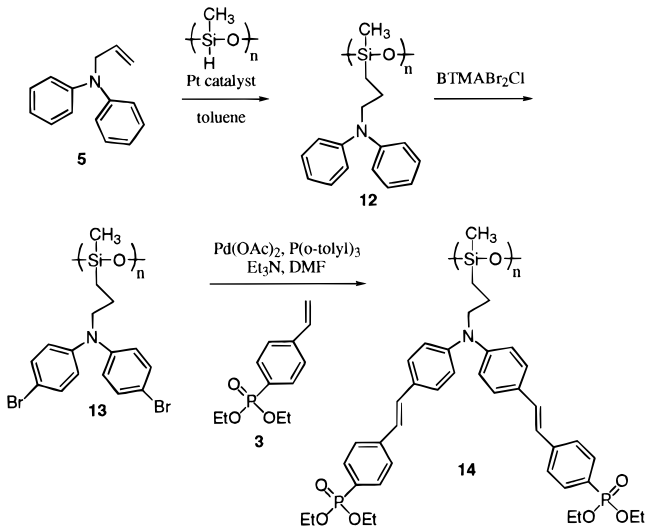
Figure 3. FT-IR spectra (films cast on KBr) of (a) poly[methyl-3-(*N*,*N*-diphenylamino)propylsiloxane] (**12**), (b) poly[methyl-3-(*N*,*N*-bis(4-bromophenyl)amino)propylsiloxane] (**13**), and (c) poly[methyl-3-(*N*,*N*-(4,4′-bis(diethyl 4-phosphonatestyryl)diphenylamino))propylsiloxane] (**14**).

Relatively efficient formation of the stilbene moieties afforded polysiloxane **8**, bearing on average one charge-transporting carbazole and 1.5 carbazole-based NLO chromophores per repeat unit. The nitrogen in the carbazole ring and the phosphonate ester moiety serve as the NLO chromophore's electron-donating and electron-withdrawing groups, respectively.

Synthesis of the corresponding nitro derivative of **8**, poly[methyl-3-(3,6-bis(4-nitrostyryl)carbazolyl)propylsiloxane] (**11**), was accomplished in a manner analogous to the preparation of **8** (Scheme 2). A Heck-type coupling occurred between the dibromocarbazole polymer **7** and 4-nitrostyrene[48] (**10**), resulting in an orange−red solid polymer. Characteristic aromatic NO_2 stretching bands were observed in the IR spectrum at 1515 and 1344 cm^{-1}. As anticipated, resonances due to styrene olefinic protons were absent in the ^1H NMR spectrum of **11**, while signals ascribed to methyl and methylene hydrogens adjacent to Si were present at −0.50 to −0.05 and 0.15−0.60 ppm, respectively. Methylene hydrogens α and β to nitrogen were observed at 3.55−4.20 and 1.40−1.80 ppm, respectively. The aromatic and stilbene olefinic hydrogens appeared as broad multiplets in the regions of 6.40−6.80, 6.85−7.50, and 7.90−8.25 ppm. The T_g of **11** was 90 °C, as measured by DSC, while the M_n and M_w were 10 200 and 12 900, respectively. The UV−visible absorption λ_{max} appeared at 310 nm, though the absorption extended from 270 to 500 nm. Elemental analysis results suggested that 54% of the repeat units of **11** contained two nitrostilbene moieties while 39% of the repeat units of **11** were functionalized with one nitrostilbene group, representing an efficiency of 82% for the Heck reaction. This polymer was soluble in such common organic as CH_2Cl_2, $CHCl_3$, CH_3CN, THF, and DMF.

The preparation of the diphenylamine analogue of **8** was desired in order to eventually study charge transport differences between photorefractive carbazole and diphenylamine-containing polymers. The sequence of

Scheme 3



reactions executed to accomplish this is shown in Scheme 3. Poly[methyl-3-(*N*,*N*-diphenylamino)propylsiloxane] (**12**) was prepared in 79% isolated yield via hydrosilylation of (*N*-phenyl-*N*-2-propenylamino)benzene[46] (**5**) with PHMS, using dichloro(dicyclopentadiene)platinum(II) as catalyst, in toluene at 60 °C. Absence of the Si−H stretch at 2150 cm^{-1} indicated completion of the reaction (Figure 3a). ^1H NMR analysis (Figure 4a) revealed resonances for methyl and methylene hydrogens adjacent to Si at −0.40−0.10 and 0.25−0.50 ppm, respectively. Methylene hydrogens α and β to nitrogen were observed at 3.40−3.65 and 1.46−1.72 ppm, respectively. Aromatic protons were observed at 6.80−7.05 (six hydrogens) and 7.10−7.25 (four hydrogens). Elemental analysis indicated that 86% of the repeat units underwent addition with allyldiphenylamine **5**, somewhat lower than in the reaction with allylcarbazole **4**, while the M_n and M_w were 5800 and 9400, respectively. Hence, the charge-transporting

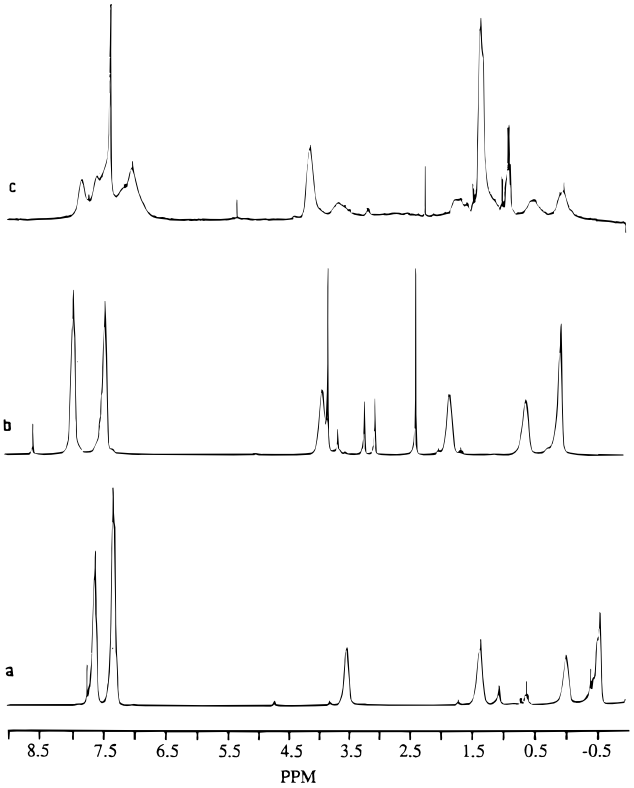


Figure 4. 300 MHz ^{1}H NMR spectra of (a) poly[methyl-3-(*N*,*N*-diphenylamino)propylsiloxane] (**12**) in $CDCl_3$, (b) poly[methyl 3-(*N*,*N*-bis(4-bromophenyl)amino)propylsiloxane] (**13**) DMF-d_7, and (c) poly[methyl 3-(*N*,*N*−(4-bis(diethyl 4-phosphonatestyryl)diphenylamino)) propylsiloxane] (**14**) in $CDCl_3$.

diphenylamine moieties reside on 86% of the repeat units of polysiloxane **12**.

Regiospecific bromination of **12**, conducted with $BTMABr_2Cl$ in THF/CH_3OH solution, afforded poly[methyl-3-(*N*,*N*-bis(4-bromophenyl)amino)propylsiloxane] (**13**). IR and ^{1}H NMR spectra were secured for **13** and are illustrated in Figures 3b and 4b, respectively. In the ^{1}H NMR spectrum (Figure 4b), the methyl and methylene proton resonances were relatively unchanged, occurring in similar positions to those in parent **12**. Evidence for regiospecific bromination was gained by examination of the aromatic region in the ^{1}H NMR spectrum. Two broad peaks of equal area were observed at 6.75−7.10 (protons ortho to N) and 7.25−7.51 (protons ortho to Br), expected only for the symmetrical dibromination product **13**. The M_n and M_w were 6800 and 9500, respectively. From the elemental analysis, it was ascertained that the bromination was nearly quantitative (99%), resulting in 85% bromination overall.

The final step was assembling the stilbene linkage, accomplished via Heck-type cross coupling of poly[methyl-3-(*N*,*N*-bis(4-bromophenyl)amino)propylsiloxane] (**13**) and vinylbenzenephosphonic acid diethyl ester (**3**). The resulting polymer, poly[methyl 3-(*N*,*N*−(4,4′-bis(diethyl 4-phosphonatestyryl)diphenylamino))propylsiloxane] (**14**), was obtained as a bright, fluorescent yellow−green solid and was characterized by IR and ^{1}H NMR spectroscopy (Figures 3c and 4c, respectively). The C═C stretch (stilbene) was observed in the IR spectrum at 1594 cm^{-1} while the characteristic P═O absorption was evident at 1240 cm^{-1}. In the ^{1}H NMR spectrum the methyl and methylene proton resonances were broad and their positions were relatively unchanged relative to **12** and **13**. Expectedly absent were resonances due to styrene olefinic protons, whereas phosphonate ethyl ester CH_3 and CH_2 signals were clearly observable at 1.05−1.35 and 3.80−4.25 ppm, respectively. Aromatic and stilbene olefinic protons occurred in the region of 6.70−7.90 ppm.

The UV−visible absorption of **14** ranged from 240 to 460 nm with a λ_{max} = 390 nm. The M_n and M_w were 8900 and 13 400, respectively. The elemental analysis provided an estimate that 30% of the repeat units underwent substitution to form two stilbenoid groups while 55% of the repeat units contained only one stilbene construct, a less efficient reaction than that in the case of analogous carbazole-based polymer. Thus, a third polysiloxane was obtained with charge transport moieties on nearly every repeat unit and at least one NLO construct (ca. 1.2 on average) per repeat unit. Consistent with the fully functionalized polysiloxanes **8** and **11**, the diphenylamine analogue **14** was also very soluble in several common organic solvents (e.g., CH_2Cl_2, $CHCl_3$, CH_3CN, THF, and DMF).

Conclusions

A series of three highly efficient reactions, Pt-catalyzed hydrosilylation, regiospecific bromination, and Pd-catalyzed cross coupling, were performed on a polymer and led to the formation of three new, highly functionalized polysiloxanes expected to exhibit second-order nonlinear optical and photoconductive properties. Relatively efficient formation of the stilbene moieties produced siloxane polymers in which each repeat unit bears a charge-transporting moiety, either carbazole or diphenylamine, and at least 1.5 or 1.2 arylamine-based NLO chromophores per repeat unit for carbazole and diphenylamine-based systems, respectively. Each arylamine CT moiety contains up to two NLO chromophores. The nitrogen in the arylamine serves as an electron-donor while, by exploiting the same synthetic methodology, either a phosphonate ester or nitro group can be incorporated to serve as the electron-withdrawing groups. Such versatile synthetic methodology affords control in the design of UV−visible absorption and, presumably, electrooptic and charge transport characteristics, prospects we are currently exploring. These "single-component" polymers have all but charge-generating functionality covalently attached, representing a novel class of materials for the study of photorefractivity. The synthetic methodology reported in the preceding affords a high density of CT and NLO functionalities with nearly every repeat unit bearing a CT and at least one NLO moiety. In addition, polymers **8**, **11**, and **14** are all quite soluble in several common organic solvents, permitting particularly facile processing.

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