Linear Polymers for Nonlinear Optics. 3. Efficient Grafting of Chromophores to Styrenic Polymers via Palladium-Catalyzed Carbonylation and Coupling Reactions†

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ABSTRACT: Various chromophores useful for second-order nonlinear optics (NLO) have been attached to a preformed polystyrene backbone via palladium-catalyzed carbonylation reactions. In favorable circumstances, the grafting reaction was nearly quantitative, leading to a high concentration of NLO-active chromophores in the resulting polymers. The polymers obtained in this way were amorphous, exhibited good solubility, and possessed high glass transition temperatures.

Introduction

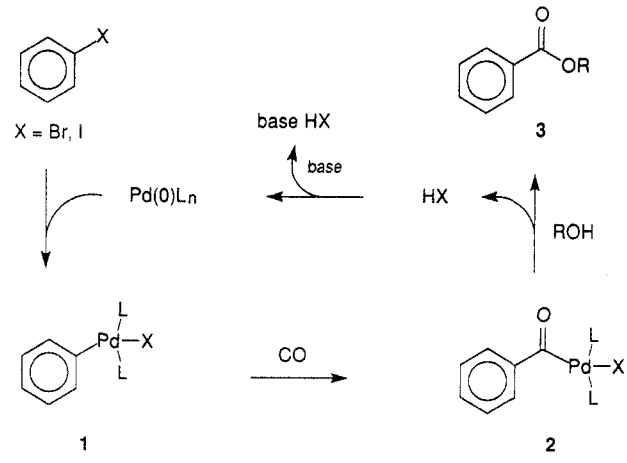
Organic materials for second-order nonlinear optics (NLO) have been an active topic of research for the past few years.[1-3] Because simple means exist for creating high-quality thin films of polymers and because certain organic chromophores exhibit substantial nonlinear optical properties, researchers have sought methods for synthesizing polymeric materials containing these chromophores. In this way, relatively inexpensive, highly efficient devices might be constructed based on optical waveguide technology.

While the earliest research in this area was based on polymers that were doped with low molar mass chromophores, the advantages of covalently attaching the chromophores to the polymer backbone have been recognized. A large number of such polymers have been synthesized, either by polymerization of monomeric units bearing active chromophores or by grafting the active species onto preformed polymers. The former technique has been limited by the difficulties in synthesizing and polymerizing these highly functionalized monomers (especially in the case of the free-radical polymerization of stilbene-containing compounds).[4,5] The latter technique has been employed using a variety of substrates such as poly(hydroxystyrene),[6] poly(vinylbenzyl chloride),[7,8] poly(acryloyl chloride),[9,10] poly(dichlorophosphazene),[11] and brominated poly(phenylene oxide).[12] Unfortunately, these highly reactive polymers are unstable toward adventitious oxygen or water. Additionally, in some of the reported examples, several synthetic steps had to be performed on the polymer to effect the desired grafting.[7,8] As a result, the loading levels that could be achieved by grafting were low, leading to poor NLO performance.

Azobenzene-containing polymers could be prepared by diazonium coupling onto stable polymers containing aniline units;[13,14] however, no polymers containing a high proportion of dye-substituted repeat units have been reported. In addition, polycondensation reactions have been employed to produce a wide variety of NLO chromophore-containing materials,[15-19] although the reported molecular weights are seldom large.

Palladium-catalyzed carbonylation and condensation reactions between aromatic halides and amines and alcohols have proved useful in the preparation of amides[20-23] and esters.[24-31] The generally high yields of products obtained from these reactions, and recent successes in preparing high molecular weight polymers via this chemistry,[32,33] prompted us to explore grafting reactions of NLO chromophores onto preformed polymer backbones using palladium-catalyzed carbonylation reactions.

Scheme I. Carbonylation Mechanism for Ester Formation



The mechanism of ester formation, as outlined in Scheme I, involves the oxidative addition of a coordinatively unsaturated Pd(0) species to an aromatic halide, producing a Pd(II) complex 1. Carbon monoxide then inserts in the aryl–palladium bond, giving acyl complex 2. This step is followed by attack of the alcohol, leading to the regeneration of the active Pd(0) catalyst and liberation of the free ester 3. (In the scheme, L represents unspecified ligands, usually phosphines, amines, or CO.)

This reaction seemed ideally suited as a grafting method because it occurs under relatively mild conditions and tolerates a number of different functional groups. The aromatic halide is hydrolytically stable and only becomes activated in the presence of the Pd catalyst. The potential for incorporating stilbene chromophores in high concentration is particularly significant because of their increased transparency when compared to analogous azobenzene derivatives (the stilbenes have a relatively blue-shifted absorption spectrum), with little change in NLO properties. Previous attempts to polymerize stilbene-containing acrylic monomers in high concentrations were only partially successful and led, at best, to cross-linked materials.[4,5]

In this paper we report a series of polymers in which various stilbene- or azobenzene-based chromophores bearing pendant alcohol groups were attached to a

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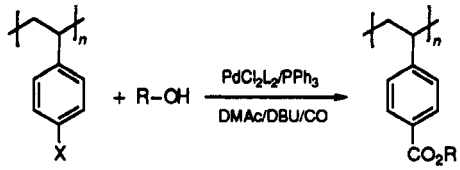
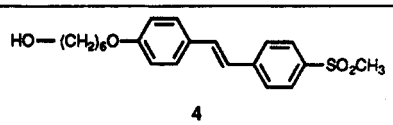
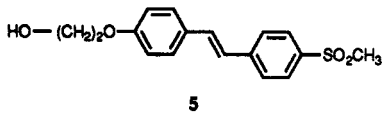
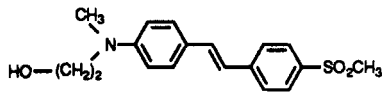
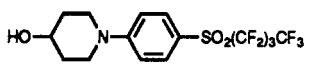
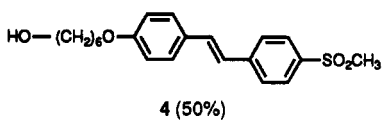
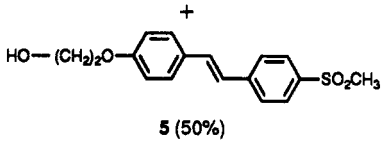
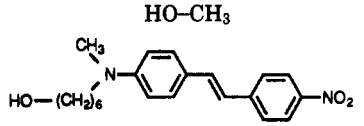
Table I. Polymer Grafting Reactions



X	R-OH	polymer code	% loading	T_g (°C)
Br		11	95	106
	4			
Br		12	99	145
	5			
Br		13	96	162
	6			
Br		14	83	142
	7			
				
	4 (50%)			
Br	+	15	99	123
				
	5 (50%)			
Br	$HO-CH_3$	16	68–75	nd
I		17	99	119
	8			

preformed poly(4-halostyrene) backbone (Table I). The resulting polymers can be considered as derivatives of poly(styrene-4-carboxylate). Nonlinear optical experiments on two of these polymers have been reported elsewhere.[34]

Experimental Section

General Procedures. Reactions were performed in a 120-mL pressure reaction vessel (containing a stirbar) equipped with a pressure gauge, a pressure release valve, a gas inlet, and a straight ball valve for degassing and sample withdrawal.

Model reactions were monitored on an Hewlett-Packard 5890 gas chromatograph using a 15 m × 0.25 μm DB-5 column (0.32 mm i.d.) and a flame ionization detector. Helium flow rate through the column was 4.0 mL/min. The GC parameters employed for analysis were as follows: injection port, 250 °C; detector, 350 °C; temperature ramp, from 50 °C (hold 1 min) to 300 °C (hold 10 min) at 20 °C/min. Size-exclusion chromatography (SEC) was performed in *N,N*-dimethylformamide (DMF) containing 0.01 M $LiNO_3$ or in tetrahydrofuran (THF), using three 10-mm Waters HT linear columns and one 300-Å HT column. All samples were filtered prior to injection, and results are reported as poly(methyl methacrylate) (PMMA) or polystyrene (PS) equivalent molecular weights unless otherwise noted. Absolute molecular weight measurements were obtained by low-angle laser light scattering (LALLS). Palladium, bromine, and iodine contents were determined by neutron activation analysis, and sulfur analyses by combustion. ^1H and ^{13}C NMR spectra were acquired on a 300-MHz spectrometer using DMSO-d_6 or $CDCl_3$ as both solvent and internal reference. Chromatography was performed on a radial layer chromatographic device using 4-mm PF-254 silica gel plates.

Chemicals. Carbon monoxide (CO; UPC grade, Air Products), *N,N*-dimethylacetamide (DMAc; anhydrous, Aldrich), and bis(triphenylphosphine)palladium(II) chloride ($PdCl_2L_2$; Aldrich) were used as received. Triphenylphosphine (PPh_3; Eastman Kodak Co.) was recrystallized from hexanes, 2,6-di-*tert*-butyl-4-methylphenol (BHT; Aldrich) was recrystallized from ethanol, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; Aldrich) and *p*-bromotoluene (Kodak) were fractionally distilled under reduced pressure.

Poly(4-bromostyrene) was prepared using conventional free-radical polymerization (AIBN initiator) in a chlorobenzene solution. The polymer was purified by repeated precipitation into methanol, followed by drying in a vacuum oven. $\overline{M}_n$ = 23 200, $\overline{M}_w$ = 40 600 by SEC (THF, PS equivalent).

The nonlinear optical chromophores 4–10 were prepared using standard synthetic procedures.[4,35] Synthetic procedures and spectral data are given in the supplementary material.

Preparation of Poly(p-iodostyrene). In a modification of a literature procedure,[36] a solution of *p*-iodoacetophenone (23.5 g, 96 mmol) and isopropyl alcohol (290 mL) was treated with aluminum isopropoxide (29.4 g, 144 mmol) and heated to distill off acetone formed in the reduction. When acetone distillation was complete (3 h), the reaction mixture was treated with concentrated HCl (35 mL) and ice (100 g). The mixture was extracted with ethyl acetate, dried, dissolved in dichloromethane, chromatographed on silica gel (eluting with heptane), and concentrated to give 20 g (84%) of *p*-iodophenylmethylcarbinol as an intermediate, mp 40–42 °C (lit.[36] mp 40–42 °C). This intermediate was heated to 200 °C in the presence of $KHSO_4$ (0.3 g) and hydroquinone (0.3 g) under vacuum (135 mmHg). Only 0.60 g (3%) of *p*-iodostyrene distilled over: mp 44–44.5 °C (lit.[36] mp 44–44.5 °C); ^1H NMR ($CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2 H), 7.13 (d, *J* = 8.2 Hz, 2 H), 6.33 (dd, *J* = 17.6, 10.9 Hz, 1 H), 5.75 (d, *J* = 17.6 Hz, 1 H), 5.27 (d, *J* = 10.9 Hz, 1 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 137.6, 135.9, 128.0, 127.4, 114.7, 93.0. The material remaining in the flask was dissolved in $CHCl_3$, precipitated twice into methanol from $CHCl_3$, and dried to give 8.8 g (47%) of poly(*p*-iodostyrene): ^1H NMR ($CDCl_3$) δ 7.4 (br, 2 H), 6.2 (br, 2 H), 1.5 (br, 1 H), 1.3 (br, 2 H); $^{13}C\{^1H\}$ NMR ($CDCL_3$) δ 143.9, 137.4, 129.5, 91.3, 43.5, 40.3. Absolute: $\overline{M}_n$ = 15 600; $\overline{M}_w$ = 45 100. PS equivalent: $\overline{M}_n$ = 10 500; $\overline{M}_w$ = 26 600.

Representative Polymer Grafting Reaction. (a) Preparation of NLO Polymer 12. The reaction vessel was charged with 4′-(2-hydroxyethoxy)-4-(methylsulfonyl)stilbene (**5**; 6.08 g, 19.1 mmol), poly(*p*-bromostyrene) (3.50 g, 19.1 mmol), $PdCl_2L_2$ (402 mg, 0.57 mmol), PPh_3 (302 mg, 1.15 mmol), BHT (42 mg, 0.19 mmol), and DMAc (40 mL). The contents of the vessel was degassed and purged with argon three times and then evacuated and filled with 15 psig CO. When the reagents had dissolved, the pressure was released and DBU (3.43 mL, 22.92 mmol) was added. The vessel was repressurized to 90 psig CO and heated to 115 °C. After 23 h, the reaction mixture was filtered through Celite, washing with DMAc, and the filtrate was concentrated to ca. 30 mL and was poured into excess methanol. The precipitated polymer was washed extensively with methanol, dried in air, redissolved in DMAc, and reprecipitated into a methanol/water mixture (3:1). Extensive washing with methanol and methanol/water was followed by drying in vacuo at 90 °C for 16 h to give 6.64 g of a white polymer (78%). Anal. Calcd for $C_{26}H_{24}O_5S$: C, 69.62; H, 5.39; S, 7.15. Found: C, 69.05; H, 5.37; S, 8.04; Br, 0.38. T_g = 155 °C, 1st heat; 145 °C, 2nd heat; 143 °C, 3rd heat.

(b) Preparation of NLO Polymer 11. The reaction vessel was charged with 4′-(6-hydroxyhexoxy)-4-(methylsulfonyl)stilbene (**4**; 14.32 g, 38.2 mmol), poly(*p*-bromostyrene) (7.00 g, 38.2 mmol), $PdCl_2L_2$ (804 mg, 1.15 mmol), PPh_3 (603 mg, 2.30 mmol), BHT (84 mg, 0.38 mmol), DBU (6.86 mL, 45.84 mmol), and DMAc (90 mL) and treated as before. After 29 h, the polymer was precipitated twice into methanol and once into water and then vacuum dried to give 17.7 g (92%) of a white polymer. Anal. Calcd for $C_{30}H_{32}O_5S$: C, 71.40; H, 6.39; S, 6.35. Found: C, 70.21; H, 6.15; S, 7.30; Br, 2.3. T_g = 109 °C, 1st heat; 105 °C, 2nd heat.

(c) Preparation of NLO Polymer 13. The reaction vessel was charged with 4′-[(2-hydroxyethyl)methylamino]-4-(meth-

ylsulfonyl)stilbene (6; 6.33 g, 19.1 mmol), poly(*p*-bromostyrene) (3.50 g, 19.1 mmol), $PdCl_2L_2$ (402 mg, 0.57 mmol), PPh_3 (300 mg, 1.15 mmol), BHT (45 mg, 0.20 mmol), DBU (3.45 mL, 22.9 mmol), and DMAc (40 mL). After 18 h, the polymer was precipitated twice into methanol and then twice into water and then vacuum dried to give 6.40 g (72%) of a yellow polymer. Anal. Calcd for $C_{27}H_{27}NO_4S$: C, 70.26; H, 5.90; N, 3.03; S, 6.94. Found: C, 69.70; H, 5.85; N, 2.98; S, 6.63; Br, 0.80. T_g = 162 °C, 1st heat. $\overline{M}_n$ = 71 000; $\overline{M}_w$ = 155 000 (PMMA equivalent).

(d) Preparation of NLO Polymer 14. The reaction vessel was charged with 1-[4-[(nonafluorobutyl)sulfonyl]phenyl]-4-hydroxypiperidine (7; 5.00 g, 11.23 mmol), poly(*p*-bromostyrene) (2.056 g, 11.23 mmol), $PdCl_2L_2$ (236 mg, 0.34 mmol), PPh_3 (177 mg, 0.68 mmol), DBU (2.02 mL, 13.47 mmol), and DMAc (34 mL) and treated as before. After 22 h, the polymer was precipitated twice into methanol and then vacuum dried to give 4.58 g (69%) of an off-white polymer. Anal. Calcd for $C_{24}H_{20}F_9NO_4S$: C, 48.90; H, 3.42; N, 2.38; S, 6.35; F, 29.01. Found: C, 50.23; H, 3.70; N, 2.28; S, 7.30; F, 23.51; Br, 5.7. T_g = 142 °C, 1st heat; 140 °C, 2nd heat; 140 °C, 3rd heat. $\overline{M}_n$ = 31 000; $\overline{M}_w$ = 45 000 (PMMA equivalent). $\overline{M}_n$ = 33 900; $\overline{M}_w$ = 91 600 (absolute).

(e) Preparation of NLO Copolymer 15. The reaction vessel was charged with 4′-(6-hydroxyhexoxy)-4-(methylsulfonyl)stilbene (4; 7.15 g, 19.1 mmol), 4′-(2-hydroxyethoxy)-4-(methylsulfonyl)stilbene (5; 6.08 g, 19.1 mmol), poly(*p*-bromostyrene) (7.00 g, 38.2 mmol), $PdCl_2L_2$ (804 mg, 1.15 mmol), PPh_3 (603 mg, 2.30 mmol), BHT (84 mg, 0.38 mmol), DBU (6.86 mL, 45.84 mmol), and DMAc (90 mL) and treated as before. After 23 h, the polymer was precipitated once into methanol and once into methanol/water and then vacuum dried to give 14.8 g (81%) of polymer. Anal. Calcd for $C_{28}H_{28}O_5S$: C, 70.57; H, 5.92; S, 6.73. Found: C, 69.31; H, 5.76; S, 7.39; Br, 0.5. T_g = 126 °C, 2nd heat; 121 °C, 3rd heat. $\overline{M}_n$ = 61 400; $\overline{M}_w$ = 93 700 (PMMA equivalent). $\overline{M}_n$ = 122 000; $\overline{M}_w$ = 186 000 (absolute).

(f) Preparation of Poly[4-(carbomethoxy)styrene] (16). The reaction vessel was charged with anhydrous methanol (8.0 mL, 198 mmol), poly(*p*-bromostyrene) (7.14 g, 39.0 mmol), $PdCl_2L_2$ (410 mg, 0.60 mmol), PPh_3 (307 mg, 1.2 mmol), BHT (86 mg, 0.39 mmol), DBU (7.00 mL, 46.8 mmol), and DMAc (70 mL) and treated as before. After 28 h, the polymer was precipitated once into methanol, treated with Norit (charcoal), then precipitated into methanol again, and vacuum dried to give 5.23 g (83%) of polymer. $\overline{M}_n$ = 11 500; $\overline{M}_w$ = 17 700 (PMMA equivalent). Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H. 6.21. Found: C, 68.65; H, 5.57. ^1H NMR: ratio of Me to aromatic and aliphatic protons indicates 68–75% carbomethoxy group incorporation.

(g) Preparation of NLO Polymer 17. The reaction vessel was charged with 4′-[(6-hydroxyhexyl)methylamino]-4-nitrostilbene (8; 1.063 g, 3.00 mmol), poly(*p*-iodostyrene) (0.690 g, 3.00 mmol), $PdCl_2L_2$ (63 mg, 0.09 mmol), PPh_3 (47 mg, 0.18 mmol), BHT (13 mg, 0.06 mmol), DBU (0.54 mL, 3.60 mmol), and DMAc (18 mL) and treated as before. After 1.25 h, the polymer was diluted with DMAc, centrifuged to remove gel slugs, concentrated in vacuo, and precipitated into methanol. The red polymer was washed extensively with methanol and then vacuum dried to give 1.015 g (70%) of polymer. Anal. Calcd for $C_{30}H_{32}N_2O_4$: C, 74.36; H, 6.66; N, 5.78. Found: C, 73.38; H, 6.66; N, 5.94; I, 0.37. T_g = 116 °C, 2nd heat; 122 °C, 3rd heat. $\overline{M}_n$ = 14 600; $\overline{M}_w$ = 18 900 (PMMA equivalent).

Model Reactions. Preparation of 18. The reaction vessel was charged with *p*-bromotoluene (93 μL, 0.76 mmol), 4′-[(2-hydroxyethyl)methylamino]-4-(methylsulfonyl)stilbene (6; 0.250 g, 0.76 mmol), $PdCl_2L_2$ (32 mg, 0.045 mmol), PPh_3 (24 mg, 0.09 mmol), DBU (135 μL, 0.91 mmol), and DMAc (4 mL). After 2.4 h, the reaction mixture was concentrated, dissolved in $CHCl_3$, and chromatographed with 4:1 CH_2Cl_2/Et_2O to give 160 mg (47%) of product: mp 126–127.5 °C; ^1H NMR ($CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 4 H), 7.61 (d, *J* = 8.4 Hz, 2 H), 7.43 (d, *J* = 8.7 Hz, 2 H), 7.22 (m, 3 H), 6.90 (d, *J* = 16.2 Hz, 1 H), 6.77 (d, *J* = 8.7 Hz, 2 H), 4.49 (t, *J* = 5.9 Hz, 2 H), 3.78 (t, *J* = 5.9 Hz, 2 H), 3.09 (s, 3 H), 3.06 (s, 3 H), 2.39 (s, 3 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 166.3, 149.0, 143.6, 143.5, 137.3, 132.4, 129.4, 128.9, 128.1, 127.5, 126.8, 126.1, 124.5, 121.7, 111.9, 61.6, 50.7, 44.4, 38.6, 21.4. Anal. Calcd for $C_{26}H_{27}NO_4S$: C, 69.46; H, 6.05; N, 3.12; S, 7.13. Found: C, 69.65; H, 6.12; N, 2.97; S, 6.98.

Preparation of 19. The reaction vessel was charged with *p*-iodotoluene (218 mg, 1.00 mmol), 4′-[(6-hydroxyhexyl)methylamino]-4-nitrostilbene (8; 354 mg, 1.00 mmol), $PdCl_2L_2$ (21 mg, 0.03 mmol), PPh_3 (16 mg, 0.06 mmol), DBU (182 μL, 1.20 mmol), and DMAc (8 mL). After 22 h, the reaction mixture was cooled, filtered through Celite, and concentrated. The reaction mixture was chromatographed on silica gel with 1:1 hexanes/EtOAc to give a crude product. The product was rechromatographed on silica gel with 6:1 toluene/EtOAc to give 269 mg of 83% product and 17% starting alcohol (48% isolated yield). An analytical sample was obtained by recrystallization from heptane: mp 117–118.5 °C; ^1H NMR ($CDCl_3$) δ 8.18 (d, *J* = 8.7 Hz, 2 H), 7.92 (d, *J* = 8.1 Hz, 2 H), 7.55 (d, *J* = 8.7 Hz, 2 H), 7.42 (d, *J* = 8.7 Hz, 2 H), 7.23 (m, 3 H), 6.90 (d, *J* = 16.2 Hz, 1 H), 6.67 (d, *J* = 8.7 Hz, 2 H), 4.30 (t, *J* = 6.5 Hz, 2 H), 3.37 (t, *J* = 7.4 Hz, 2 H), 2.99 (s, 3 H), 2.40 (s, 3 H), 1.77 (m, 2 H), 1.64 (m, 2 H), 1.47 (m, 4 H). Anal. Calcd for $C_{29}H_{32}N_2O_4$: C, 73.71; H, 6.83; N, 5.93. Found: C, 73.57; H, 6.91; N, 5.78.

Preparation of 20. The reaction vessel was charged with *p*-bromotoluene (316 μL, 2.57 mmol), 4′-[(6-hydroxyhexyl)-methylamino]-4-(methylsulfonyl)azobenzene (9; 1.00 g, 2.57 mmol), $PdCl_2L_2$ (108 mg, 0.15 mmol), PPh_3 (79 mg, 0.3 mmol), DBU (460 mL, 3.08 mmol), and DMAc (7.8 mL). After 17 h, the reaction mixture was cooled, diluted with water, and extracted with $CHCl_3$. The extracts were combined, dried with Na_2SO_4, concentrated, and chromatographed with 4:1 CH_2Cl_2/Et_2O to give a crude product. The product was dissolved in 6 mL of toluene and then triturated with hexanes to give a microcrystalline solid that was washed with hexanes: mp 80–81 °C; ^1H NMR ($CDCl_3$) δ 8.02 (d, *J* = 8.6 Hz, 2 H), 7.95 (d, *J* = 8.6 Hz, 2 H), 7.93 (d, *J* = 8.0 Hz, 2 H), 7.89 (d, *J* = 9.1 Hz, 2 H), 7.23 (d, *J* = 8.0 Hz, 2 H), 6.72 (d, *J* = 9.1 Hz, 2 H), 4.31 (t, *J* = 6.5 Hz, 2 H), 3.44 (t, *J* = 7.4 Hz, 2 H), 3.08 (s, 3 H), 3.07 (s, 3 H), 2.39 (s, 3 H), 1.8–1.3 (m, 8 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 166.6, 156.3, 152.2, 143.4, 143.3, 139.6, 129.4, 129.0, 128.3, 127.7, 125.9, 112.6, 111.2, 64.5, 52.4, 44.6, 38.6, 28.6, 26.9, 26.6, 25.9, 21.6. Anal. Calcd for $C_{28}H_{33}N_3O_4S$: C, 66.25; H, 6.55; N, 8.28; S, 6.31. Found: C, 65.13; H, 6.46; N, 7.99; S, 6.20.

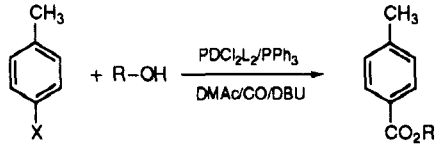
Results and Discussion

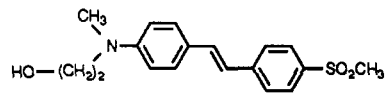
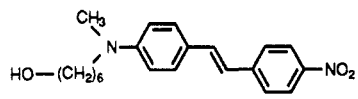
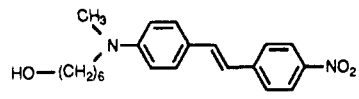
Functionalized NLO Dyes. A diverse series of "push–pull" NLO chromophores with pendant hydroxyl groups (4–10, Tables I and II) were prepared by well-established methods.[4,35] Details of the synthesis of previously unpublished compounds are given in the supplementary material.

Model Reactions. To test the efficacy of the Heck carbonylation reaction for the grafting of NLO chromophores onto poly(4-halostyrene), we carried out model reactions using 4-bromotoluene or 4-iodotoluene (Table II). The progress of these coupling reactions was monitored by gas chromatography. Typically, the reactions were run in *N*,*N*-dimethylacetamide (DMAc) at 120 °C for several hours using equimolar amounts of aryl halide and alcohol, 90 psig carbon monoxide, 2–6 mol % of Pd catalyst, 4–12 mol % of triphenylphosphine, and 1.2 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as base.

We found that both azobenzene and stilbene chromophores with methylsulfonyl electron-acceptor groups (6 and 9) reacted well with bromotoluene, but nitrostilbene (8, DANS-type) and nitroazobenzene (10, Disperse Red-type) chromophores were unreactive. However, a good yield of coupled product was obtained with the DANS-type chromophore, 8, when the more reactive iodotoluene was employed as substrate. In this case, the nitro functionality remained intact although reduction has been noted in some Pd-mediated carbonylation reactions.[37] (Note that the yields in the model reactions represent actual isolated quantities after purification and are not optimized).

Table II. Model Reactions



X	R-OH	product code	yield (%)
Br		18	47
	6		
Br			0
	8		
I		19	48
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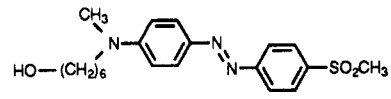
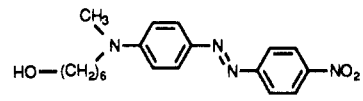
Br		20	66
	9		
Br			0
	10		

Polymer Grafting Reactions. Encouraged by the success of the model reactions, we attempted analogous reactions mainly using poly(4-bromostyrene). The selection of this substrate has many advantages: 4-Bromostyrene monomer is commercially available and easily polymerized in multigram quantities by conventional free-radical means. The resulting poly(4-bromostyrene) is stable under ambient conditions and can be stored indefinitely. The more reactive 4-iodostyrene monomer and polymer are not commercially available. We synthesized poly(4-iodostyrene) during an attempt to prepare its monomer by a literature procedure.[36] (The monomer polymerized spontaneously during isolation.)

The efficiency of the grafting reaction performed as described in the Experimental Section is uniformly high (83–99%) with the functionalized NLO chromophores (Table I). Both primary and secondary alcohols could be employed, and even an apparently random copolymer (15) could be synthesized using a mixed chromophore feed. In all cases, the amount of residual palladium in the isolated polymer was negligible.

The inclusion of a small amount of inhibitor (BHT) in the grafting reaction mixture helped to prevent cross-linking reactions that plague conventional free-radical polymerizations of stilbene-containing monomers. A DANS-type chromophore was grafted in quantitative yield using poly(4-iodostyrene) as substrate. Soluble, high-MW polymers with such a large loading of the DANS chromophore are difficult to prepare by other means.[4,5]

In addition to the azobenzene and stilbene chromophores, we also successfully grafted a chromophore based on 4-[(perfluorobutyl)sulfonyl]aniline (14). This chromophore was chosen because of its relatively blue-shifted absorption band, necessary for practical frequency doubling applications. Noteworthy here is the high level of loading obtained even with secondary alcohol 7.

We also attempted to prepare the simple model polymer poly[4-(carbomethoxy)styrene] (16) via grafting of methanol to poly(4-bromostyrene). However, the yields were somewhat poorer than with the chromophoric alcohols. It is possible that, even though we used a 5-fold excess of methanol, much of this volatile alcohol was lost from the reaction vessel during vacuum-degassing steps.

All of the polymers were amorphous materials, soluble in strong solvents such as DMAc or (in some cases) THF. When the spacer between the ester functionality and the chromophore was short [i.e., $(CH_2)_2$], the glass transition temperatures of the polymers were relatively high, a desirable feature for preservation of poling-induced order. Molecular weights and distributions were consistent with those of the starting polymers, considering the additional weight of the grafted units.

Optical Properties. All of the polymers could be spin-cast from solutions in dipolar, aprotic solvents to produce uniform, intact films. Polymers 14 and 15 were studied most extensively.[34] At relatively long wavelengths, far from absorption bands, films of 14 and 15 exhibited excellent optical transparency, and good quality waveguides could be constructed. At shorter wavelengths (<500 nm, but still above the absorption bands of the chromophores), a small absorption from an as yet unidentified impurity was observed. The absorption appeared as a tail extending above 400 nm from the bands attributable to the chromophores, as opposed to a distinct peak. That this undesirable absorption is due to a byproduct of the grating reaction is evidenced by four observations: (1) Polymer 16, which has the chromophore replaced by a nonabsorbing methyl group, also exhibited some absorption above 400 nm. (2) Solutions of the polymers also showed the absorption. (3) The absorption could not be removed by fractionation of the polymers. (4) The anomalous tail was absent from a sample of conventional (i.e., unsubstituted) polystyrene exposed to the grafting conditions (no chemical reaction should occur) and isolated in the same way as polymers 11–17. These observations are inconsistent with chromophore aggregation or catalyst residues as the primary cause of the undesirable attenuation below 500 nm.

Polymers 14 and 15 were poled at ca. 100 V/μm and exhibited electrooptic coefficients consistent with their structure (ca. 0.5 pm/v at 830 nm and 2.0 pm/v at 548 nm).[34]

Summary

We have demonstrated that high loadings of NLO chromophores containing stilbene, azobenzene, sulfone, and nitro groups can be readily grafted onto polymer backbones through the Pd-catalyzed carbonylation and coupling reactions of poly(4-halostyrene). This method represents a facile means to achieve high densities of a variety of chromophores on a stable support.

Supplementary Material Available: Synthesis of NLO chromophores 4–7 and related intermediates (6 pages). Ordering information is given on any current masthead page.

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