Synthesis and Characterization of Soluble, High Molecular Weight Poly(aromatic diacetylenes)

Elizabeth W. Kwock, Teaster Baird, Jr., and Timothy M. Miller*

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

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ABSTRACT: New polymers containing aromatic diacetylenes designed to be more soluble and mechanically flexible and less thermally reactive while retaining the thermooxidative stability of earlier materials are described. Preparations of the new monomers 4,4′-diethynylbenzophenone and 4,4′-bis(3-ethynylphenoxy)-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl are described. Soluble copolymers can be prepared in quantitative yield by Glaser coupling, using several ratios of 1,3-diethynylbenzene and 4,4′-ethynylphenyl ether, and 4,4′-ethynylphenyl ether and 4,4′-bis(3-ethynylphenoxy)-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl. Of the polymers containing 4,4′-diethynylbenzophenone, only the one containing 3:1 1,3-diethynylbenzene:4,4′-diethynylbenzophenone is soluble in *o*-dichlorobenzene. The molecular weights of one series of polymers are changed by addition of varying quantities of monofunctional phenylacetylene. Size exclusion chromatography of the copolymers versus polystyrene standards yields M_n's and M_w/M_n's from 5000 to 46 700 and 2.51 to 4.84, respectively. The polymers cross-link thermally and give peak exotherm temperatures ranging from 228 to 285 °C, as measured by differential scanning calorimetry. They retain greater than 95% of their mass under N_2 up to 550 °C and form strong, coherent, optically transparent films in thicknesses of 1–20 μm.

Introduction

There is a scientific interest in and need for polymers having combinations of favorable properties such as high thermal stability and good solubility, good film forming properties and toughness, and high strength without crystallinity. In many cases these properties oppose each other and compromises have to be made. Diacetylene containing polymers were discovered initially in the early 1960s by Hay and co-workers but have not received nearly as much attention as other classes of aromatic polymers.[1,2] Hay's materials were difficult to dissolve and highly thermally reactive[1,3] They did, however, retain virtually all of their mass when pyrolyzed under N_2, and some materials were shown to cross-link on irradiation with UV light.[4] Many others have examined materials in which diacetylene moieties are joined by aliphatic spacers.[5–8] Recently, Stille and Whitesides made soluble diacetylene containing aromatic polymers by incorporating a solubilizing aliphatic side group on the thiophene nucleus.[9,10] Neenan and Callstrom have demonstrated that oligomers derived from aryldiacetylenes produce glassy carbon when pyrolyzed to 600 °C which constitutes a new low temperature synthetic route to glassy carbon.[11] This class of polymers has several interesting features that we thought worthy of exploration. Once monomers are prepared, synthesis of polymers is quite simple involving only O_2 and a catalytic amount of Cu(I). The only byproduct of polymerization is water and the yields are essentially quantitative. The polymerization mechanism should allow for simple production of random copolymers and probably block copolymers as well by simple substitution of aromatic nuclei. Finally, the polymers may be cross-linked thermally or photochemically without evolving volatile side products. We sought to explore whether solubilities and thermal reactivities of these materials can be modified by changing their aromatic backbone.

Here, we describe the syntheses of several aromatic diacetylenes and copolymers of these. Ratios of monomers required to impart solubility were found and molecular weights in one case varied systematically by varying the quantity of the endcap, phenylacetylene. The polymers were characterized by NMR spectroscopy, size exclusion chromatography, and thermal analysis.

Results and Discussion

Monomer Syntheses. Syntheses of monomers are shown in Schemes I and II. Aromatic acetylenes are most easily prepared using Pd/Cu-catalyzed coupling of (trimethylsilyl)acetylene to an aryl bromide or aryl iodide followed by removal of the trimethylsilyl protecting group.[12] The requisite dibromo derivatives of anthracene, benzene, benzophenone, and phenyl ether are commercially available, and reaction with (trimethylsilyl)acetylenes proceeds without difficulty. The crude products from these reaction mixtures were purified by passage through short columns of silica gel and recrystallization where necessary. Treatment with a catalytic quantity of KOH in MeOH removed the trimethylsilyl protecting group yielding the free diethynyl aromatics.

We planned to prepare monomer 4 from the parent dibromide or diiodide using the same chemistry. Both the dibromide and diiodide were made by reaction of the 3-halophenol with decafluorobiphenyl in the presence of K_2CO_3 in *N,N*-dimethylacetamide.[13] Treatment of either of these with trimethylsilylacetylene in diisopropylamine using Pd/Cu catalysis afforded a complex mixture of products which appeared to contain little if any of the diacetylene. We do not understand the course of this reaction. We prepared 4 in a lengthier route by reacting 2 mol of 3-ethynylphenol with decafluorobiphenyl. Reaction of tetrahydropyranyl-protected 3-iodophenol with (trimethylsilyl)acetylene followed by sequential removal of the trimethylsilyl and THP groups afforded 3-ethynylphenol (Scheme II).[14]

Monomers 1, 2, and 5 are known compounds whose spectral properties agreed with the literature values.[12,15–17] Monomers 3 and 4 were characterized by elemental analysis, NMR, and mass spectroscopies, which were consistent with their assigned structures.

Polymer Syntheses. The procedure of White was followed using CuCl, *N,N,N′,N′*-tetramethylethylenediamine, and pyridine at ca. 80 °C in *o*-dichlorobenzene at

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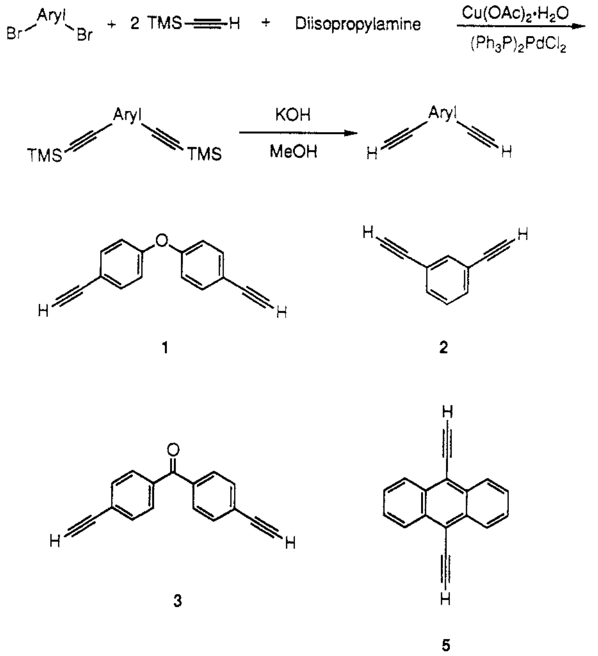
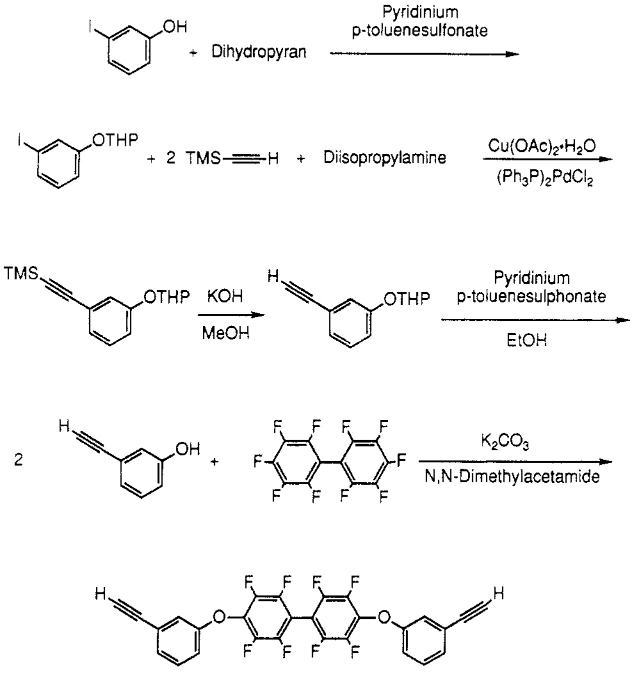
Scheme I



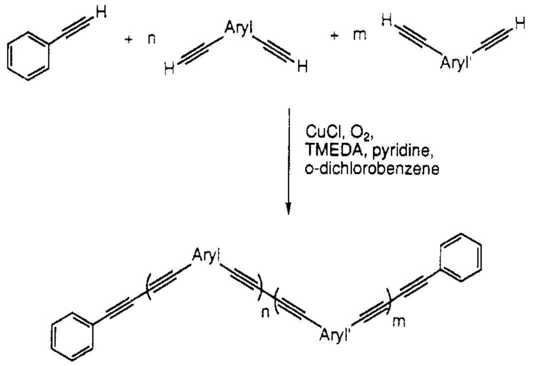
Scheme II



4

polymer concentrations of typically 6% (wt/vol) (Scheme III).[3] Phenylacetylene was used as an endcapping agent to limit molecular weights, thus preventing solutions from becoming too viscous. Reaction mixtures containing soluble polymers were generally diluted with *p*-dioxane and precipitated into methanol containing concentrated HCl. The polymers were isolated by filtration, washed with methanol, and dried. Yields were essentially quantitative (Table I). Reaction of monomers **1** and **2** in the ratios of 3:1, 1:1, and 1:3 afforded soluble polymers. Polymerization of **1** alone or **1** and **2** in the ratios of 10:1 and 1:10 afforded insoluble, presumably oligomeric, mixtures after 10–20 min. The amount of phenylacetylene in the polymer containing 3:1 **1**:**2** was varied from 0 to 10%. A soluble terpolymer containing **1**, **2**, and 1% of **5** was also prepared.

Scheme III



Reaction of **1** and **4** in the ratios of 3:1, 1:1, and 1:3 with 5% phenylacetylene also afforded soluble polymers. Reactions of **2** and **3** in the ratio of 1:1, 1:3, or 1:10 and **1** and **3** in the ratios of 1:3 or 3:1 yielded insoluble materials. Only reaction of **2** and **3** in the ratio of 3:1 afforded a soluble polymer. The insolubility of most copolymers containing **3** is somewhat surprising given the solubilities of copolymers containing **1**. *o*-Dichlorobenzene is probably a poor solvent for polymers containing the strong ketone dipole and possibly soluble high molecular weight materials could be made in other solvents.

The polymers are all white fibrous materials except for poly(**1**-*co*-**2**-*co*-**5**) which is yellow. They can be redissolved readily in a several solvents including THF, cyclohexanone, *p*-dioxane, and *N*-methylpyrrolidinone in the case of poly(**2**-*co*-**3**). The data in Table I show that in many cases more than 10% solutions can be prepared with heating and are stable to precipitation for greater than 1 h at room temperature. The copolymers containing **4** are more soluble than the others. The exceptions are those copolymers containing **1** or **3** which are not endcapped or only endcapped very lightly. These polymers swell considerably in hot solvents but do not form solutions. This solubility contrasts with the solubilities of copolymers of mainly *m*-diethynylbenzene and *p*-diethynylbenzene. Two percent solutions of these polymers in *o*-dichlorobenzene precipitate when cooled below 55 °C.[3] Elemental analyses of our materials are consistent with the proposed structures and demonstrate that the polymers have high chemical purity. The polymers form smooth, coherent, strong, and creasable films when cast from solution in thicknesses of 5–10 μm.

NMR Spectra of Polymers. ^{1}H NMR spectra of the polymers were recorded in dilute THF-d_8 solutions in most cases and compared to spectra of the monomers in the same solvent. The spectra, high yields, and elemental analyses demonstrate that the ratios of monomers in the polymer are the same as their feed ratios. We have not observed, by ^{1}H NMR spectroscopy, residual ethynyl protons due to unreacted acetylenes in any of our polymers. The ^{1}H NMR spectra of copolymers of **1** and **2** are particularly informative. The chemical shift of the proton ortho to both ethynyl groups on the 1,3-diethynylbenzene unit of the polymer is sensitive to the identity of the adjacent monomers. This proton resonates at 7.75, 7.72, and 7.69 ppm when surrounded by two diethynylbenzenes, a diethynylbenzene and a bis(ethynylphenyl) ether, and two bis(ethynylphenyl) ethers, respectively. These assignments were made by comparing spectra of **1** and **2** and of the poly(**1**-*co*-**2**) containing 3:1, 1:1, and 1:3 ratios of **1**:**2**. The integrals of the three resonances in the three spectra vary from 1:6:9 to 1:2:1 to 9:6:1, as expected for a random copolymerization. The acetylene region of the ^{13}C NMR spectra of the polymers also demonstrates that the terminal

Table I. Poly(aromatic diacetylenes)

									solubilities^d	
monomers	ratios	% phenylacetylene	yield (%)	M_w^{a}	M_n^{a}	M_w/M_n^{a}	T_{peak}^{b} (°C)	ΔH^{c} (J/g)	cyclohexanone	*N*-methylpyrrolidinone
1	1	0	precip							
1, 2	10:1	5	precip							
1, 2	3:1	0	99	155 500	46 700	3.33	243	290	O	O
1, 2	3:1	1	99	62 000	17 800	3.48	253	470	O	O
1, 2	3:1	5	98	33 600	13 400	2.51	258	390	++	++
1, 2	3:1	10	85	19 200	5 700	3.37	261	460	+	++
1, 2	1:1	5	77	37 600	8 300	4.53	246	527	++	++
1, 2	1:3	5	82	30 300	10 200	2.97	243	500	++	++
1, 2	1:3	0	81	110 000	44 400	2.49	231	550	O	O
1, 2	1:10	5	precip							
1, 2, 5	3:1:0.04	5	92	44 700	9 300	4.81	257	530	++	++
1, 3	3:1	5	precip							
1, 3	1:3	5	precip							
1, 4	3:1	5	92	28 000	6 000	4.80	277	330	++	++
1, 4	1:1	5	95	23 600	6 200	4.67	285	310	++	++
1, 4	1:3	5	95	24 000	5 000	4.80	272	300	++	++
1, 4	1:3	0	90	81 700	39 800	2.05	287	204	++	++
2, 3	3:1	0	82	111 900	52 400	2.13	229	535	O	O
2, 3	3:1	5	92	24 000	5 000	4.80	228	580	+	++
2, 3	1:1	5	precip							
2, 3	1:3	5	precip							
2, 3	1:10	5	precip							
3	1	5	precip							

[a] Size exclusion chromatography values versus polystyrene standards. [b] T_{peak} is the peak exotherm temperature in the differential scanning calorimetric trace. [c] ΔH is the heat evolved in the exotherm from differential scanning calorimetry. [d] O indicates that a 10% solution cannot be prepared, + indicates that a 10% solution can be prepared but the polymer precipitates at room temperature within 1 h, and ++ indicates that a 10% solution is stable at room temperature for greater than 1 h.

ethynyl groups are transformed into diethynyl moieties in the polymers. The ^{13}C resonances for terminal carbons disappear and are replaced by new resonances typical of diacetylenes. ^{19}F NMR spectra of copolymers of **1** and **4** are essentially unchanged from that of monomer **4**.

Size Exclusion Chromatography. Size exclusion chromatograms were measured using THF as the eluant and calibrated against polystyrene standards. The measured M_n's varied from 5000 to 46 700 (Table I). The M_n's and M_w's for the series of poly(**1**-*co*-**2**) decrease with increasing amounts of phenylacetylene, as expected. Many of the polymers prepared contained 5% phenylacetylene as a chain terminator (moles of phenylacetylene per mole of difunctional monomers) and should therefore contain on average only 40 repeat units which should give M_n's that range from 6000 to 18 000 depending on the repeat unit molecular weights. The measured M_n's do not correlate well with the molecular weights of the repeat units. The measured M_n's are both higher and lower than the calculated M_n's depending upon the particular polymer. We do not know whether these differences reflect changes in the degree of polymerization or differences in stiffness of polymer chains. The polydispersities range from 2.5 to 5 and do not seem to correlate with M_n.

Thermal Analysis. The polymers were analyzed by thermal gravimetric analysis under a N_2 atmosphere, and none lost more that 5% of its weight up to 550 °C. Despite their greater mechanical flexibility and solubilities which generally reduce thermal stability, they have thermal stabilities comparable to polymers consisting of only aromatic rings and diacetylenes.[1]

Differential scanning calorimetry of the polymers demonstrated that they all undergo an exothermic reaction whose peak temperature varies from 228 to 285 °C. This exotherm is presumably caused by reaction of the diacetylene moieties in the polymers. We have not observed a glass transition in any of the materials between 30 °C and the temperature of the exotherm or up to 375 °C. There is surprisingly little variation in the peak temperature of the exotherm. We expected that polymers having more **2** might have exotherms closer to that observed for polymers consisting of *p*-diethynylbenzene and **2**. Copolymers of **1** and **4** have slightly higher peak exotherms than the other materials, which appears reasonable, however, the low value for poly(**2**-*co*-**3**) is not easily interpreted. We suspect that the exothermic reaction in these materials does not take place until the polymer chains begin to have some mobility which usually manifests itself as a glass transition but here is obscured by the heat evolved in the cross-linking reaction.

Conclusions

The polymers described have significantly greater solubility and undergo thermal cross-linking at significantly higher temperatures than the previously known materials in this class. In several instances, they form transparent, coherent, strong films. These properties may give these polymers utility in microelectronic fabrication which we are presently exploring as well as determination of their physical properties.

Experimental Section

General Information. All reagents and solvents unless otherwise specified were obtained from Aldrich Chemical and were used without further purification. *o*-Dichlorobenzene, *p*-dioxane, and tetrahydrofuran were Aldrich HPLC grade. Melting points were obtained on a Mel Temp melting point apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 360 spectrometer at 360.1 and 90.5 MHz, respectively, and referenced to TMS. ^{19}F NMR spectra were recorded at 338.8 MHz and referenced to C_6F_6. Analytical TLCs were run on commercial Merck plates coated with silica gel GF254 (0.25 mm thick). Polymerizations were followed using a Beckman solvent delivery system (1 mL/min), a 1000-Å μ-Spherogel column, and an adjustable wavelength UV/vis detector operated at 254 nm using *p*-dioxane (Aldrich, HPLC grade) as the eluant. Analytical size exclusion chromatography data were obtained using a Waters HPLC with 100-, 500-, 10^3, and 10^4-Å Ultrastyragel columns in series at 30 °C using THF as eluant. Elemental analyses were obtained from Robertson-Microlit, Madison NJ. Thermal gravimetric analyses were carried out under nitrogen in a Perkin-Elmer TGA-7 using a heating rate of 10 °C/min. The calorimetric data were obtained on a Perkin-Elmer DSC-7 at a scanning rate of 15 °C/min under a flow (20 cm^3/min) of nitrogen. The temperature scale was calibrated using the melting points of indium and zinc and is accurate to ±0.1 °C. Samples typically weighed 4–9 mg, and aluminum containers were used.

1,3-Bis((trimethylsilyl)ethynyl)benzene was obtained from Farchan Laboratories and purified by flushing through a short column of silica gel with hexanes followed by recrystallization from MeOH; mp 60–62 (lit. mp 57–59 °C[12]). Treatment of 1,3-bis((trimethylethylsilyl)ethynyl)benzene with methanolic KOH afforded 1,3-diethynylbenzene, **2**. Monomer **2** was purified by flushing through a short column of silica gel with *n*-hexanes affording an essentially colorless oil. 9,10-Diethynylanthracene, **5**, was prepared according to a literature procedure.[17]

4,4′-Bis((Trimethylsilyl)ethynyl)diphenyl Ether. Procedure A. A 1-L, four-neck round-bottomed flask equipped with an overhead stirrer, water-cooled condenser, addition funnel, and Ar inlet was charged with bis(4-bromophenyl) ether (28.25 g, 86.13 mmol), bis(triphenylphosphine)palladium dichloride (1.442 g, 2.054 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.404 g, 2.02 mmol), and diisopropylamine (300 mL). The vessel was sealed and purged with Ar. (Trimethylsilyl)acetylene (25 g, 250 mmol) was added via addition funnel over 10 min, and the originally green solution turned brown. The reaction flask was heated to 65 °C with a heating mantle beginning 45 min after the addition was complete. The reaction was monitored by thin layer chromatography (TLC) using 9:1 hexanes:CH_2Cl_2 and was complete in 24 h. The reaction mixture was filtered through Celite, and the salts were washed with copious amounts of CH_2Cl_2. The volatiles were removed under reduced pressure, yielding a black oil which solidified overnight under vacuum. The black solid was dissolved with the minimum quantity of hexanes and flushed through silica gel with hexanes, yielding a colorless solid. The recovered compound was recrystallized from hot MeOH, yielding white crystals (27.22 g, 87%), mp 103–106 °C. ^{1}H NMR ($CDCl_3$): δ 7.44 (d, J = 9.3 Hz, 4 H), (d, J = 9.3 Hz, 4 H), 0.245 (s, 18 H).

4,4′-Diethynyldiphenyl Ether, 1. Procedure B. A 500-mL round-bottomed flask equipped with a magnetic stir bar was charged with 4,4′-bis((trimethylsilyl)ethynyl)diphenyl ether (25.0 g, 68.9 mmol), THF (100 mL), and MeOH (200 mL). Potassium hydroxide (0.486 g, 8.66 mmol) was dissolved in 5 mL of water and then added to the stirred solution. TLC of the reaction mixture after 30 min indicated that the reaction was complete. The volatiles were removed under reduced pressure. The resulting solid was dissolved in diethyl ether (300 mL) extracted with distilled water (2 × 250 mL), washed with brine, dried over $MgSO_4$, and filtered. The ether was removed under reduced pressure. The yellow powder was sublimed (82 °C, 0.1 mmHg), yielding a yellow crystalline solid (14.5 g, 93%), mp 79.4–81.2 °C, lit. 74.5–75 °C.[16] ^{1}H NMR (THF-d_8): δ 7.45 (d, J = 8.6 Hz, 4 H), 6.97 (d, J = 8.6 Hz, 4 H), 3.49 (s, 2 H). ^{13}C NMR (THF-d_8): δ 158.01, 134.56, 118.79, 117.90, 83.58, 75.37.

2-(3-Iodophenoxy)tetrahydro-2*H*-pyran. A 1-L round-bottomed flask equipped with a magnetic stir bar was charged with iodophenol (17.56 g, 79.81 mmol), pyridinium *p*-toluenesulfonate (PPTS) (2.54 g, 10.7 mmol), and 250 mL of anhydrous CH_2Cl_2. A solution of dihydropyran (8.52 g, 101 mmol) in CH_2Cl_2 (50 mL) was added to the iodophenol solution which was allowed to stir overnight. The reaction was monitored by TLC. More dihydropyran (1.698 g, 20.19 mmol) was added, and the mixture was allowed to stir. The reaction mixture was extracted with distilled H_2O and 1 M NaOH, washed with brine, dried over $MgSO_4$, and filtered, and the volatiles were removed under reduced pressure, yielding a yellow orange solid. Recrystallization from 200 mL of hot hexanes gave crystals (16.45 g, 68%), mp 62–64 °C. ^{1}H NMR ($CDCl_3$): δ 6.45–6.90 (m, 4 H), 5.46 (t, J = 3.1 Hz, 1 H), 3.85 (m, 1 H), 3.60 (m, 1 H), 1.50–2.10 (m, 6 H).

2-(3-((Trimethylsilyl)ethynyl)phenoxy)tetrahydro-2*H*-pyran. Procedure A was followed using 15.21 g (50.01 mmol) of 2-(3-iodophenoxy)tetrahydro-2*H*-pyran, 0.704 g (1.00 mmol) of bis(triphenylphosphine)palladium dichloride, 0.055 g (0.56 mmol) of copper(I) chloride, 10.0 mL (70.6 mmol) of (trimethylsilyl)acetylene, and 475 mL of diisopropylamine at room temperature. The reaction was monitored by TLC and appeared to be complete after 75 min. The crude product was flushed through silica gel using *n*-hexanes, yielding a colorless oil weighing 9.96 g (73%). ^{1}H NMR ($CDCl_3$): δ 6.96–7.20 (m, 4 H), 5.40 (t, J = 3.1 Hz, 1 H), 3.85 (m, 1 H), 3.60 (m, 1 H), 1.50–2.00 (m, 6 H), 0.22 (s, 9 H).

2-(3-Ethynylphenoxy)tetrahydro-2*H*-pyran. Procedure B was followed using 9.9 g (36 mmol) of 2-(3-((trimethylsilyl)ethynyl)phenoxy)tetrahydro-2*H*-pyran, 0.42 g (7.4 mmol) of potassium hydroxide in 7 mL of H_2O, and ca. 300 mL of MeOH. The solvent was removed under reduced pressure and the resulting solid dissolved in CH_2Cl_2. The organic layer was extracted with distilled H_2O and brine, then dried over $MgSO_4$, and filtered. The solvents were removed under reduced pressure, yielding an orange solid (4.9 g, 67%). ^{1}H NMR ($CDCl_3$): δ 7.00–7.23 (m, 4 H), 5.40 (t, J = 3.2 Hz, 1 H), 3.88 (m, 1 H), 3.60 (m, 1 H), 1.55–2.05 (m, 6 H).

3-Ethynylphenol. A 500-mL round-bottomed flask equipped with a magnetic stir bar was charged with 2-(3-ethynylphenoxy)-tetrahydro-2*H*-pyran (4.88 g, 24.1 mmol), PPTS (0.607 g, 2.56 mmol), and 80 mL of EtOH. The solution was heated and stirred at 65 °C for 1 h. The volatiles were removed in vacuo, and the residue was dissolved in ether which was extracted with H_2O, followed by 1 N NaOH. The resulting aqueous basic solution was acidified with concentrated HCl and extracted with ether. The ethereal solution was washed with brine, dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude oil was purified using Kugelrohr distillation (80 °C, 3 mmHg), yielding a clear yellow oil (1.95 g, 68%). ^{1}H NMR ($CDCl_3$): δ 7.17–7.23 (m, 1 H), 7.06–7.10 (m, 1 H), 6.95–6.97 (m, 1 H), 6.82–6.86 (m, 1 H), 5.05 (bs, 1 H), 3.06 (s, 1 H).

4,4-Bis(3-ethynylphenoxy)-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl, 4. A 50-mL Schlenk flask equipped with an Ar inlet and septum, was charged with 3-ethynylphenol (1.507 g, 12.76 mmol), decafluorobiphenyl (1.812 g, 5.42 mmol) and potassium carbonate (1.789 g, 12.94 mmol). The Schlenk flask was evacuated and filled with Ar twice. Anhydrous *N,N*-dimethylacetamide (25 mL) was added via cannula and the flask heated in an oil bath to 55 °C. The reaction was monitored by TLC and judged complete after 6.5 h. The volatiles were removed via vacuum transfer, and the remaining solid was dissolved in CH_2Cl_2 and distilled H_2O. The organic layer was extracted twice with distilled water, washed with brine, dried over $MgSO_4$, and filtered, and the volatiles were removed under reduced pressure. The crude product was recrystallized from 15 mL of hot EtOH, yielding **4** (1.86 g, 65%), mp 91–95 °C. Anal. Calcd for $C_{28}H_{10}O_2F_8$: C, 63.42; H, 1.90; F, 28.65. Found: C, 63.26; H, 1.89; F, 28.70. ^{1}H NMR (THF-d_8): δ 7.37 (t, J = 8 Hz, 2 H), 7.29 (s, 2 H), 7.26 (m, 2 H), 7.12 (d, J = 8 Hz, 2 H), 3.66 (s, 2 H). ^{13}C NMR (THF-d_8): δ 157.80, 146.0 (d, J_{CF} = 264 Hz), 143.25 (d, J_{CF} = 271 Hz), 136.96 (t, $^2J_{CF}$ = 12.3 Hz), 130.97, 128.79, 128.34, 119.81, 117.30, 103.66, 83.45, 80.10. ^{19}F NMR ($CDCl_3$): δ −138.7 (d, ^3J = 15 Hz, 4 F), −153.9 (d, ^3J = 15 Hz, 4 F). Mass spectrum (*m/e*): 530 (M^+), 483, 265, 237, 101, 75.

4,4′-Bis((trimethylsilyl)ethynyl)benzophenone. Procedure A was followed using 30.03 g (88.32 mmol) of dibromobenzophenone, 0.322 g (1.61 mmol) of $Cu(OAc)_2 \cdot H_2O$, 1.241 g (1.768 mmol) of bis(triphenylphosphine)palladium dichloride, 26 mL (184 mmol) of (trimethylsilyl)acetylene, and 300 mL of diisopropylamine at 80 °C overnight. The crude material obtained after filtration of the salts was flushed through silica gel (100 g) with 1:1 hexanes:CH_2Cl_2. The resulting yellow solid (52 g) was recrystallized from hot hexanes (400 mL), yielding faintly yellow crystals (19.35 g, 58%), mp 173–175 °C. ^{1}H NMR ($CDCl_3$): δ 7.72 (d, J = 8 Hz, 4 H), 7.55 (d, J = 8 Hz, 4 H), 0.23 (s, 18 H).

4,4′-Diethynylbenzophenone, 3. Procedure B was followed using 3.03 g (8.09 mmol) of 4,4′-bis((trimethylsilyl)ethynyl)-benzophenone, 1.188 g (21.18 mmol) of potassium hydroxide, 30 mL of THF, and 20 mL of MeOH. The volatiles were removed under reduced pressure, and the resulting solid was dissolved in CH_2Cl_2. The organic layer was extracted with distilled water and brine and then dried over $MgSO_4$. The solvent was removed under reduced pressure, and the resulting yellow solid was dried under vacuum. Recrystallization of the solid in EtOH resulted in faintly yellow flakes (1.35 g, 73%), mp 165–167 °C. Anal. Calcd for $C_{17}H_{10}O$: C, 88.67; H, 4.38; O, 6.95. Found: C, 88.31; H, 4.14; O, 7.20. ^{1}H NMR (*o*-dichlorobenzene-d_4): δ 7.65 (d, J

= 8.1 Hz, 4 H), 7.45 (d, *J* = 8.1 Hz, 4 H), 3.21 (s, 2 H). ^{13}C NMR (THF-d_8): δ 194.44, 138.04, 132.67, 130.57, 127.44, 83.44, 81.98. Mass spectrum (*m*/*e*): 230 (M$^+$), 202, 129, 101, 75.

Polymerization Procedure C: 3:1 Poly(1-*co*-2), 5% Endcapped. A 100-mL round-bottomed flask was charged with CuCl (0.084 g, 0.85 mmol), tetramethylethylenediamine (TMEDA) (0.102 g, 0.874 mmol), 1.4 mL of pyridine, and 40 mL of anhydrous *o*-dichlorobenzene (ODCB). Oxygen was bubbled through the catalyst mixture, and it was heated to 75 °C. Monomers **1** (2.630 g, 12.050 mmol), **2** (0.514 g, 4.07 mmol), and phenylacetylene (0.083 g, 0.813 mmol) were dissolved in 16 mL of ODCB and added to the stirred catalyst mixture. The reaction was followed by size exclusion chromatography (SEC). When polymerization seemed to be complete as determined by SEC, the green viscous solution was diluted with *p*-dioxane and precipitated into 600 mL of acidic methanol (2 mL of concentrated HCl/100 mL of MeOH). The fibrous off-white solid was filtered, washed with MeOH, and dried by pulling air through it (3.13 g, 98%). Anal. Calcd for $C_{19.87}H_{9.67}O$: C, 90.26; H, 3.96; O, 6.05. Found: C, 89.99; H, 3.52; O, 6.08. ^{1}H NMR (THF-d_8): δ 7.75 (s, 1 H), 7.72 (s, 6 H), 7.69 (s, 9 H), 7.52–7.63 (m, 230 H), 7.35–7.45 (m, 26 H), 7.05 (d, *J* = 8.7 Hz, 192 H). ^{13}C NMR (THF-d_8): δ 158.71, 158.64, 158.50, 158.40, 135.36, 135.21, 133.94, 133.18, 131.45, 130.01, 129.41, 129.01, 123.45, 123.40, 123.10, 120.13, 120.05, 118.03, 117.95, 117.68, 117.60, 82.31, 81.55, 81.36, 80.66, 80.61, 75.41, 75.00, 74.40, 74.25, 73.87.

3:1 Poly(1-*co*-2), 0% Endcapped. Procedure C was followed using 0.017 g (0.17 mmol) of CuCl, 0.024 g (0.21 mmol) of TMEDA, 0.35 mL of pyridine, 0.674 g (3.09 mmol) of **1**, 0.130 g (1.03 mmol) of **2**, and 14 mL of ODCB, yielding 0.787 g (99%) of polymer. Anal. Calcd for $C_{19.33}H_{9.33}O$: C, 90.14; H, 3.65; O, 6.21. Found: C, 89.19; H, 3.42; O, 6.95. ^{1}H NMR (THF-d_8): δ 7.74 (s, 1 H), 7.72 (s, 6 H), 7.69 (s, 9 H), 7.52–7.60 (m, 224 H), 7.37–7.45 (m, 16 H), 7.05 (d, *J* = 8.6 Hz, 192 H). ^{13}C NMR (THF-d_8): δ 158.69, 158.61, 158.45, 158.37, 136.64, 135.34, 135.21, 133.93, 131.46, 130.01, 129.03, 123.38, 123.05, 120.10, 120.05, 117.97, 117.93, 117.63, 117.55, 82.31, 81.55, 81.37, 80.66, 75.46, 75.41, 74.98, 74.24, 73.87.

3:1 Poly(1-*co*-2), 1% Endcapped. Procedure C was followed using 0.018 g (0.18 mmol) of CuCl, 0.022 g (0.19 mmol) of TMEDA, 0.35 mL of pyridine, 0.697 g (3.19 mmol) of **1**, 0.134 g (1.06 mmol) of **2**, 5 μL (0.5 mmol) of phenylacetylene, and 14 mL of ODCB, yielding 0.787 g (99%) of polymer. Anal. Calcd for $C_{19.44}H_{9.40}O$: C, 90.16; H, 3.66; O, 6.18. Found: C, 89.54; H, 3.14; O, 6.82. ^{1}H NMR (THF-d_8): δ 7.75 (s, 1 H), 7.72 (s, 6 H), 7.70 (s, 9 H), 7.53–7.60 (m, 225 H), 7.38–7.45 (m, 18 H), 7.05 (d, *J* = 8.6 Hz, 192 H). ^{13}C NMR (THF-d_8): δ 158.69, 158.60, 158.45, 158.37, 136.71, 136.61, 135.34, 135.21, 134.94, 134.13, 133.92, 133.18, 133.08, 131.44, 129.99, 129.01, 123.37, 123.07, 120.10, 120.02, 118.00, 117.93, 117.64, 117.57, 82.31, 81.55, 81.37, 80.67, 75.41, 75.00, 74.25, 73.88.

3:1 Poly(1-*co*-2), 10% Endcapped. Procedure C was followed using 0.022 g (0.22 mmol) of CuCl, 0.027 g (0.23 mmol) of TMEDA, 0.35 mL of pyridine, 0.655 g (3.00 mmol) of **1**, 0.129 g (1.02 mmol) of **2**, 0.042 g (0.41 mmol) of phenylacetylene, and 13 mL of ODCB, yielding 0.787 g (99%) of polymer. Anal. Calcd for $C_{20.40}H_{10.0}O$: C, 90.38; H, 3.72; O, 5.90. Found: C, 90.11; H, 3.57; O, 5.67. ^{1}H NMR (THF-d_8): δ 7.75 (s, 1 H), 7.72 (s, 6 H), 7.70 (s, 9 H), 7.51–7.60 (m, 237 H), 7.35–7.45 (m, 35 H), 7.05 (d, *J* = 8.6 Hz, 192 H). ^{13}C NMR (THF-d_8): δ 158.69, 158.45, 158.37, 136.73, 136.61, 135.34, 135.20, 134.14, 133.93, 133.29, 133.19, 130.16, 129.98, 129.42, 123.37, 123.08, 122.61, 120.10, 120.03, 118.01, 117.92, 117.57, 82.31, 81.55, 81.37, 80.67, 80.61, 75.41, 74.30, 74.25, 73.87.

1:1 Poly(1-*co*-2), 5% Endcapped. Procedure C was followed using 0.022 g (0.22 mmol) of CuCl, 30 μL (0.20 mmol) of TMEDA, 0.35 mL of pyridine, 0.455 g (2.09 mmol) of **1**, 0.267 g (2.12 mmol) of **2**, 22 μL (0.20 mmol) of phenylacetylene, and 12 mL of ODCB, yielding 0.550 g (77%) of polymer. Anal. Calcd for $C_{20.40}H_{10.0}O$: C, 90.38; H, 3.72; O, 5.90. Found: C, 90.11; H, 3.57; O, 5.67. ^{1}H NMR (THF-d_8): δ 7.75 (s, 1 H), 7.72 (s, 2 H), 7.70 (s, 1 H), 7.53–7.63 (m, 25 H), 7.35–7.45 (m, 5 H), 7.05 (d, *J* = 8.6 Hz, 16 H). ^{13}C NMR (THF-d_8): δ 158.72, 158.63, 158.50, 136.75, 135.37, 135.23, 134.26, 134.18, 134.05, 133.96, 130.07, 129.46, 129.03, 123.40, 123.13, 120.12, 120.03, 118.03, 117.95, 117.67, 117.58, 82.32, 81.54, 81.36, 80.67, 80.61, 75.46, 75.41, 75.03, 74.98, 74.25, 73.87.

1:3 Poly(1-*co*-2), 5% Endcapped. Procedure C was followed using 0.022 g (0.22 mmol) of CuCl, 35 μL (0.23 mmol) of TMEDA, 0.35 mL of pyridine, 0.221 g (1.01 mmol) of **1**, 0.384 g (3.04 mmol) of **2**, 22 μL (0.20 mmol) of phenylacetylene, and 12 mL of ODCB, yielding 0.490 g (82%) of polymer. Anal. Calcd for $C_{47.60}H_{5.00}O$: C, 93.90; H, 3.48; O, 2.63. Found: C, 93.57; H, 3.24; O, 2.99. ^{1}H NMR (THF-d_8): δ 7.73 (s, 9 H), 7.72 (s, 6 H), 7.69 (s, 1 H), 7.54–7.63 (m, 34 H), 7.34–7.45 (m, 19 H), 7.06 (d, *J* = 8.6 Hz, 21 H). ^{13}C NMR (THF-d_8): δ 158.71, 158.63, 136.88, 136.82, 136.71, 136.58, 135.37, 135.23, 134.26, 134.18, 134.04, 133.94, 130.05, 129.47, 123.45, 123.13, 120.11, 120.03, 118.03, 117.65, 82.35, 81.55, 81.42, 81.33, 80.61, 75.49, 75.05, 74.97, 74.27, 73.90.

1:3 Poly(1-*co*-2), 0% Endcapped. Procedure C was followed using 0.023 g (0.23 mmol) of CuCl, 35 μL 0.23 mmol) of TMEDA, 0.35 mL of pyridine, 0.228 g (1.05 mmol) of **1**, 0.394 g (3.12 mmol) of **2**, and 12 mL of ODCB, yielding 0.498 g (81%) of polymer. Anal. Calcd for $C_{47.60}H_{5.00}O$: C, 93.84; H, 3.43; O, 2.72. Found: C, 93.64; H, 3.19; O, 3.33. ^{1}H NMR (THF-d_8): δ 7.74 (s. 9 H), 7.71 (s, 6 H), 7.69 (s, 1 H), 7.52–7.62 (m, 53 H), 7.38–7.46 (m, 16 H), 7.05 (d, *J* = 8 Hz, 21 H). ^{13}C NMR (THF-d_8): δ 158.59, 158.37, 136.80, 135.34, 135.21, 134.23, 130.03, 123.45, 123.39, 123.10, 120.09, 120.00, 118.00, 117.63, 82.34, 81.39, 81.34, 80.61, 75.48, 75.05, 74.97, 74.27, 73.90.

Poly(1-*co*-2-*co*-5), 5% Endcapped. Procedure C was followed using 0.022 g (0.22 mmol) of CuCl, 0.042 g (0.36 mmol) of TMEDA, 0.399 g of pyridine, 0.892 g (4.09 mmol) of **1**, 0.190 g (1.51 mmol) of **2**, 0.011 g (0.049 mmol) of **5**, 0.030 g (0.29 mmol) of phenylacetylene, and 14 mL of ODCB, yielding 1.01 g (91%) of polymer. Anal. Calcd for $C_{20.10}H_{9.77}O$: C, 90.33; H, 3.69; O, 5.98. Found: C, 90.11; H, 3.57; O, 5.67. ^{1}H NMR (THF-d_8): δ 8.59 (q, *J* = 3.1 Hz, 2.56 H), 7.75 (s, 1 H), 7.72 (s, 6 H), 7.69 (s, 9 H), 7.52–7.63 (m, 233 H), 7.35–7.45 (m, 26 H), 7.05 (d, *J* = 8.7 Hz, 192 H). ^{13}C NMR (THF-d_8): δ 158.72, 158.63, 158.50, 136.59, 135.37, 134.18, 133.96, 130.03, 123.40, 120.13, 120.08, 117.95, 82.33, 81.55, 80.67, 75.41, 74.25, 73.87.

3:1 Poly(1-*co*-4), 5% Endcapped. Procedure C was followed using 0.015 g (0.15 mmol) of CuCl, 25 μL (0.17 mmol) of TMEDA, 0.10 mL of pyridine, 0.272 g (1.25 mmol) of **1**, 0.214 g (0.403 mmol) of **4**, 18 μL (0.16 mmol) of phenylacetylene, and 12 mL of ODCB, yielding 0.458 g (92%) of polymer. Anal. Calcd for $C_{15.52}H_{6.60}OF_{1.90}$: C, 77.85; H, 2.78; O, 6.68; F, 12.69. Found: C, 77.15; H, 3.10; F, 12.63. ^{1}H NMR (THF-d_8): δ 7.56 (d, *J* = 8.6 Hz, 30 H), 7.50–7.53 (m, 1 H), 7.42 (t, *J* = 7.9 Hz, 5 H), 7.33–7.39 (m, 11 H), 7.22–7.30 (m, 5 H), 7.05 (d, *J* = 8.6 Hz, 30 H). ^{13}C NMR (THF-d_8): δ 158.72, 158.50. 158.39, 157.88, 147.42, 144.37, 141.44, 135.34, 135.23, 133.20, 131.29, 130.19, 129.46, 129.25, 129.14, 124.45, 120.10, 120.06, 119.95, 118.22, 118.03, 117.95, 117.58, 82.37, 81.63, 81.55, 80.91, 75.38, 74.90, 74.25, 73.82. ^{19}F NMR: δ −138.06, −153.13.

1:1 Poly(1-*co*-4), 5% Endcapped. Procedure C was followed using 0.016 g (0.16 mmol) of CuCl, 25 μL (0.17 mmol) of TMEDA, 0.10 mL of pyridine, 0.147 g (0.674 mmol) of **1**, 0.354 g (0.668 mmol) of **4**, 18 μL (0.16 mmol) of phenylacetylene, and 12 mL of ODCB, yielding 0.481 g (95%) of polymer. Anal. Calcd for $C_{14.93}H_{5.50}OF_{2.67}$: C, 71.30; H, 2.20; F, 20.14. Found: C, 71.21; H, 1.80; F, 19.77. ^{1}H NMR (THF-d_8): δ 7.56 (d, *J* = 8.6 Hz, 20 H), 7.50–7.53 (m, 1 H), 7.42 (t, *J* = 7.9 Hz, 10 H), 7.33–7.39 (m, 22 H), 7.22–7.30 (m, 10 H), 7.05 (d, *J* = 8.6 Hz, 20 H). ^{13}C NMR (THF-d_8): δ 158.61, 158.30, 157.88, 147.28, 144.45, 141.51, 135.80, 135.30, 135.20, 133.16, 131.38, 131.26, 130.49, 129.47, 129.19, 124.45, 124.13, 120.11, 120.06, 119.95, 118.35, 118.25, 118.17, 118.03, 117.57, 82.34, 81.63, 80.89, 75.38, 74.90, 74.03, 73.81. ^{19}F NMR: δ −138.07, −153.17.

1:3 Poly(1-*co*-4), 5% Endcapped. Procedure C was followed using 0.017 g (0.17 mmol) of CuCl, 35 μL (0.19 mmol) of TMEDA, 0.10 mL of pyridine, 0.061 g (0.279 mmol) of **1**, 0.442 g (0.833 mmol) of **2**, 18 μL (0.16 mmol) of phenylacetylene, and 12 mL of ODCB, yielding 0.489 g (95%) of polymer. Anal. Calcd for $C_{14.51}H_{4.71}OF_{3.43}$: C, 67.01; H, 1.83; F, 25.02. Found: C, 67.17; H, 1.56; F, 24.20. ^{1}H NMR (THF-d_8): δ 7.56 (d, *J* = 8.6 Hz, 10 H), 7.50–7.53 (m, 1 H), 7.42 (t, *J* = 7.9 Hz, 15 H), 7.33–7.39 (m, 32 H), 7.22–7.29 (m, 15 H), 7.05 (d, *J* = 8.6 Hz, 10 H). ^{13}C NMR (THF-d_8): δ 158.71, 158.63, 158.33, 157.88, 147.33, 144.20, 141.48, 135.96, 135.82, 135.68, 135.32, 138.21, 133.26, 133.18, 133.10, 131.46, 130.41, 130.16, 129.41, 129.25, 129.15, 129.00, 124.47, 124.12, 122.32, 120.11, 120.06, 119.98, 118.56, 118.24, 118.17, 118.03, 117.66, 117.57, 82.34, 81.63, 80.89, 75.38, 74.90, 74.03, 73.81. ^{19}F NMR (THF-d_8): δ −138.06, −153.19.

1:3 Poly(1-*co*-4), 0% Endcapped. Procedure C was followed using 0.008 g (0.08 mmol) of CuCl, 9 μL (0.06 mmol) of TMEDA, 0.05 mL of pyridine, 0.071 g (0.33 mmol) of 1, 0.502 g (0.947 mmol) of 4, and 8 mL of ODCB, yielding 0.516 g (90%) of polymer. Anal. Calcd for $C_{14.51}H_{4.71}OF_{3.43}$: C, 66.76; H, 1.80; F, 25.22. Found: C, 66.27; H, 1.32; F, 25.47. ^{1}H NMR (THF-d_8): δ 7.56 (d, J = 8 Hz, 2 H), 7.42 (t, J = 8 Hz, 3 H), 7.33–39 (m, 6 H), 7.22–7.29 (m, 3 H), 7.05 (d, J = 8.6 Hz, 2 H). ^{13}C NMR (THF-d_8): 158.71, 158.63, 157.88, 147.41, 144.62, 144.35, 144.21, 141.57, 141.41, 135.94, 135.80, 135.34, 131.33, 129.25, 129.15, 124.45, 124.13, 120.11, 119.97, 118.37, 118.19, 117.63, 82.36, 81.64, 80.91, 75.38, 74.90, 74.27, 73.82.

3:1 Poly(2-*co*-3), 5% Endcapped. Procedure C was followed using 0.040 g (0.40 mmol) of CuCl, 0.078 g (0.67 mmol) of TMEDA, 0.735 g of pyridine, 0.947 g (7.51 mmol) of 2, 0.578 g (2.51 mmol) of 3, 0.056 g (0.55 mmol) of phenylacetylene, and 40 mL of ODCB, yielding 1.43 g (92%) of polymer. Anal. Calcd for $C_{48.60}H_{21.00}O$: C, 94.01; H, 3.41; O, 2.58. Found: C, 93.20; H, 3.00; O, 3.07. ^{1}H NMR (*o*-dichlorobenzene-d_4): δ 7.66–7.74 (m, 1 H), 7.50–7.64 (m, 2 H), 7.35–7.45 (m, 2 H), 7.10–7.20 (m, 1 H). ^{13}C NMR (*o*-dichlorobenzene-d_4): 193.25, 137.41, 136.26, 133.26, 133.15, 129.90, 129.47, 128.79, 128.52, 127.69, 125.96, 122.48, 122.43, 122.32, 82.01, 81.48, 81.07, 77.29, 75.46, 75.40, 75.33.

3:1 Poly(2-*co*-3), 0% Endcapped. Procedure C was followed using 0.020 g (0.20 mmol) of CuCl, 30 μL (0.20 mmol) of TMEDA, 0.35 mL of pyridine, 0.386 g (3.06 mmol) of 2, 0.231 g (1.00 mmol) of 3, and 20 mL of ODCB, yielding 0.499 g (82%) of polymer. Anal. Calcd for $C_{48.60}H_{21.00}O$: C, 93.98; H, 3.36; O, 2.66. Found: C, 93.20; H, 3.13; O, 3.29. ^{1}H NMR (*o*-dichlorobenzene-d_4): δ 7.66–7.74 (m, 1 H), 7.50–7.64 (m, 2 H), 7.35–7.45 (m, 2 H), 7.10–7.20 (m, 1 H). ^{13}C NMR (*o*-dichlorobenzene-d_4): 193.23, 137.60, 137.50, 136.29, 133.15, 132.19, 130.45, 129.88, 128.80, 127.92, 127.69, 127.57, 126.00, 125.88, 122.55, 122.51, 122.40, 82.09, 81.56, 81.15, 77.32, 75.51, 75.46, 75.38.

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References and Notes

(1) Hay, A. S. *J. Org. Chem.* **1960**, *25*, 1275. Newkirk, A. E.; Hay, A. S.; McDonald, R. S. *J. Polym. Sci., Polym. Chem. Ed.* **1964**, *2*, 2217. Hay, A. S. U.S. Pat. 3,300,456, 1967.

(2) Neenan, T. X.; Callstrom, M. R.; Scarmoutzos, L. M.; Stewart, K. R.; Whitesides, G. M.; Howes, V. R. *Macromolecules* **1988**, *21*, 3528.

(3) White, D. M. *Poly. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1971**, *12* (1), 155.

(4) Hay, A. S.; Bolon, D. A.; Leimer, K. R.; Clark, R. F. *Polym. Lett.* **1970**, *8*, 97.

(5) Stanford, J. L.; Young, R. J.; Day, R. J. *Polymer* **1991**, *32*, 1713.

(6) Nallicheri, R. A.; Rubner, M. F. *Macromolecules* **1991**, *24*, 517.

(7) Wegner, G. *Makromol. Chem.* **1970**, *134*, 219.

(8) Liang, R.-C.; Reiser, A. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 451.

(9) Callstrom, M. R.; Neenan, T. X.; Whitesides, G. M. *Macromolecules* **1988**, *21*, 3530.

(10) Rutherford, D. R.; Stille, J. K. *Macromolecules* **1988**, *21*, 3532. Rutherford, D. R.; Stille, J. K.; Elliott, C. M.; Reichert, V. R. *Macromolecules* **1992**, *25*, 2294.

(11) Pocard, N. L.; Alsmeyer, D. C.; McCreery, R. L.; Neenan, T. X.; Callstrom, M. R. *J. Mater. Chem.* **1992**, *2*, 771. Callstrom, M. R.; Neenan, T. X.; McCreery, R. L.; Alsmeyer, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 4954.

(12) Neenan, T. X.; Whitesides, G. M. *J. Org. Chem.* **1988**, *53*, 2489.

(13) Mercer, F.; Goodman, T.; Wojtowicz, J.; Duff, D. *J. Polym. Sci., Polym. Chem. Ed.* **1992**, *30*, 1767. Irvin, J. A.; Neef, C. J.; Kane, K. M.; Cassidy, P. E.; Tullos, G.; St. Clair, A. K. *J. Polym. Sci., Polym. Chem. Ed.* **1992**, *30*, 1675.

(14) Bohlmann, F.; Albrecht, K.-D.; Schmidt, G. *Chem. Ber.* **1966**, *99*, 2822.

(15) Ratto, J. M.; Dynes, P. J.; Hamermesh, C. L. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 1035.

(16) Havens, S. J.; Hergenrother, P. M. *J. Org. Chem.* **1985**, *50*, 1763.

(17) Kobayashi, E.; Jiang, J.; Ohta, H.; Furukawa, J. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 2641.