Macromolecules **2005,** *38,* 4147−4156

Design and Synthesis of New Polymeric Materials for Organic Nonvolatile Electrical Bistable Storage Devices: Poly(biphenylmethylene)s

Matthias Beinhoff,[†] Luisa D. Bozano,[†] J. Campbell Scott,[†] and Kenneth R. Carter*[,‡]

Polymer Science & Engineering Department, University of Massachusetts Amherst, Conte Center for Polymer Research, 120 Governors Drive, Amherst, Massachusetts 01003, and IBM Almaden Research Center, NSF Center for Polymeric Interfaces and Macromolecular Assemblies, 650 Harry Road, San Jose, California 95120-6099

Received March 3, 2004; Revised Manuscript Received December 9, 2004

ABSTRACT: The synthesis of new polymers, poly(biphenylmethylene)s, derived from bistriflates of bisphenol-type monomers, by Ni(0)-mediated polymerization has been presented. These polymers are interesting because of the nature of the polymer backbone that contains biphenyl units separated by substituted methylene units. The solubility, mechanical properties, and electrical properties of the polymers can be altered by proper selection of the methylene substituents. Polymers and oligomers had molecular weights ranging from 2000 to 15 000 g/mol, as measured by calibrated gel permeation chromatography (GPC), though light scattering and MALDI studies indicate that GPC tends to underestimate the molecular weights of these polymers. The polymers have T_g's between 230 and 300 °C and have thermal stabilities ranging from 400 to 493 °C. Thermally cross-linkable, 4-phenylethenyl end-capped oligomers were synthesized and fabricated into thin-film electronic devices, and preliminary results on their characterization are discussed. The unique structure of the polymer backbone makes these materials potentially interesting in electrical applications where large-band-gap polymers with good electron/hole mobility and good thermal and oxidative stability are required.

Introduction

The modern electronics industry has an ever-increasing demand for polymeric materials with new or fine-tuned properties. Most research is devoted to conjugated polymers that are, for example, applied as semiconductors[1] or in electroluminescent devices,[2] and the synthesis of these materials is often a challenge for chemists. Within the past decade, many polymers containing conjugated phenyl groups such as poly(*p*-phenylene)s (PPPs), polyfluorenes (PFs), and poly(phenylene-ethenylene)s (PPEs) have been synthesized. Various transition-metal-catalyzed step-growth polymerization techniques (Suzuki,[3,4] Yamamoto,[5,6] Haghihara/Sonogashira[7]) were utilized successfully. Monomers with aromatic bromides are utilized in most cases, less often aryl iodides, chlorides, and sulfonates, and polymers with $M_n \leq 10\,000$ g/mol are generally obtained, which have been found to be sufficient for most applications.

The use of halogenated aromatic monomers is limited by their availability. Often their preparation by direct halogenation of aryl substrates results in the formation of several regioisomers, polyhalogenation, and purification can be a tedious task. The leaving group ability generally increases from chloride to bromide to iodide. Sulfonates, however, are an attractive alternative to the halides. They can conveniently be prepared from a myriad of commercially available phenol derivatives, and they show reactivity in the range of analogous bromide and iodides. In model studies, Percec and coworkers investigated Ni-catalyzed homo- and cross-coupling reactions of various aromatic sulfonates, with the triflate group as the most reactive leaving group.[8] The optimized methodology was applied in Ni-catalyzed step-growth polymerizations of selected bissulfonates of hydroquinones.[9−12]

Another widely used protocol in the synthesis of PPPs and related polymers, especially PFs, is the Ni-mediated Yamamoto-type polycondensation of bishalogen monomers.[5,6] For the polymerization of dibromofluorenes, polymers with a very high M_n of 30 000 up to 200 000 g/mol were reported.[13] Conventional external heating[14] and microwave-assisted[15] procedures are readily available.

Both Ni-catalyzed and Ni-mediated reaction schemes take advantage of the fact that only one monomer (AA-type monomer) is needed, unlike the Suzuki polycondensation that requires either two monomers (AA- and BB-type monomers) or a monomer carrying two different leaving groups (AB-type monomer), which may require application of precise stoichiometry and extensive monomer synthesis and purification. However, one reason Ni-based polycondensations are not applied more often is the lower molecular weight sometimes obtained when the leaving group carries an ortho substituent other than hydrogen.[8]

Thermally cross-linkable semiconducting polymers were introduced in recent years.[16−18] Functionalized with thermally polymerizable endgroups such as 4-phenylethenyl, thin films of these materials were fashioned into electronic devices by spin-coating. Thermal treatment of these films renders them insoluble in common organic solvents, allowing for coating of successive polymer layers. This method of device fabrication can have an advantageous effect on the properties of the

---

* Author to whom correspondence should be addressed. Phone: 413-577-1416. Fax: 413-545-0082. E-mail: krcarter@polysci.umass.edu.

[†] IBM Almaden Research Center.

[‡] University of Massachusetts Amherst.

10.1021/ma049572k CCC: $30.25 © 2005 American Chemical Society
Published on Web 04/09/2005

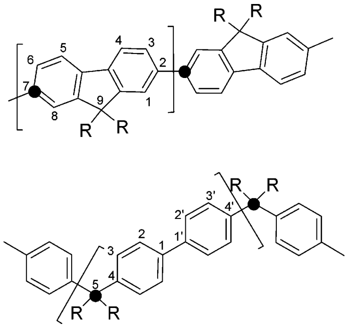


Figure 1. Structural comparison of polyfluorene (above; repeating unit length: 8.4 Å, ●↔●) and poly(biphenylmethylene) (below; repeating unit length: 10.3 Å, ●↔●).

resulting materials. Cross-linkable polyfluorenes, for example, were found to exhibit less aggregation and excimer emission compared to their un-cross-linked analogues.[16,17]

In the development of nonvolatile organic memory, which involves electrical characterization of thin-film devices,[19,20] wide-band-gap materials that possess good electron/hole transport properties are needed. The reason that well-known semiconducting polymers such as polyfluorene and polythiophene do not work while other wide band gap materials perform quite well is a matter of current study.[21] We therefore desired to further explore a new class of processable oligomers and polymers, namely poly(biphenylmethylene)s. This work was inspired by a publication by Sheares and coworkers[22] who have reported hexafluoromethyl-substituted poly(biphenylmethylene)s. This class of macromolecules has a high content of aromatic units, consisting of short, conjugated biphenyl segments bridged by nonconjugated methylene units. Its structure is slightly similar to polyphenylenes such as polyfluorene, as depicted in Figure 1. One difference is the missing carbon−carbon bond between two phenyl rings in the fluorene five-membered ring. The second is the varying substitution pattern of the methylene group. Whereas in polyfluorene it occurs in the meta position the methylene substituent (2,7 bond), in poly(biphenylmethylene)s the para positions are connected (1,1′ bond). In contrast to polyfluorene, the methylene group introduces a kink into the backbone of an otherwise semirigid poly(biphenylmethylene) backbone, increasing the degrees of freedom. Though a methylene unit interrupts the conjugation between two biphenyl groups, such polymeric material may have interesting electronic properties. It has been suggested that 2,2-diphenylpropanes in the butterfly conformation have a spatial overlap between the p atomic orbitals on the phenyl carbon atoms adjacent to the bridge.[23] These structural characteristics should have a strong influence on the material's properties such as solubility, morphology, and electronic behavior. Specifically, we were motivated to explore these materials for the development of new organic bistable devices where wide-band-gap materials with low intrinsic electrical conduction perform best.[24,25] To the best of our knowledge, such polymers have not yet been reported in the literature with the exception of the mentioned report,[22] and the suggestion in a patent of similar structures.[26]

Herein we report on the monomer and polymer synthesis of a variety of poly(biphenylmethylene)s, carrying different substituents, applying Yamamoto-type polycondensation conditions. Through controlled endcapping reactions, cross-linkable materials were also prepared. The thermal, optical, and mechanical properties of representative examples were investigated. Selected cross-linkable oligomers were fabricated into electronic test devices, and preliminary results of their characterization are presented.

Experimental Section

Materials. Phenol (**1**), cyclododecanone (**2**), bisphenol A (**3a**), hexafluorobisphenol A (4,4′-hexafluoroisopropylidene)-bisphenol (**3b**), bisphenol TP (4,4′-(diphenylmethylidene)-bisphenol (**3c**), 4,4′-(*9H*-fluoren-9-ylidene)bisphenol (**3d**), bisphenol Z (4,4′-cyclohexylidenebisphenol (**3e**), trifluoromethane sulfonic anhydride (triflic anhydride), 4-bromostyrene (**6**), 2,2′-bipyridyl, and 1,5-cyclooctadiene were purchased from Aldrich or TCI and used without further purification. The active Ni(0) coupling reagent, bis(1,5-cyclooctadiene)nickel(0), was purchased from Strem Chemicals and handled under inert atmosphere. Pyridine was used as received. Anhydrous toluene and dimethylformamide (DMF) were stored and used in a glovebox. All nickel-mediated cross-coupling reactions were carried out under oxygen-free conditions. 4,4′-Cyclododecylidenebisphenol[27] (**3f**) and bis-4-trifluoromethanesulfonyloxyphenylsulfone (**4g**)[28] are each mentioned in the literature, though insufficient experimental and characterization data are available; therefore, their preparation and characterization are described in full detail. Poly{[1,1′-biphenyl]-4,4′-diyl-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]} (**5b**) was prepared in a different way than in the reference.[22] All other compounds are new. Previously published protocols were utilized for Ni(0)-mediated polymerizations: both conventional heating[14] and microwave assisted.[15]

Microwave Reactor. The microwave heating was performed in a SmithCreator single-mode microwave cavity producing continuous radiation at a frequency of 2.45 GHz (Personal Chemistry, Inc.). Reactions were conducted under nitrogen in 9 mL, heavy-walled Pyrex glass reaction vials sealed with aluminum crimp caps fitted with a silicone septum. Reaction mixtures were stirred internally with a magnetic stir bar during the irradiation. Reaction times and temperatures are operator selectable. Reaction temperature is constantly monitored by infrared thermometry on the outer surface of the reaction vial, the pressure by a transducer on the top of the vial's septum, and the microwave output power is automatically adjusted by the software algorithm to maintain programmed temperature profiles. The instrument's upper operating limits are 250 °C and 25 bar. After the irradiation period, the reaction vessel is cooled rapidly to ambient temperature (and pressure) by compressed air (gas jet cooling).

Characterization. All NMR spectra were acquired at 22 °C on a Bruker AF 400 (400 MHz) spectrometer and internally referenced via residual solvent signal ($CHCl_3$: ^1H, $\delta = 7.24$ ppm; ^{13}C, $\delta = 77.00$ ppm; THF: ^1H, $\delta = 1.73$; 3.58 ppm; DMSO: ^1H, $\delta = 2.50$ ppm). ^{19}F NMR chemical shifts were internally referenced to hexafluorobenzene (^{19}F, $\delta = -164.9$ ppm). All chemical-shift values are given in ppm. ^{19}F NMR experiments were run with a relaxation delay time of 10 s per pulse. Gas chromatography/mass spectrometry (GC-MS) was performed using an Agilent 6890 Series GC (equipped with a 30 m HP-5MS column) interfaced with a HP 5973 mass-selective detector. Gel permeation chromatography (GPC) was performed on a Waters chromatograph (four Waters Styragel HR columns HR1, HR2, HR4, and HR5E in series) connected to a Waters 410 differential refractometer with THF as the eluent. Molecular weight standards were narrow polydispersity polystyrenes. Thermal gravimetric analysis was performed using a Perkin-Elmer TGS-2, under nitrogen atmosphere with a heating rate of 10 °C/min. A TA Instruments 2920 MDSC was used to perform modulated differential scanning calorimetric (MDSC) measurements. Samples were scanned under nitrogen from −50 to 250 °C at a rate of 4 °C/min and a rate modulation of 1 °C. Glass transition temperatures (T_g's) were determined by the inflection point of the complex heat capacity

(C_p). Thermal-mechanical analysis (DMA) was performed on a DMA 983 from TA Instruments. Samples were scanned from −50 to 250 °C at a rate of 5 °C/min under nitrogen. The T_g was determined by the maximum of loss tangent (tan δ). UV/vis absorption spectra were recorded using a Perkin-Elmer UV−vis spectrometer Lambda 9 or HP 8452A diode array spectrometer. Fluorescence was measured using a SA Instruments FL3-11 fluorimeter. Spectra were taken from spun-cast films on 1 in. quartz wafers. Polymer films were prepared on precleaned quartz substrates, and spectroscopic measurements were performed in air. Current voltage characteristics were measured under a nitrogen atmosphere using a computer interfaced Keithley Source-Measure Unit Model 238. The devices were tested at room temperature for DC measurements and in the pulse mode of the source-measure unit.

Device Fabrication and Characterization. Thin film test devices were prepared using 1 in. square glass substrates that were pre-patterned with indium tin oxide (ITO) (Thin Solid Films, Inc., sputtered ITO, 1500 Å). Before the device fabrication, the substrates were first washed with DI water, then IPA, and finally dried for 10 min in an oven. The ITO substrates were then treated with oxygen plasma for 45 min to remove any additional organic residues. After the cleaning process, the substrates were moved into a nitrogen atmosphere drybox for all subsequent processing and electrical characterization. The polymer layers were prepared by spin-coating from THF or *p*-xylene solutions of approximately 5−10 wt% solids. Different spin speeds were used to control the thickness of the films, which were measured independently by AFM. Solvent removal and cross-linking of 4-phenylethenyl-encapped materials were induced by treatment at 150 °C for 1 h. All subsequent metal-layer evaporations were carried out at a pressure of 10^{-6} Torr. A calibrated crystal quartz monitor was used to control the thickness of the layers. During the deposition, the samples were rotated to ensure uniformity of thickness. Each substrate holds six test areas that were 3.12 mm^2 in size. All subsequent electrical characterization was performed in a tandem drybox to avoid exposing the devices to air.

Synthesis. *4,4′-Cyclododecylidenebisphenol (**3f**).* Method (a). Hydrogen chloride was bubbled through a stirred mixture of phenol (**1**) (7.70 g, 81.82 mmol, 5.20 equiv), cyclododecanone (**2**) (2.85 g, 15.63 mmol), and mercaptoacetic acid (0.20 mL, 2.88 mmol, 0.18 equiv) for 15 min at 40 °C. Upon being stirred at room temperature, the reaction mixture solidified overnight. Ethyl acetate (30 mL) was added, and the mixture was neutralized by addition of diluted aqueous sodium hydroxide. The phases were separated, the aqueous one was extracted with ethyl acetate, the combined organic layers were dried over $MgSO_4$, filtered, and the solvent was evaporated. The residue was purified by column chromatography on silica gel (hexanes/ethyl acetate = 5:1 → 2:1). The resulting oil was recrystallized from methanol to yield 4.11 g (75%) of **3f** as a colorless solid.

Method (b). To a stirred solution of acetic acid (3.0 mL), sulfuric acid (96%, 2.5 mL) and mercaptoacetic acid (0.20 mL, 2.88 mmol, 0.19 equiv), phenol (7.3 g, 77.68 mmol, 5.01 equiv) and cyclododecanone (2.83 g, 15.52 mmol) were added at 0 °C. The reaction mixture solidified after 1.5 h and was let stand overnight. After workup and purification (see Method (a)), 4.21 g of bisphenol **3f** was obtained (77%). mp = 206 °C (207−208.5 °C);[27] $R_f = 0.16$ (hexanes/EtOAc = 4:1); ^{1}H NMR (400 MHz) δ 7.00 (d, $^3J = 8.7$ Hz, 4H), 6.69 (d, $^3J = 8.7$ Hz, 4H), 4.48 (s, br, 1H, *OH*), 1.97 (m, br, 4H), 1.27−1.33 (m, 14H), 0.90 (m, br, 4H); ^{13}C NMR (101 MHz) δ 152.9, 142.4, 128.7, 114.4, 47.2, 33.3, 26.5, 26.2, 22.2, 22.0, 20.0; Anal. Calcd for $C_{24}H_{32}O_2$ (352.51): C, 81.77; H, 9.15. Found: C, 81.85; H, 9.06.

*Typical Procedure for the Synthesis of Bistriflates **4a−g**.* 1,1′-Bis(4-trifluoromethanesulfonyloxyphenyl)cyclododecane (**4f**). To a solution of 4,4′-cyclododecylidenebisphenol (**3g**) (4.45 g, 12.60 mmol) in pyridine (40 mL) was added trifluoromethanesulfonic acid anhydride (6.40 mL, 37.91 mmol, 3.0 equiv) within 30 min at 0 °C. The brownish solution was stirred at room temperature overnight. Pyridine was distilled off under reduced pressure, and the residue was dissolved in ethyl acetate. The solution was washed with diluted hydrochloric acid, dried over $MgSO_4$, filtered, and the solvent was evaporated. The residue was purified by column chromatography on silica gel (hexanes/ethyl acetate = 9:1). Recrystallization from CH_2Cl_2/hexanes afforded 7.34 g (95%) of **4f**. The GC-MS spectrum showed a single peak with the mass 467 au, which corresponds to $[M\text{-}OSO_2CF_3]^+$. Colorless solid; mp = 91 °C; $R_f = 0.86$ (hexanes/EtOAc = 10:1); ^{1}H NMR (400 MHz) δ 7.20−7.10 (m, 8H), 1.99 (m, br, 4H), 1.31 (m, br, 14H), 0.82 (m, br, 4H); ^{13}C NMR (101 MHz) δ 149.3, 147.5, 129.3, 120.7, 118.9 (q, J {C,F} = 321 Hz, *CF$_3$*), 48.4, 33.2, 26.3, 26.0, 22.1, 21.8, 18.8; ^{19}F NMR (376 MHz) δ −76.1; Anal. Calcd for $C_{26}H_{30}F_6O_6S_2$ (616.64): C, 50.64; H, 4.90. Found: C, 50.36; H, 4.86.

2,2-Bis(4-trifluoromethanesulfonyloxyphenyl)propane (**4a**). Yield: 93% (6.88 g); colorless solid; mp = 57 °C (58−59 °C);[29] ^{1}H NMR (400 MHz) δ 7.27 (d, $^3J = 8.9$ Hz, 4H), 7.18 (d, $^3J = 8.9$ Hz, 4H), 1.68 (s, 6H); ^{13}C NMR (101 MHz) δ 150.2, 147.7, 128.6, 121.0, 118.7 (q, J {C,F} = 321 Hz, *CF$_3$*), 42.8, 30.7; ^{19}F NMR (376 MHz) δ −76.0; $C_{20}H_{18}F_6O_6S_2$ (532.48).

2,2-Bis(4-trifluoromethanesulfonyloxyphenyl)hexafluoropropane (**4b**). Yield: 95% (7.99 g); colorless needles; mp = 97−98 °C (97.5−98.5 °C);[30,31] $R_f = 0.80$ (hexanes/EtOAc = 10:1); ^{1}H NMR (400 MHz) δ 7.47 (d, 4H), 7.32 (d, 4H); ^{13}C NMR (101 MHz) δ 149.9, 133.1, 132.2, 123.6 (q, J {C,F} = 286 Hz, C-*CF$_3$*), 121.6, 118.7 (q, J {C,F} = 322 Hz, SO$_2$-*CF$_3$*), 64.0 (septet, J {C,F} = 26 Hz, *C*-CF$_3$); ^{19}F NMR (376 MHz) δ −75.9 (s, 6F, SO$_2$−CF$_3$), −67.0 (s, 6F, C−CF$_3$); Anal. Calcd for $C_{17}H_8F_{12}O_6S_2$ (600.36): C, 34.01; H, 1.34. Found: C, 34.14; H, 1.44.

Bis-4-trifluoromethanesulfonyloxyphenyl-bisphenylmethane (**4c**). Yield: 91% (4.68 g); recrystallyzed from CH_2Cl_2/hexanes; colorless solid; mp = 121 °C; $R_f = 0.72$ (hexanes/EtOAc = 10:1); ^{1}H NMR (400 MHz) δ 7.30−7.21 (m, 10H), 7.21 (d, $^3J = 8.8$ Hz, 4H), 7.15 (d, $^3J = 8.8$ Hz, 4H); ^{13}C NMR (101 MHz) δ 147.8, 146.6, 145.2, 132.7, 130.8, 128.0, 126.7, 120.5, 118.7 (q, J {C,F} = 321 Hz, *CF$_3$*), 64.3; ^{19}F NMR (376 MHz) δ −76.0; Anal. Calcd for $C_{27}H_{18}F_6O_6S_2$ (616.55): C, 52.60; H, 2.94. Found: C, 52.46; H, 2.99.

9,9-Bis(4-trifluoromethanesulfonyloxyphenyl)fluorene (**4d**). Yield: 94% (16.65 g); colorless crystals; mp = 154−155 °C; $R_f = 0.58$ (hexanes/EtOAc = 10:1); ^{1}H NMR (400 MHz) δ 7.79 (d, $^3J = 7.6$ Hz, 2H), 7.42−7.38 (m, 2H), 7.33−7.28 (m, 4H), 7.24 (d, $^3J = 8.9$ Hz, 4H), 7.13 (d, $^3J = 8.9$ Hz, 4H); ^{13}C NMR (101 MHz) δ 149.6, 148.5, 145.8, 140.0, 129.8, 128.2, 125.9, 121.3, 120.7, 120.5 118.7 (q, J {C,F} = 321 Hz, *CF$_3$*), 64.4; ^{19}F NMR (376 MHz) δ −76.0; Anal. Calcd for $C_{27}H_{16}F_6O_6S_2$ (614.54): C, 52.77; H, 2.62. Found: C, 52.79; H, 2.70.

1,1-Bis(4-trifluoromethanesulfonyloxyphenyl)cyclohexane (**4e**). Yield: 96% (16.71 g); recrystallyzed from CH_2Cl_2/hexanes; colorless needles; mp = 70 °C; $R_f = 0.76$ (hexanes/EtOAc = 10:1); ^{1}H NMR (400 MHz) δ 7.30 (d, $^3J = 8.9$ Hz, 4H), 7.17 (d, $^3J = 8.9$ Hz, 4H), 2.24 (m, 4H), 1.51 (m, 6H); ^{13}C NMR (101 MHz) δ 148.2, 147.5, 129.0, 121.2, 118.7 (q, J {C,F} = 321 Hz, *CF$_3$*), 46.0, 37.2, 26.0, 22.0; ^{19}F NMR (376 MHz) δ −76.0; Anal. Calcd for $C_{20}H_{18}F_6O_6S_2$ (532.48): C, 45.11; H, 3.41. Found: C, 45.34; H, 3.42.

Bis-4-trifluoromethanesulfonyloxyphenylsulfone (**4g**). Yield: 96% (7.38 g); recrystallized from CH_2Cl_2/hexanes; long, colorless needles; mp = 115 °C; $R_f = 0.57$ (hexanes/EtOAc = 4:1); ^{1}H NMR (400 MHz) δ 8.05 (d, $^3J = 8.9$ Hz, 4H), 7.43 (d, $^3J = 8.9$ Hz, 4H); ^{13}C NMR (101 MHz) δ 152.7, 140.9, 130.4, 122.8, 118.6 (q, J {C,F} = 321 Hz, *CF$_3$*); ^{19}F NMR (376 MHz) δ −76.0; Anal. Calcd for $C_{14}H_8F_6O_8S_3$ (514.40): C, 32.69; H, 1.59. Found: C, 32.47; H, 1.56.

*Typical Procedure for the Homopolymerization of Bistriflates **4a−g** to Polymers **5a−g** Carrying Triflate Endgroups (See Table 1 for Yields, M_n, PDI, DP, Decomposition Temperatures, and T_g).* Poly{[1,1′-biphenyl]-4,4′-diyl-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]} (**5b**).

Method (a): Conventional External Heating. A solution of bis(1,5-cyclooctadiene)nickel(0) (894 mg, 3.3 mmol), 2,2′-bipyridyl (528 mg, 3.4 mmol), and 1,5-cyclooctadiene (0.40 mL, 3.3 mmol) in degassed anhydrous toluene (10 mL) and DMF (10 mL) was stirred at 80 °C for 30 min. Via a cannula, a solution of **4b** (874 mg, 1.46 mmol) in degassed anhydrous toluene (40 mL) was then added. After the mixture was stirred for 24 h at 80 °C, the resulting dispersion was poured into a vigorously

Table 1. Experimental Data of Homopolymers 5

method[a]	monomer[b]	polymer[c]	yield[d] (%)	M_n[e] (g/mol)	PDI[f]	DP[g]	T_g[h] (°C)	decomp[i] (°C)
a	**4a**	**5a**		1418	1.39	5	n.o.[k]	
a	**4b**	**5b**	78	14855	2.07	49	265	495
a	**4c**	**5c**	94	oligomeric				
a	**4d**	**5d**	93	6720	1.52	21	n.o.	>497
a	**4e**	**5e**	52	2610[j]	1.80	11	287	454
a	**4f**	**5f**		oligomeric				
a	**4g**	**5g**		oligomeric				
b	**4a**	**5a**	50	2259	1.53	12	n.o.	
b, 250	**4b**	**5b**	69	10920	1.44	36		
b, 200			40	11711	1.33	38		
b, 150			72	4319	1.54	14		
b	**4c**	**5c**	87	oligomeric				
b	**4d**	**5d**	59	3322	1.64	10		
b	**4e**	**5e**	25	oligomeric				
b	**4f**	**5f**	67	oligomeric				
			43	2075[j]				
b	**4g**	**5g**		oligomeric				

[a] a: conventional heating, 16−24 h at 80 °C; b: microwave-assisted heating, 10 min at 200 °C, unless otherwise noted. [b] See Scheme 1 for structures. [c] See Scheme 2 for structures. [d] Isolated yield. Calculated by M_n/M(repeating unit); hence, in oligomers the triflate endgroups tend to increase the value. [e] Values are for the THF-soluble fractions of the obtained polymers. [f] Polydipersity index, M_n/M_w. [g] Degree of polymerization. [h] Glass transition tempearture. [i] Decomposition, 5% weight loss in TGA under nitrogen. [j] Sample contained lower-molecular-weight fractions (multimodal distribution) that are not included in this value since they could not be quantified by GPC. [k] Not observed.

stirred 1:1 mixture of methanol and concentrated hydrochloric acid (100 mL). The phase-separated toluene layer was removed with a pipet and dropped into methanol. The precipitated material was centrifugated and dried in a vacuum to give the title compound **5b** as a colorless powder (345 mg, 78%). M_n (GPC) = 14.855, PDI = 2.07, DP = 49. There was found a considerable loss of material due to fractionation. Oligomeric material of **5b** was easily soluble in methanol. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.61 (m, ^3J {H,H} = 8.1 Hz, 4H), 7.50 (m, ^3J {H,H} = 8.1 Hz, 4H), 7.39 (m, Ph−OTf endgroup), 5.32 (m, Ph−OTf endgroup); ^{19}F NMR (376 MHz, CDCl$_3$) δ −76.2 (SO$_2$−CF$_3$), −67.0 (C−CF$_3$).

Method (b): Microwave-Assisted Heating. To a freshly prepared solution of bis(1,5-cyclooctadiene)nickel(0) (168 mg, 0.6 mmol), 2,2′-bipyridyl (77 mg, 0.5 mmol), and 1,5-cyclooctadiene (0.10 mL, 0.8 mmol) in anhydrous toluene (4 mL) and DMF (1 mL) was added a solution of **4b** (153 mg, 0.26 mmol) in anhydrous toluene (1 mL) via a cannula. Prior to heating, the mixture was stirred in the sealed vial at room temperature for 10 min then heated in the microwave reactor at 200 °C for 10 min. The resulting dispersion was passed through a 0.45 μm syringe filter and poured into a stirred mixture of methanol and concentrated hydrochloric acid (1:1, 20 mL). The toluene used for washing the vial was added, and the phase-separated toluene layer was removed with a pipet and dropped under stirring into methanol. The precipitated material was centrifugated and dried in a vacuum to give polymer **5b** as a colorless powder (46 mg, 60%). M_n (GPC) = 11.700, PDI = 1.33, DP = 38. There was found a considerable loss of material due to fractionation. Oligomeric material of **5b** was easily soluble in methanol.

Polymer (5a). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.49 (d, 4H), 7.29 (d, 4H), 1.72 (s, 6H); ^{19}F NMR (376 MHz, CDCl$_3$) δ −76.0.

Polymer (5c). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.44 (m, 4H), 7.27−7.08 (m, 14H), ^{19}F NMR (376 MHz, CDCl$_3$) δ −76.0.

Polymer (5d). ^{1}H NMR (400 MHz, d_8-THF) δ 7.98 (m, 2H), 7.62−7.51 (m, 8H), 7.42 (m, 6H); ^{19}F NMR (376 MHz, d_8-THF) δ −74.9.

Polymer (5e). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.48 (d, 4H), 7.31 (s, 4H), 2.30 (m, 4H), 1.55 (m, 6H); ^{19}F NMR (376 MHz, CDCl$_3$) δ −75.9.

Polymer (5f). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.41 (s, br, 4H), 7.18 (s, 4H), 2.04 (s, br, 4H), 1.31 (s, br, 14H), 0.91 (s, br, 4H); ^{19}F NMR (376 MHz, CDCl$_3$) δ −76.2.

Polymer (5g). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.04 (m, 4H), 7.68 (m, 4H); ^{19}F NMR (376 MHz, CDCl$_3$) δ −76.0.

*Typical Procedure for the Copolymerization of Bistriflates **4a−g** and 4-Bromostyrene (**6**) to Polymers **7a−g** Carrying 4-Phenylethenyl Endgroups (See Table 2 for Yields, M_n, PDI, DP, Decomposition Temperatures, and T_g).* Poly{[1,1′-biphenyl]-4,4′-diyl-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]} (7b).

Method (a): Conventional External Heating. A solution of bis(1,5-cyclooctadiene)nickel(0) (274 mg, 1.0 mmol), 2,2′-bipyridyl (188 mg, 1.2 mmol), and 1,5-cyclooctadiene (1.2 mL, 1.0 mmol) in degassed anhydrous toluene (7 mL) and DMF (1 mL) was stirred at 80 °C for 25 min. Via a cannula, a solution of **4b** (301 mg, 0.50 mmol) and 4-bromostyrene (**6**) (17 mg, 0.09 mmol) in degassed anhydrous toluene (3 mL) was then added. After the mixture was stirred for 24 h at 80 °C, the resulting dispersion was poured into a vigorously stirred 1:1 mixture of methanol and concentrated hydrochloric acid (25 mL). The phase-separated toluene layer was removed with a pipet and dropped into methanol, and the precipitated material was centrifugated and dried in a vacuum to give the polymer **7b** as a colorless solid (97 mg, 63%). M_n (GPC) = 8.580, PDI = 1.63, DP = 28. There was found a considerable loss of material due to fractionation. Oligomeric material of **7b** was easily soluble in methanol. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.60 (m, 4H), 7.51 (m, 4H), 6.74 (m, 1H), 5.79 (d, ^3J {H,H} = 17 Hz, 1H), 5.28 (d, ^3J {H,H} = 11 Hz, 1H); ^{13}C NMR (101 MHz) δ 140.4, 132.9, 130.8, 126.9, 124.2 (q, J {C,F} = 287 Hz, *CF$_3$*), 64.3 (septett, J {C,F} = 26 Hz, *C*-CF$_3$); ^{19}F NMR (376 MHz, CDCl$_3$) δ −66.7.

Method (b): Microwave-Assisted Heating Using a Catalyst Stock Solution. In a glovebox, a 0.2727 mM catalyst stock solution was prepared consisting of bis(1,5-cyclooctadiene)-nickel(0) (1.50 g, 5.4 mmol), 2,2′-bipyridyl (850 mg, 5.4 mmol), and 1,5-cyclooctadiene (0.68 mL, 5.5 mmol) in anhydrous toluene (10 mL) and DMF (10 mL). Polymerization was accomplished by adding 4.3 mL of the catalyst solution (1.17 mmol of the active Ni(0) complex) to a 10 mL reaction vial already charged with **4b** (339 mg, 0.57 mmol) and 4-bromostyrene (**6**) (10 mg, 0.06 mmol). The reaction vial was sealed and placed in the microwave reactor and heated to 250 °C for 10 min. After cooling, the reaction solution was filtered (0.45 μm) and precipitated into a stirred 1:1 mixture of methanol and concentrated hydrochloric acid (35 mL). The separated toluene phase was removed with a pipet and dropped into methanol, and the precipitated material was centrifugated and dried in a vacuum to give the title compound **7b** as a colorless solid (124 mg, 72%). M_n (GPC) = 6.706, PDI = 1.64, DP = 22. There was found a considerable loss of material due to fractionation. Oligomeric material of **7b** was easily soluble in methanol.

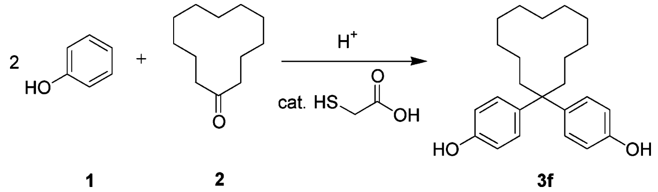
Polymer (7a). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.45 (d, 4H), 7.21 (d, 4H), 6.67 (m, 1H), 5.70 (m, 1H), 5.18 (m, 1H), 1.66 (s, CH$_3$).

Table 2. Experimental Data of Homopolymers 7

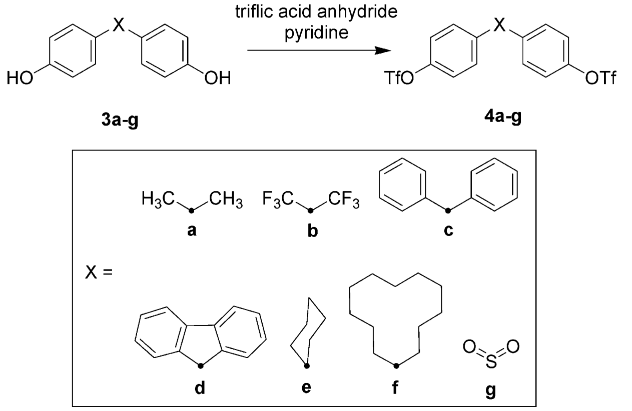
method[a]	monomers[b]	polymer[c]	yield[d] (%)	M_n[e] (g/mol)	PDI[f]	DP[g]	T_g[h] (°C)	decomp[i] (°C)
a	**4a, 6**	**7a**	61	2106	1.23	11	n.o.[k]	489
a	**4b, 6**	**7b**	63	8580	1.63	28	232	493
a	**4c, 6**	**7c**	98	oligomeric				
a	**4d, 6**	**7d**	74	3637	1.82	11	297	430
a	**4e, 6**	**7e**	60	oligomeric				
a	**4f, 6**	**7f**	81	oligomeric				
a	**4g, 6**	**7g**	85	oligomeric				
b, 250	**4b, 6**	**7b**	72	6706	1.64	22	250	470
b	**4c, 6**	**7c**	62	oligomeric			n.o.	
b	**4d, 6**	**7d**	79	3107	1.67	10	n.o.	421
b	**4d, 6**	**7d**	93	3493	1.66	11	n.o.	
b, 250	**4e, 6**	**7e**	47	3752[j]				401
b	**4f, 6**	**7f**	58	oligomeric				
b	**4g, 6**	**7g**	76	oligomeric				

[a] a: conventional heating, 16−24 h at 80 °C; b: microwave assisted heating, 10 min at 200 °C, unless otherwise noted. [b] See Scheme 1 for structures. [c] See Scheme 2 for structures. [d] Isolated yield. Calculated by M_n/M(repeating unit); hence, in oligomers the triflate endgroups tend to increase the value. [e] Values are for the THF-soluble fractions of the obtained polymers. [f] Polydispersity index, M_n/M_w. [g] Degree of polymerization. [h] Glass transition tempearture. [i] Decomposition, 5% weight loss in TGA under nitrogen. [j] Sample contained lower-molecular-weight fractions (multimodal distribution) that are not included in this value since they could not be quantified by GPC. [k] Not observed.

Scheme 1. Synthesis of 4,4′-Cyclododecylidenebisphenol (3f)

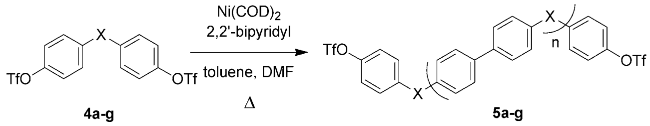


Scheme 2. Monomer Synthesis[a]



[a] The symbol • indicates the point of connection.

Scheme 3. Polymer Synthesis[a]



[a] For a legend see Scheme 2.

Polymer (7c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (m, 4H), 7.28 (m, 14H), 6.78 (m, 1H), 5.80 (m, 1H), 5.25 (m, 1H).

Polymer (7d). ^{1}H NMR (400 MHz, d_8-THF) δ 7.96 (s, br, 2H), 7.68−7.31 (m, 14H), 6.89 (m, 1H), 5.93 (d, ^3J {H,H} = 18 Hz, 1H), 5.35 (d, ^3J {H,H} = 11 Hz, 1H).

Polymer (7e). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (m, 4H), 7.34 (m, 4H), 6.73 (m, 1H), 5.76 (m, 1H), 5.24 (m, 1H), 2.32 (m, 4H), 1.59 (m, 6H).

Polymer (7f). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (m, 4H), 7.17 (m, 4H), 6.67 (m, 1H), 5.70 (m, 1H), 5.18 (m, 1H), 2.04 (m, br, 4H), 1.30 (m, br, 14H), 0.90 (m, br, 4H);

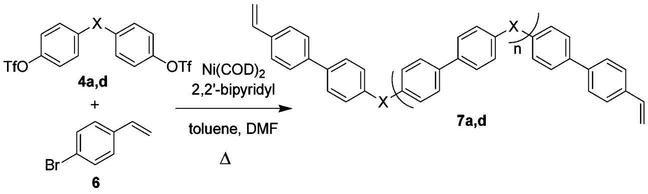
Polymer (7g). ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.08 (m, 4H), 7.92 (m, 4H), 6.80 (m, 1H), 5.92 (m, 1H), 5.33 (m, 1H).

Results and Discussion

Synthesis. Commercially available bisphenol A-type compounds **3a**−**g** served as starting materials for the synthesis of the bistriflate monomers, with the exception of the cyclododecyl derivative, which required the synthesis of 4,4′-cyclododecylidenebisphenol (**3f**). The monomer **3f** was prepared by acid-catalyzed condensation of 2 equiv of phenol (**1**) and cyclododecanone (**2**) in the presence of catalytic amounts of mercapto acetic acid (Scheme 1).[32] Two different protocols were successfully applied toward the synthesis of **3f**: (a) the mixture was repeatedly saturated with gaseous hydrogen chloride and stirred at room temperature or (b) the reaction mixture was stirred in a 1:1 mixture of concentrated sulfuric acid and glacial acetic acid. Both methods afforded the bisphenol **3f** in 75 and 77% yield, respectively. The bistriflate monomers **4a**−**g** were obtained in yields >95% by reaction of their respective bisphenols **3a**−**g** with trifluoromethane sulfonic acid anhydride in pyridine (Scheme 2). Purification by column chromatography on silica gel and recrystallization ensured purities of virtually 100% (GC-MS).

The macromolecular synthetic scheme involves the Ni(0)-mediated Yamamoto-type polycondensation (reductive aryl−aryl coupling) of the bistriflates monomers using a catalyst system consisting of bis(1,5-cyclooctadiene)nickel(0), 2,2′-bipyridyl, and free 1,5-cyclooctadiene (COD) in toluene or toluene/DMF mixtures (Scheme 3).[33] Two series of poly(biphenylmethylene)s have been synthesized for this study: homopolymers **5** from monomers **4**, carrying triflate endgroups (Scheme 3), and homopolymers **7** from monomers **4** and 4-bromostyrene (**6**, between 5 and 10 mol% vs triflate groups) leading to 4-phenylethenyl end-capped polymers (Scheme 4). The polymerization results are displayed in Tables 1 and 2. The end-capping procedure not only allows for stoichiometric control of molecular weight but also introduces thermally cross-linkable functionality into the oligomer that can be used to produce polymeric networks for application in electronic devices by spin-coating (vide infra). Preparation of polymers **5** and **7** was carried out via two different routes: (a) conventional external heating in a Schlenk flask at 85 °C for 16−24 h and (b) heating in a microwave reactor for 10 min at temperatures ranging from 150 to 250 °C. The

Scheme 4. 4-Phenylethenyl End-Capped Polymer Synthesis[a]



[a] For a legend see Scheme 2.

utilization of microwaves has become a widespread tool in organic synthesis in recent years, with the main benefits of significant rate enhancements and higher product yields with less occurrence of side reaction pathways.[34,35] Transition-metal-catalyzed or -mediated, microwave-assisted reaction protocols both on the molecular[35] and the macromolecular[15] level are readily available.

The synthesis of a first set of homopolymers **5** (Scheme 3, Table 1) by both heating methods gave low-molecular-weight oligomers and higher-molecular-weight polymers in typical yields ranging from 40 to 95%. The materials had number average weights (M_n) up to 6.700 g/mol, polydispersity indexes (PDI) of 1.4–2.0 and degrees of polymerizations (DP) up to 38 (THF soluble fractions), as measured by GPC relative to polystyrene (PS) standards.

Interestingly, Sheares and co-workers found that GPC underestimates the molecular weight of a polymer analogous to **5b** by a factor of 1.4 when compared to the more reliable data obtained by multiple-angle laser light scattering (MALLS).[22,36] Comparison of the molecular weight of polymer **5b** made in this study measured by GPC and quasi-elastic light scattering (QELS) results in underestimation of the M_n value measured by GPC by a factor of 1.6–1.8 (Figure 2). The deviation from the theoretical PDI value of 2.0 and comparably low yields of good soluble polymers are consistent with other polymers prepared by transition-metal-catalyzed or -mediated step-growth polymerization methods, possibly due to the loss of some lower-molecular-weight oligomeric material via fractionation during workup. For material with low THF solubility, GPC results may only reflect the lower-molecular-weight fraction that is soluble. The predominant limiting factor in obtaining high molecular weight appeared to be the low solubility of a number of the polymers. After the polymerization reaction, insoluble, precipitated polymeric material is not clearly visible in the crude reaction mixture since the crude slurry also contains finely dispersed Ni black particles and Ni salts. Of all the materials, only the hexafluoromethyl-substituted polymer **5b** showed very good solubility in a number of common organic solvents such as toluene, chloroform, THF, *N*-methylpyrrolidone (NMP), and propylene glycol methyl ether acetate (PGMEA); hence, the highest M_n were observed for **5b**. While the fluorenyl polymer **5d** is reasonably soluble, all other materials were only sparingly soluble in organic solvents. Oligomer **5d** with a M_n of 3300 is readily soluble in THF, whereas material with a M_n of 6700 (GPC values vs PS) did not dissolve completely upon shaking the mixture for 16 h. Replacement of the cyclohexyl group in polymer **5e** by a cyclododecyl group in polymer **5f** did not result in a distinct enhancement of the solubility. In the end, the moderate molecular weights of these poly(biphenylmethylene)s are not a setback for the targeted application because generally the electronic properties of semiconducting polymers level off with DPs of roughly 5–10 repeat units.[14] Difficulties in preparing good, robust thin films from low-molecular-weight polymers and oligomers is overcome by synthesizing cross-linkable materials.

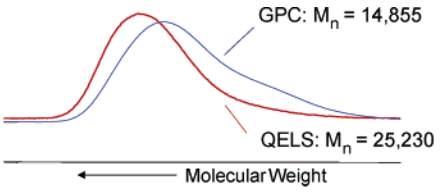


Figure 2. Comparison of GPC and quasi-elastic light scattering (QELS) results on molecular-weight determination of polymer **5b**. GPC underestimates the M_n value by a factor of 1.6–1.8.

The presence of residual triflate endgroups in polymers **5** was determined by ^{19}F NMR spectroscopy, which proved to be a valuable sensitive tool for determining the amount of fluorine-containing triflate groups. Triflate endgroups in the homopolymers series **5** exhibited a strong signal at about −76 ppm in the ^{19}F NMR spectra in chloroform, essentially the same value as observed for the respective monomers. However, when d_8-THF was used as the solvent, the signal underwent a downfield shift to −74.9 ppm. The amount of triflate endgroups could be quantified by comparing their signals with the signals from added hexafluorobenzene of known concentration.[37]

Polymers **7a–f** with 4-phenylethenyl endgroups were prepared by copolymerization of bistriflate monomers **4a–g** and 4-bromostyrene (**6**) (Scheme 4, Table 2). Using essentially the same reaction conditions as outlined above, the monofunctional endcapping agent **6** was used in ratios of 5–10% vs triflate groups. As expected from the calculated stoichiometric imbalance, DP 10 were achieved. Surprisingly, 4-phenylethenyl end-capped polymers **7** could conveniently be prepared in the high-temperature microwave reactor as well. No noticeable consumption of the vinyl group and hence no cross-linkage was observed during polymerization, even at temperatures as high as 250 °C for 10 min. This result shows the utility of the efficiency of microwave-heated reactions even when using functional organic substrates. All GPC elution curves for the polymers from these reactions were monomodal. As expected, thin films prepared from these materials form insoluble cross-linked networks when heated, dried, and cured at 150 °C for >1 h (see below).

There was no observed difference in solubility of material of comparable molecular weight with either triflate or 4-phenylethenyl endgroups. Polymer solubility plays a crucial role in the fabrication of electronic devices by spin-coating. The poor solubility of some of the polymers, even low-molecular-weight oligomers, may be to some extent be due to the tendency toward crystallization or the rigid nature of the polymer backbone. The lower reactivity of some of the monomers we utilized is likely another cause of the low molecular weights we observed in some cases. We attempted to discern whether we were observing molecular-weight limitations imposed by solubility versus reactivity by attempting to synthesize random copolymers consisting of two different triflate monomer. For example, combinations of the fluorenyl-substituted monomer **4d** with

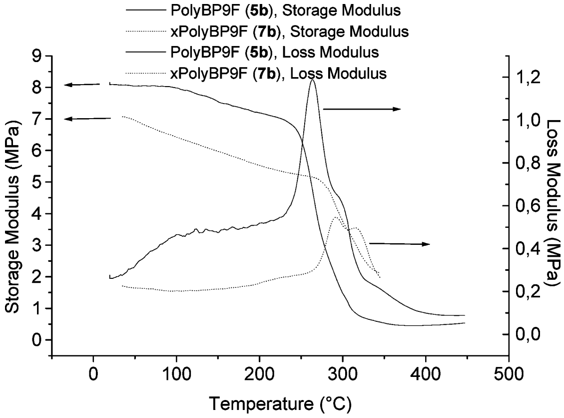


Figure 3. Dynamic mechanical analysis (DMA). Storage and Loss Modulus for **5b** (—–) and **7b** (···).

either the hexafluoromethyl compound **4b** or the cyclododecyl monomer **4f** were used in a 1:1 ratio to synthesize random copolymers. No significant changes in the molecular weight or solubility of the resulting copolymers were observed. This led us to believe that low reactivity of the cyclododecyl monomer is the primary reason that it fails to give high-molecular-weight polymer—while we note that the oligomeric copolymers also have extremely low solubility. No crystallinty was observed by DSC measurements. At the time of the study, WAXD facilities were not available; however, future collaborative WAXD studies have been proposed.

The 4-phenylethenyl end-capped polymers, series **7,** showed the expected resonances of the vinyl protons in the ^{1}H NMR spectra at 5.32 (d), 5.90 (d), and 6.85 ppm (m), respectively. However, some of the ^{19}F NMR spectra of the 4-phenylethenyl end-capped polymers still showed a trace of the triflate signal at −76 ppm. This indicates that the end-capping with 4-bromostyrene (**6**) did not reach 100% completion in these cases. It was possible to quantitatively replace all of the triflate endgroups in a secondary, follow-up Ni(0)-meditated cross-coupling reaction of these materials with an excess of 4-bromostyrene (**6**).

Characterization. Selected materials were examined by TGA and MDSC, (see Tables 1 and 2 for details). Polymers **5** and **7** showed good thermal stability. Less than 5% weight loss values well above 300 °C were observed for most samples by TGA (10 °C/min, under nitrogen), some were stable up to about 490 °C, e.g., the hexafluoromethyl- and fluorenyl-substituted polymers **5b** and **5d**. MDSC data did not clearly reveal values for T_g's for most of the materials. This is likely due to the high degree of crystallinity in the solid state, though no melting transitions were noted. However, the observed T_g's were in the range of 220−300 °C, and the thermal mechanical properties observed in DMA measurements (see below) show that these materials possess thermo-mechanical response and measurable T_g's consistent with the T_g's observed by DSC for the other samples. Polymer **5b** forms thin, free-standing, non-crosslinked films from a 20 wt% solution in PGMEA. The T_g measured for this cast film was slightly lower (255 °C) than that of the amorphous solid polymer powder (265 °C), though both samples were taken from the same batch.

Dynamic mechanical analysis (DMA) was performed for polymers **5b** and **7b** (Figure 3). The observed T_g, as measured by the large drop in the storage modulus and the maximum of the loss modulus, increases from 263 °C for the linear polymer **5b** to 292 °C for the cross-linked polymer **7b**. The linear polymer undergoes a sharp seven-decade drop in modulus at T_g, whereas the drop in modulus observed with the cross-linked system is much less dramatic and at a much higher temperature. These data confirms that we have indeed incorporated better thermo-mechanical stability as a result of the mild cross-linking introduced into the system (**7b**). The loss of mechanical properties at nearly 300 °C is a result of a failure of the cross-linked vinyl linkages at that temperature with concurrent loss of mechanical stability as the system reverts to a non-cross-linked, low-molecular-weight, linear morphology.

The absorption and photoluminescence behavior for selected polymers **5** and **7** were measured on spun-cast thin films on quartz substrates. Typical spectra are displayed in Figure 4 (polymers **5d** and **7d**). The absorption spectra all show two broad bands with λ_{max} ranging from 210 to 225 nm and 270 to 290 nm, respectively, and a weak shoulder at 310 nm. Since the backbones of the two polymers are identical, the absorp-

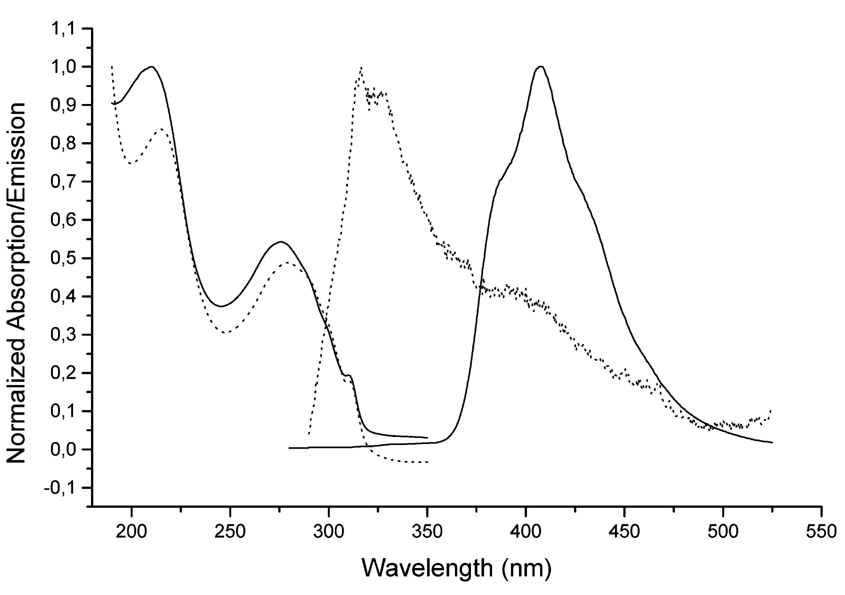


Figure 4. Absorption and photoluminescence spectra of polymers **5d** (···) and **7d** (—–).

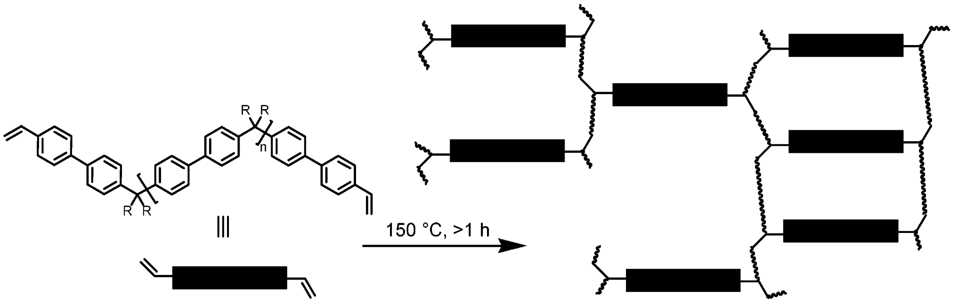


Figure 5. Schematic representation of the formation of a cross-linked film.

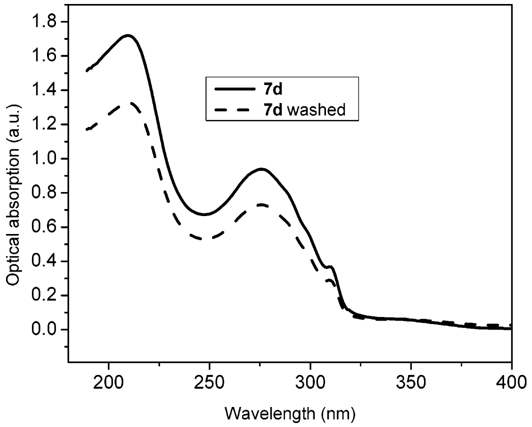


Figure 6. UV absorbance spectra of **7d** after thermal curing (1 h, 150 °C) and after curing and solvent rinsing (THF).

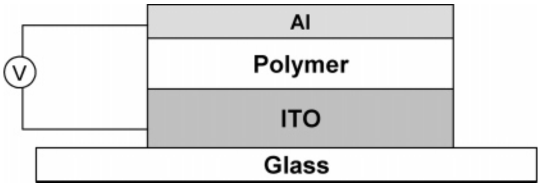


Figure 7. Device structure of the fabricated devices.

tion spectra are very similar. The 4-phenylethenyl endgroups of polymer **7** do not noticeably alter the absorption spectra since 4-vinylbiphenyl absorbs (in solution) at 274 nm.[38] The emission spectra exhibit also broad bands with varying intensities and $\lambda_{\max}$ ranging from 315 to 325 nm for polymers **5** with triflate endgroups and at about 405 nm for polymers **7** with 4-vinylbiphenyl endgroups. The latter one has clear shoulders on both the high- and low-wavelength sides which look like a vibronic progression, with 0−1 stronger than 0−0. Moreover, the emission is much stronger than of polymers **5**. The large red-shift in the emission band of **7** results from rapid exciton transfer to the 4-vinylbiphenyl endgroups. These have more-extended conjugation and, therefore, lower exciton energy than the biphenyl units in the chain. Thus, backbone units dominate the absorption, but the endgroups are responsible for the emission.

Electronic Devices. The cross-linkable, 4-phenylethenyl end-capped oligomers **7b** and **7d** were successfully utilized in electronic device fabrication. To prepare thin film samples for UV/vis and photoluminescence characterization, the polymers were spin-cast on a 1 in. quartz wafers from 5 to 10 wt% THF or *p*-xylene solutions and subsequently baked at 150 °C under N_2 for 1 h to effect solvent removal and curing. This curing involves the thermally initiated cross-linking of the oligomer 4-phenylethenyl endgroups. The cross-linking process is represented in Figure 5. The resulting network films have decreased solubility in organic processing solvents and are more robust than analogous non-cross-linked films. The advantages of these types of curable systems have been explored previously.[16,17] To demonstrate the increased solvent resistance of the cured oligomers, the absorption spectra of the cured film before and after rinsing the substrate with THF solvent are shown in Figure 6. Though a slight reduction of absorption after rinsing is noted, the UV−vis data suggests that greater than 80% of the polymer remains after rinsing. When non-cross-linked films are subjected to the same procedure, the film is completely removed, precluding their use in processes where multilayer films are prepared by successive solvent coating techniques. The solvent resistance imparted in **7b** and **7d** allows for their use in multilayer thin film devices.

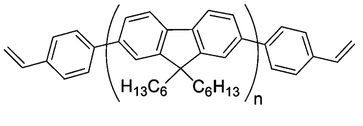
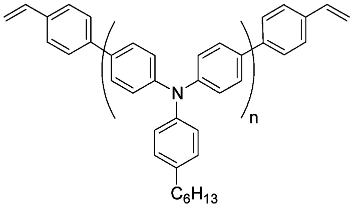
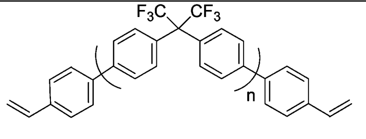
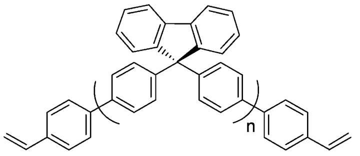
A schematic representation of the structure of the diodes-type devices that were prepared and characterized is shown in Figure 7. Devices 3.12 mm × 1 mm in area were prepared on ITO substrates (see Experimental Section). The aluminum layer was thermally evaporated at 10^{-6} Torr in a vacuum chamber. A shadow mask was used to define the size of the top electrode contact and, therefore, the device's operational area.

For electronic applications such as bistable memory devices,[21,39,40] wide band-gap polymers that possess high thermal and electronic stability and that are cross-linkable are preferable. Polymers such as x-DHF (poly (9, 9-di-*n*-hexylfluorene)), and x-HTPA (poly-[(4-*n*-hexyltriphenyl)amine]), where "x-" denotes "*cross-linkablity*", are conjugated materials that have been extensively studied for electronic applications[41] but are sensitive to both electrical and photooxidative degradation.

In Table 3, four interesting cross-linkable materials, x-DHF, x-HTPA, and the newly synthesized polymers **7b** and **7d** are compared. Their structure, electrical performances, and energy band gap are also indicated. The band-gap values for x-DHF and x-HTPA are reported in the literature,[41] while an estimation of the optical band gap of **7b** and **7d** can be derived from their absorption spectra.[42] From the comparison, we observe that the polymer **7b** and **7d** have a wider band gap than that of x-DHF and x-HTPA; this has important implications in the electrical properties, as explained below.

Applying a voltage to the polymer layer when configured between two electrodes as depicted in Figure 7 and measuring the current output, one can study the electrical properties of the different polymers. The current density is plotted as a function of applied voltage in Figure 8 using a semilogarithmic scale. Since the I−V characteristic of **7b** had similar low current behavior to the **7d** material, only three of the four materials considered are compared for clarity, x-DHF, x-HTPA, and **7d**. The thickness of the polymer layer was different

Table 3. Summary of Materials Used to Fabricate Electrical Devices

Material	**Structure**	**Current density at 4 V (A/cm^2)**	**Energy Bandgap (eV)**
xDHF		3 10^{-1}	2.8
xHTPA		3 10^{-2}	2.8
7b		1 10^{-8}	~ 4 – 4.4[a]
7d		7 10^{-8}	~ 4 - 4.4[a]

[a] the values represent the optical bandgap, that could differ form the value for the energy bandgap.

for the various materials, ranging from 50 to 100 nm (**7b**, **7d**).

There is a large observable difference between the polymers. At 4 V, the current density of the polymer **7d** (and **7b**) is 6 orders of magnitude smaller than the current observed for x-DHF and x-HTPA. Furthermore, while x-DHF and x-HTPA show rectifying properties, the polybiphenylmethylene materials show no rectification and a symmetrical I−V characteristic with respect of the voltage polarity (positive or negative). This indicates that the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) probably have similar barrier heights to the work functions of the metal electrodes. In the case of x-DHF and x-HTPA, the energy levels tend to well match the metal work function of the ITO (x-HTPA) and Al (x-DHF) electrodes, explaining the respective good hole- and electron-injection properties of these materials. The HOMO and LUMO levels of **7b** and **7d** have not yet been determined, making it difficult to interpret the low current density observed from the I−V measurements in terms of whether it is due to intrinsically low conduction or poor injection properties.

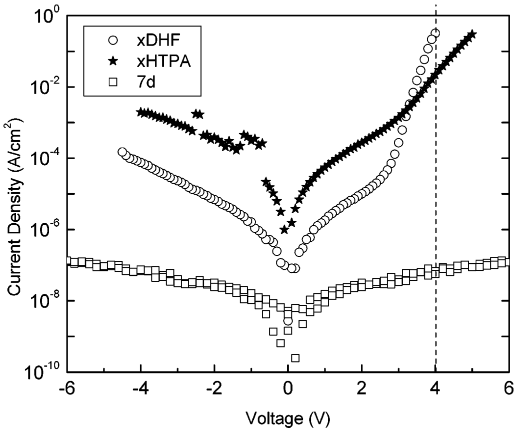


Figure 8. Comparison of the electrical properties of devices based on different polymer films for ITO/polymer/Al structure.

The three devices were tested for other electrical properties, such as lifetime and temperature dependence, and the poly(biphenylmethylene) materials demonstrated more stability than the x-DHF- and x-HTPA-based devices. Therefore, they are perhaps the best candidates so far for application as semiconducting polymers for the fabrication of memory devices where stabilty and long operational lifetimes are important. Reports on their operations in bistable organic memory devices are forthcoming.[40]

Summary

The synthesis of new polymers, poly(biphenylmethylene)s, derived from bistriflates of bisphenol-type monomers by Ni(0)-mediated polymerization has been presented. These polymers are interesting because of the nature of the polymer backbone that contains biphenyl units separated by substituted methylene units. The unique structure of the polymer backbone makes these materials potentially interesting in electrical applications where large-band-gap polymers with low current density and good thermal and oxidative stability are required. The solubility, mechanical properties, optical properties, and electrical properties of the polymers can be altered by proper selection of the methylene substituents. Thermally cross-linkable, 4-phenylethenyl end-capped oligomers were synthesized and fabricated into thin-film electronic devices, and preliminary results on their characterization were discussed.

Acknowledgment. Financial support from both the MRSEC Program of the National Science Foundation, under Award No. DMR-9808677 for the Center for Polymeric Interfaces and Macromolecular Assemblies, and the IBM Corporation are gratefully acknowledged. We thank Teddie Magbitang for help with the GPC and light scattering and Lucy Lu for thermal analysis.

References and Notes

(1) Heeger, A. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 2591−2611.
(2) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed*. **1998**, *37*, 402−428.
(3) Schlüter, A. D. *J. Polym. Sci., Part A: Polym. Chem*. **2001**, *39*, 1533−1556.
(4) Marsitzky, D.; Vestberg, R.; Blainey, T. T.; Hawker, C. J.; Carter, K. R. *J. Am. Chem. Soc.* **2001**, *123*, 6965−6972.
(5) (a) Yamamoto, T.; Morita, A.; Miyazaki, Y.; Maruyama, T.; Wakayama, H.; Zhou, Z.-h.; Nakamura, Y.; Kanbara, T.; Sasaki, S.; Kubota, K. *Macromolecules* **1992**, *25*, 1214−1223. (b) Yamamoto, T. *Prog. Polym. Sci*. **1992**, *17*, 1153−1205.
(6) Scherf, U.; List, E. J. W. *Adv. Mater*. **2002**, *14*, 477−487.
(7) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605−1644.
(8) Percec, V.; Bae, J.-Y.; Zhao, M.; Hill, D. H. *J. Org. Chem.* **1995**, *60*, 176−185 and references therein.
(9) Percec, V.; Okita, S.; Weiss, R. *Macromolecules* **1992**, *25*, 1816−1823.
(10) Percec, V.; Bae, J.-Y.; Zhao, M.; Hill, D. H. *Macromolecules* **1995**, *28*, 6726−6734.
(11) Percec, V.; Zhao, M.; Bae, J.-Y.; Hill, D. H. *Macromolecules* **1996**, *29*, 3727−3735.
(12) Typical molecular weights were in the range of $M_n = 2000-7000$ g/mol (28 examples), with three examples exceeding 10 000 and one as high as 35 000 g/mol (as measured by GPC vs a polystyrene standard).
(13) Nothofer, H.-G.; Meisel, A.; Miteva, T.; Neher, D.; Forster, M.; Oda, M.; Lieser, G.; Sainova, D.; Yasuda, A.; Knoll, W.; Scherf, U. *Macromol. Symp*. **2000**, *154*, 139−148.
(14) Klärner, G.; Miller, R. D. *Macromolecules* **1998**, *31*, 2007−2009.
(15) Carter, K. R. *Macromolecules* **2002**, *35*, 6757−6759.
(16) Klärner, G.; Lee, J.-I.; Lee, V. Y.; Chan, E.; Chen, J.-P.; Nelson, A.; Markiewicz, D.; Siemens, R.; Scott, J. C.; Miller, R. D. *Chem. Mater.* **1999**, *11*, 1800−1805.
(17) Marsitzky, D.; Murray, J.; Scott, J. C.; Carter, K. R. *Chem. Mater.* **2001**, *13*, 4285−4289.
(18) Bozano, L. D.; Carter, K. R.; Lee, V. Y.; Miller, R. D.; DiPietro, R.; Scott, J. C. *J. Appl. Phys.* **2003**, *94*, 3061−3068.
(19) Ma, L.; Pyo, S.; Ouyang, J.; Xu, Q.; Yang, Y. *Appl. Phys. Lett.* **2003**, *82*, 1419−1421.
(20) Ma, L.; Liu, J.; Pyo, S.; Xu, Q.; Yang, Y. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **2002**, *378*, 185.
(21) Bozano, L. D.; Kean, B. W.; Deline, V. R.; Salem, J. R.; Scott, J. C. *Appl. Phys. Lett.* **2004**, 607−609.
(22) Havelka-Rivard, P. A.; Nagai, K.; Freeman, B. D.; Sheares, V. V. *Macromolecules* **1999**, *32*, 6418−6424.
(23) Van Walree, C. A.; Roest, M. R.; Schuddeboom, W.; Jenneskens, L. W.; Verhoeven, J. W.; Warman, J. M.; Kooijman, H.; Spek, A. L. *J. Am. Chem. Soc*. **1996**, *118*, 8395−8407.
(24) Beinhoff, M.; Bozano, L. D.; Scott, J. C.; Carter, K. R. *Polym. Mater. Sci. Eng.* **2004**, *90*, 211.
(25) Ouyang, J.; Chu, C.-W.; Szmanda, C. R.; Ma, L.; Yang, Y. *Nat. Mater.* **2004**, *3*, 918−922.
(26) Percec, V. U.S. Patent No. 5,241,044, 1993.
(27) Liaw, D.-J.; Liaw, B.-Y. *Polymer* **1999**, *40*, 3183−3189.
(28) Jonsson, H.; Hedrick, J. L.; Labadie, J. W. *Polym. Prepr.* **1992**, *33*, 394−395.
(29) Inouye, M.; Miyake, T.; Furusyo, M.; Nakazumi, H. *J. Am. Chem. Soc.* **1995**, *117*, 12416−12425.
(30) Lau, K. S. Y.; Landis, W. J.; Kelleghan, W. J.; Beard, C. D. *J. Polym. Sci., Part A: Polym. Chem*. **1982**, *20*, 2381−2393.
(31) Sauvage, N.; Mercier, R.; Sillion, B. *Polym. Bull*. (*Berlin*) **1990**, *23*, 7−12.
(32) For general information about condensation reactions of phenol with carbonyl compounds, see: (a) Bode, K.-D. *Methods of Organic Chemistry*; Houben-Weyl: Thieme, 1976; Vol. 6/1c, pp 1021−1031. (b) Schnell, H.; Krimm, H. *Angew. Chem*. **1963**, *75*, 662−668.
(33) Similar conditions were first applied by Semmelhack et al. in molecular cross-coupling reactions (Semmelhack, M. F.; Helquist, P. M.; Jones, L. D. *J. Am. Chem. Soc.* **1971**, *93*, 5908−5910).
(34) Perreux, L.; Loupy, A. *Tetrahedron* **2001**, *57*, 9199−9223.
(35) Lidström, P.; Tierney, J.; Wathey, B.; Westeman, J. *Tetrahedron* **2001**, *57*, 9225−9283.
(36) However, GPC/PS is known to *over*estimate the M_n and M_w values and, hence, the DP of semirigid rod polymers such as PPPs and PFs by a factor of roughly 2.
(37) Hexafluorobenzene served as a reference, its signal set to −164.9 ppm.
(38) 4-Vinylbiphenyl (cyclohexane) exhibits a featureless absorption band at $\lambda_{max} = 274$ nm and a structured emission band at $\lambda_{max} = 318$ and 332 nm: Momicchiolli, F.; Bruni, M. C.; Baraldi, I. *J. Phys. Chem.* **1972**, *76*, 3983−3990.
(39) Ma, L. P.; Pyo, S.; Ouyang, J.; Xu, Q. F.; Yang, Y. *Appl. Phys. Lett.* **2003**, *82*, 1419−1421.
(40) Bozano, L. D.; Carter, K. R.; Kean, B. W.; Beinhoff, M.; Deline V. R.; Scott, J. C., manuscript in preparation.
(41) Chen, J. P.; Klaerner, G.; Lee, J. I.; Marsitzky, D.; Lee, V. Y.; Miller, R. D.; Scott, J. C. *Synth. Met.* **1999**, *107*, 129−135.
(42) The Einstein relationship, $E = hc/\lambda$, has been used to estimate the band gap from the measured absorption maximum.

MA049572K