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Palladium-Mediated Soluble Precursor Route into Poly(arylethynylenes) and Poly(arylethylenes)

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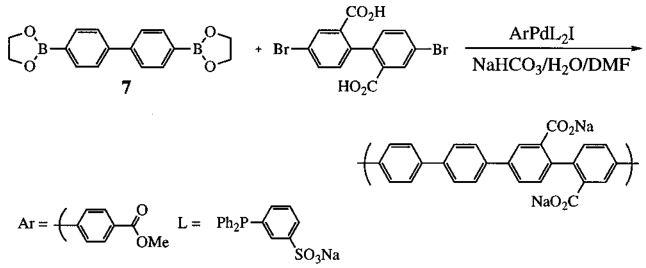
ABSTRACT: Soluble precursor polymers **8** and **14** were successfully synthesized via the palladium-mediated condensation of 4,4′-(1,3,2-dioxaborolan-2-yl)biphenyl (**7**) with the bis(*p*-bromophenyl)norbornadiene monomer **5** and the bis(*p*-bromophenyl)norbornene monomer **13**, respectively. The number-averaged molecular weights of these materials were determined by GPC−LS to be 34 000 for **8** and 75 000 for **14**. Thermolysis of **8** by a retro-Diels−Alder reaction began at 260 °C and appeared (by GC−MS analysis of the volatile byproducts) to yield a conjugated polymer with both alkyne and cyclopentadiene functionalities in the polymer backbone; however, TGA analysis indicated that the transformation was accompanied by some decomposition. The analogous thermolysis of **14** to yield the polymer with a double bond in the backbone began at 230 °C and appeared to proceed without the concomitant decomposition.

Introduction

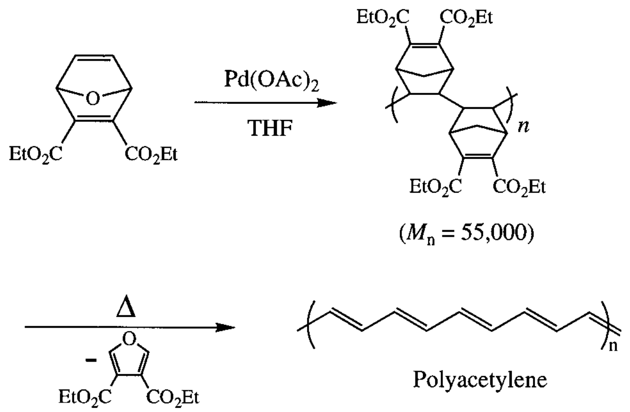
Rigid, conjugated polymers, such as poly(*p*-phenylene), poly(*p*-phenylenevinylene), and poly(*p*-phenyleneethynylene), are a class of polymers that have attracted a great deal of attention in the scientific community.[1−11] Although these materials possess such interesting properties as electroluminescence,[1] electrical conductivity (when doped),[2] liquid crystallinity,[3] high third-order optical nonlinearities,[4] and impressive mechanical properties,[5] the rigid, conjugated backbone that is generally responsible for these attributes also renders these polymers insoluble and infusible, and therefore, nonprocessible. Furthermore, classical syntheses[6] generally result in oligomeric materials since the polymers precipitate from solution before the higher molecular weights can be obtained. As a result, the technological potential of these materials has remained largely untapped. Research has been devoted to circumventing this insolubility/intractability problem, largely through the development of two basic, divergent synthetic strategies. The first of these tactics (of which there are numerous examples in the literature[7]) has been the incorporation of long, flexible side chains that disrupt the crystallinity and exploit the entropy of solvent−side chain mixing in order to gain solubility.[8] However, since the strong interchain reactions that are the root cause of the intractability of these materials are also responsible for their mechanical strength in oriented fibers, there is substantial evidence that the addition of these side chains has a detrimental effect on the desired properties of these polymers.[9] The second strategy has been to synthesize a precursor polymer containing a solubilizing functionality that can then be eliminated, generally by treatment with heat, to give the desired conjugated polymer. This latter methodology has been applied extensively in the synthesis of poly(*p*-phenylene),[10] poly(*p*-phenylenevinylene) and derivatives,[11] and polyacetylene.[12]

Previous work in our group resulted in the development of an aqueous synthesis of a water soluble poly(*p*-phenylene) utilizing a modified Suzuki coupling[13] reaction (Scheme 1).[14] Other research in our group was applied toward the development of a soluble precursor route to polyacetylene via an olefin polymerization to form the precursor followed by a retro-Diels−Alder reaction to form the conjugated polymer (Scheme 2).[12t,v] In this paper, we present a combination of these strategies to obtain a palladium-mediated (via Suzuki coupling) soluble precursor route (via retro-Diels−Alder reaction) into conjugated polymers with aromatic units (Scheme 3).

Scheme 1



Scheme 2



Results and Discussion

The synthesis of the requisite bis(*p*-bromophenyl)norbornadiene monomer is outlined in Scheme 4. Utilizing a modification of Bladon's route to the analogous nonbrominated cyclopentadiene,[15] we were able to synthesize the diarylcyclopentadiene **4**. From there, a Diels−Alder reaction with diethyl acetylenedicarboxy-

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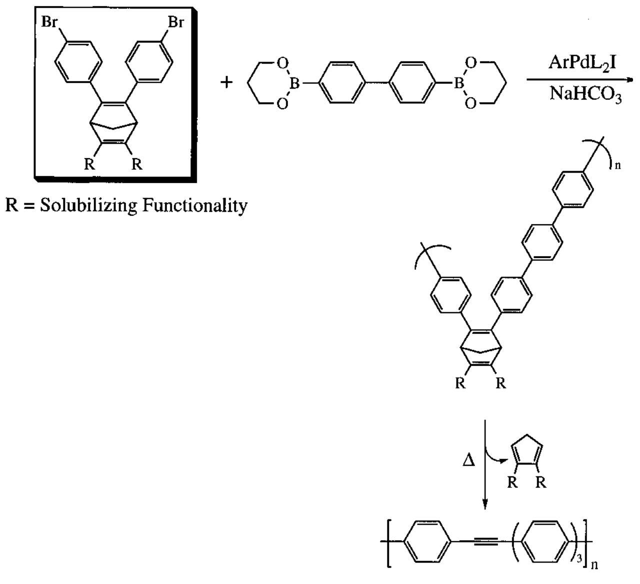
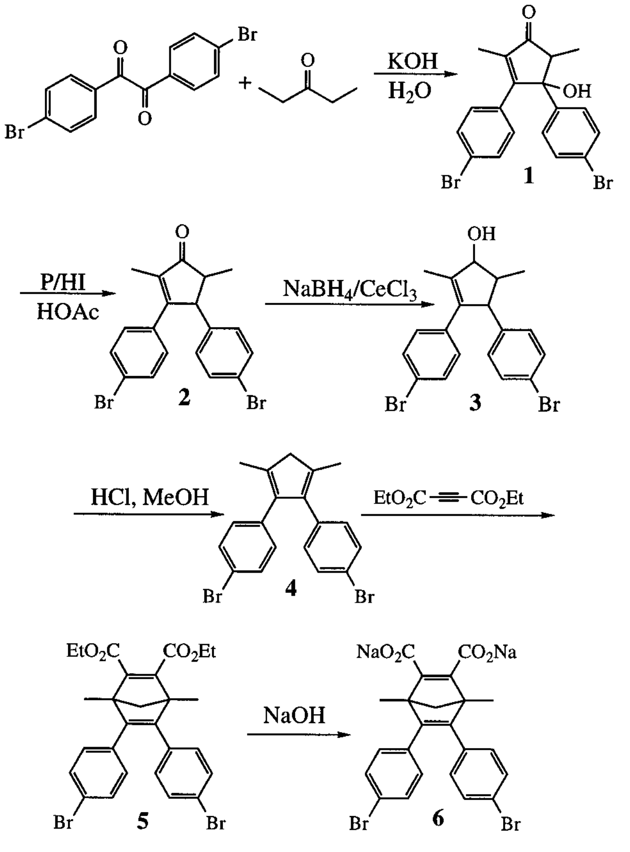
Scheme 3



Scheme 4



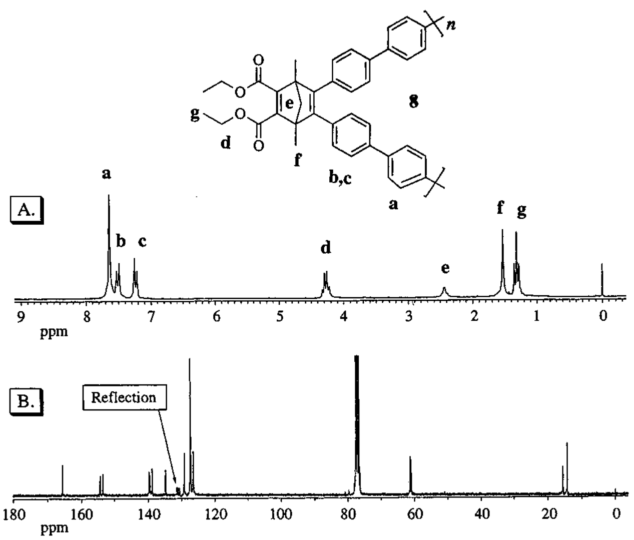
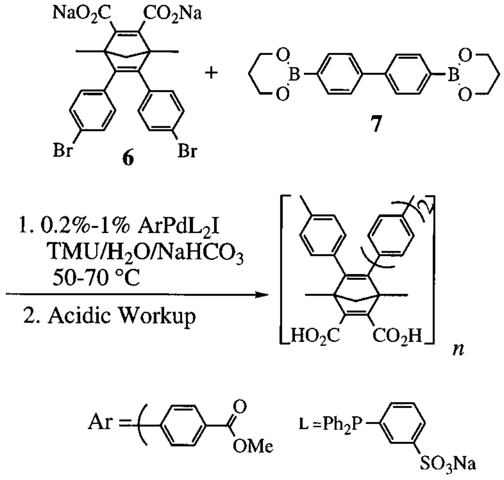
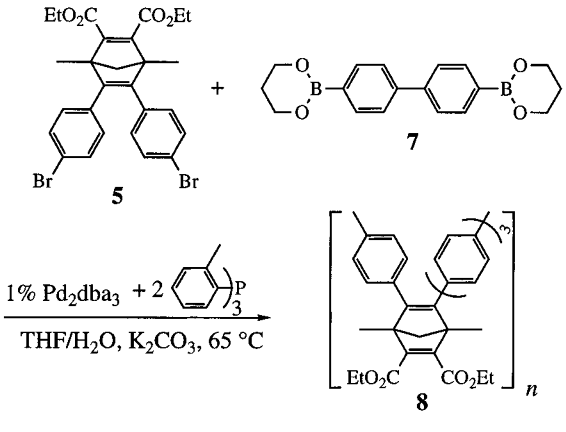


Figure 1. (A) ^{1}H and (B) ^{13}C NMR spectra for polymer **8**.

Scheme 5



Scheme 6

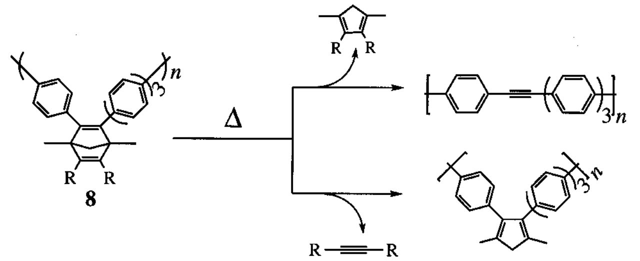


late and subsequent saponification led to monomers **5** and **6**, respectively.

Initial polymerizations (Scheme 5) of **6** with biphenylylenediboronic acid ester monomer **7** utilizing the methodology developed for the synthesis of water soluble poly(*p*-phenylenes) (Scheme 1) resulted in only oligomeric materials. However, by switching to the organic soluble monomer, **5**, and running the polymerization in THF/H$_2$O in the presence of 1% tris(dibenzylideneacetone)dipalladium(0) and the bulky tris(*o*-tolyl)phosphine ligand, we were able to synthesize polymer **8** in 96% isolated yield (Scheme 6).[16,17] The molecular weight values for polymer **8** were determined by tandem GPC−LS to be M_n = 34 000 and M_w = 59 000, with a polydispersity of 1.75. ^{1}H and ^{13}C NMR spectra for **8** are presented in Figure 1 along with peak assignments. The spectra are quite clean, and the absence of visible resonances due to end groups suggests that no oligomers were isolated with this polymer sample.

In actuality, there are two possible directions of thermolysis for this type of structure (Scheme 7). In the first, the cyclopentadiene moiety is eliminated to yield the target conjugated polymer. However, an alternative thermolysis pathway would involve the elimination of the alkyne, thus yielding a material with the cyclopentadiene unit embedded in the polymer

Scheme 7

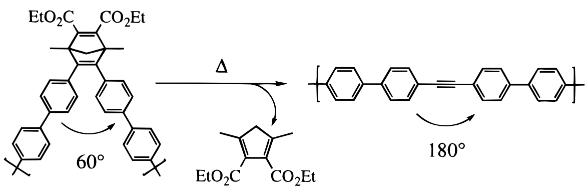


backbone. As this latter substance may have interesting properties in its own right, we would ideally like to find some means of controlling the direction of this thermolysis so that we can have access to both of these materials.

Heating a lyophilized sample of polymer **8** for 2 h at 300 °C in a Kugelrohr apparatus resulted in the formation of an insoluble brown polymer and the collection of a clear distillate. During the thermolysis, the carbonyl stretch present in virgin polymer **8** essentially disappears, while peaks at 810, 1003, and 1485 cm^{-1} become predominant (Supporting Information). These signals are indicative of *para*-substituted phenylene units and are the dominant signals in underivitized poly(*p*-phenylene).[18] Evidence for the phenylethynylene structure is obtained by Raman spectroscopy (Supporting Information). The spectrum of the product material shows a resonance clearly visible at 2215 cm^{-1}, indicating the formation of alkyne functionality in the polymer backbone.[7g] The ^{13}C solid state NMR spectrum of the theromolyzed material is dominated by the aromatic resonances (Supporting Information). A weak alkyne signal is present at 91 ppm, as is a weak alkyl signal at 13 ppm. This latter could be due to the presence of residual ester functionalities, or to the methyl groups of the cyclopentadiene units that would be present from the alternative Diels–Alder pathway.

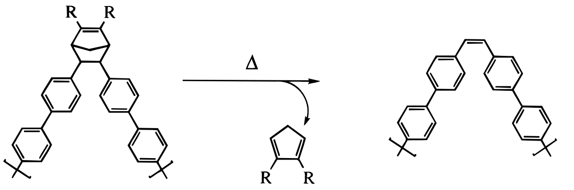
The direction of the thermolysis can be determined more definitively from analysis of the distillate. A GC–MS chromatographic analysis of the volatile byproducts of the thermolysis revealed the presense of both diethyl acetylenedicarboxylate (identified by comparison with an authentic sample) and the parent ion at 238 *m*/*e* corresponding to the cyclopentadiene byproduct from the desired thermolytic cleavage (Supporting Information). So, from this analysis it is apparent that both thermolytic pathways are present. The degree to which each pathway is occurring can be approximated from the integrations of the peaks in the GC chromatogram. Based on this analysis, the ratio of alkyne to cyclopentadiene functionalities in the thermolyzed polymer backbone is approximately 10:1. The expected weight retention for this thermolyzed polymer would be 59%, which is in good agreement with the experimentally determined value of 62%. Thermogravimetric analysis (TGA) reveals the retro-Diels–Alder onset occurs at 260 °C, and nonspecific decomposition above 350–400 °C.

In order to avoid the concomitant decomposition, we sought a means by which the temperature of the thermal conversion could be lowered. One possible reason for the high temperature of thermolysis (and the sizable presence of the alternative pathway) is the fact that the conversion from the norbornadiene unit, where the polymer substituents are 60° apart, to the alkyne functionality, where the chains are 180° apart, requires a radical change in geometry for the polymer chain (eq 1). A possible solution would be to synthesize an



(1)

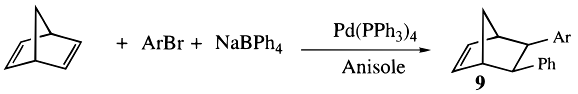
analogous polymer with a norbornene moiety in the polymer backbone. This material could undergo a retro-Diels–Alder reaction to form the conjugated polymer with a double bond embedded in the backbone (eq 2).



(2)

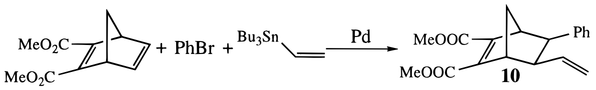
The geometrical change would be less severe, hopefully resulting in a lower temperature of thermolysis. Furthermore, there is only one possible pathway in which the conversion can take place.

Chiusoli has synthesized the diarylnorbornene **9** from a palladium-catalyzed reaction of norbornadiene with bromoarenes and sodium tetraphenylborate (eq 3).[19]

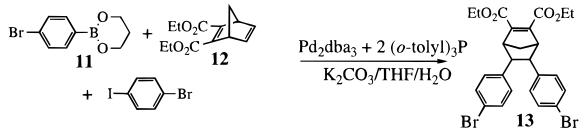


9 (3)

Also, Migita has developed tandem norbornadiene insertion–Stille coupling chemistry to synthesize, for example, the dimethyl 5-ethenyl-6-diarylnorbornene-2,3-dicarboxylate **10** (eq 4).[20] By reacting the (*p*-bromophenyl)boronic acid ester **11** with a large excess of the norbornadiene derivative **12** and *p*-bromoiodobenzene, we were able to combine these strategies to synthesize the norbornene monomer **13** in about 25% yield (eq 5). Clearly there is room for optimization in this procedure. But, the fact that this route involves monomer synthesis in one step from readily available materials makes it a notable improvement over the previous monomer system.



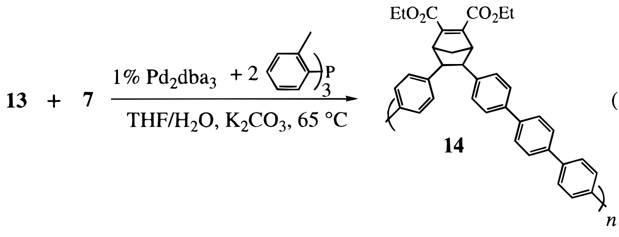
10 (4)



11 **12** **13** (5)

Polymerization of **13** with **7** under the typical conditions resulted in the formation of polymer **14** in 89% isolated yield. Polymer **14** is soluble in standard organic solvents such as THF, chloroform, and benzene; and analysis by GPC–LS reveals M_n = 75,000 for this material.

Heating a lyophilized sample of **14** under vacuum in a Kugelrohr apparatus for 1 h at 300 °C again resulted in the formation of a brown intractable material and the production of a clear distillate. IR spectra (KBr) of



(6)

14 before and after this treatment are presented in Figure 2. In the "after" spectrum, the carbonyl stretch has completely disappeared and the characteristic signals for *p*-phenylene units at 813, 1002, and 1486 cm^{-1} have again grown prominent. There is also an additional absorbance at 963 cm^{-1} due to *trans*-alkene C−H out-of-plane bending,[21] indicating that double-bond formation has taken place. The fact that there is no significant signal at 630 cm^{-1}, where the analogous *cis*-alkene C−H bending would be expected,[21] suggests that the *cis* double bonds initially formed during the retro-Diels−Alder reaction are isomerized to *trans* under the high temperatures of the thermolysis.

Thermalized **14** retained 59% of its weight, very close to the theoretical value of 61%. By TGA, the onset temperature is approximately 230 °C (lower by *ca.* 30 °C than the onset for **8**), and the weight retention before the onset of subsequent decomposition is 63%, again very close to the theoretical value of 61% (Supporting Information). Furthermore, when the instrument is isothermed at 275 °C, the result is a simple decay, suggesting a clean thermolytic conversion. However, the fact that the theoretical weight is never reached suggests that higher temperatures (or the application of a vacuum) are required to drive the pyrolysis to completion.

A GC−MS chromatogram for the distillate shows a parent ion of 210 *m*/*e*, which is consistent with the cyclopentadiene byproduct from the retro-Diels−Alder reaction of polymer **14** (Supporting Information). Since the ^{1}H NMR spectrum of the distillate appears to be quite complex, it is most likely that it is composed of a mixture of Diels−Alder adducts/oligomers of the cyclopentadiene byproduct that crack upon subjection to the 270 °C injector of the GC.

Conclusions

In summary, we have successfully synthesized two polymers, **8** and **14**, that can undergo retro-Diels−Alder reactions upon treatment with heat to form at least partially conjugated polyarylenes. For polymer **8**, two thermolysis pathways appear to be present, one which yields a triple bond in the polymer backbone, and the other which leaves a 2,3-cyclopentadiene functionality. From GC−MS analysis of the distillate, the ratio of these two processes is approximately 10:1, respectively. The temperature at which the thermal conversion occurs for **8** is quite high (befins at 260 °C), and consequently, the thermolysis appears to be accompanied by some decomposition and, furthermore, does not appear to proceed to quantitative completion, as a weak signal due to residual carbonyl is noticeable in the IR spectrum of the thermolyzed polymer. The thermal conversion of **14**, however, does appear to proceed to completion and occurs at a slightly lower temperature (begins at 230 °C). The retro-Diels−Alder reaction for this polymer yields a double bond in the polymer backbone, and the amount of concomitant decomposition seems to be less than that for **8**. In both cases, however, the spectroscopic characteristics of the functionalities generated by the thermolysis, are much weaker than expected. Though this could be due to the fact that there are four phenylene units for every alkene or alkyne formed during the conversion, the possibility that other thermolytic processes are occurring at the expense of alkene/alkyne formation cannot be ruled out.

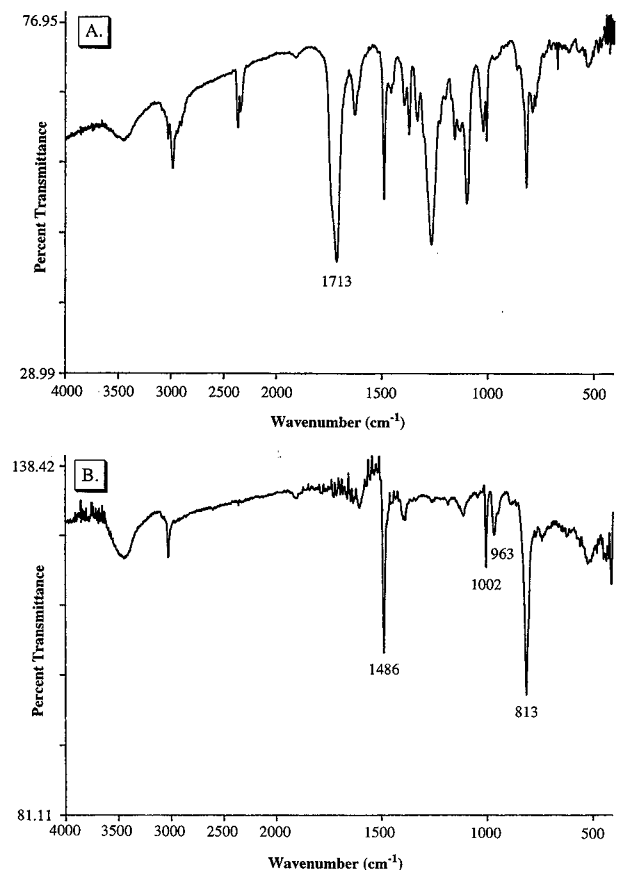


Figure 2. IR (KBr) spectra of polymer **14** (A) before and (B) after thermolysis at 300 °C for 1 h.

Experimental Section

General Information. Schlenk-line or drybox (MBraun Labmaster 100 series; maintained under positive argon pressure) techniques were used for all air-sensitive manipulations. ^{1}H NMR spectra were acquired at 200, 300, 400, and 500 MHz using Bruker AC-series, AM-series, MSL series, and AMX-series spectrometers; proton-decoupled ^{13}C spectra were obtained at corresponding frequencies. ^{1}H and ^{13}C chemical shifts are reported relative to internal TMS. Dry diethyl ether, THF, and benzene were purified by distillation from sodium/benzophenone and used immediately. Dry CH_2Cl_2 was dried over CaH_2 and vacuum-transferred prior to use. Triphenylphosphine was purchased from Aldrich, recrystallized from degassed ethanol, and sublimed under vacuum prior to use. 4-Bromoacetophenone, 1,4-dibromobenzene, *p*-iodobromobenzene, and 4-iodotoluene were purchased from Aldrich and sublimed under vacuum prior to use. The benzene adduct of tris(dibenzylideneacetone)dipalladium(0),[22] phenyl boronic anhydride,[23] 4,4′-bis(1,3,2-dioxaborolan-2-yl)biphenyl (**7**),[24] bis-[(sodiophenyl-4-sulfonyl)diphenylphosphine][4-(methylcarboxy)-phenyl]palladium(II) iodide,[24] and diethyl [2.2.1]bicyclohepta-2,5-diene-2,3-dicarboxylate[25] were all prepared via known procedures. All other chemicals were used as received from commercial suppliers. Listed melting point values are uncorrected. TGA measurements were performed on a DuPont Instruments Model 2000 thermal analysis system. IR spectra were performed on thin films cast by evaporation of THF solutions onto NaCl plates or from KBr mulls pressed into pellets utilizing a Perkin-Elmer 1600 Series FT-IR spectrometer. Raman spectra were performed on neat powders utilizing a Bruker FT-Raman spectrometer. FAB mass spectra were performed by the U. C. Berkeley Mass Spectrometry Laboratory. Analytical data were obtained by the elemental analysis facilities at the University of California at Berkeley and the University of Massachusetts at Amherst.

GC−MS measurements were performed on a Hewlett-Packard 5890 Series II gas chromatograph in line with a 5972 Series mass selective detector. The instrument was equipped with a polysiloxane capillary column, and helium was used as the carrier gas. The detector was held at 325 °C, while the injection port was maintained at 200 °C, and the oven temperature was ramped from 32 to 325 °C at 20 °C/min. The instrument was tuned to maximum sensitivity and acquired data in scan mode scanning for ions of $m/e = 1{-}510$. Tandem GPC−LS experiments were performed with a Hewlett-Packard Series 1050 HPLC pump equipped with Ultrastyragel (500, 10^3, 10^4, 10^5, and 10^6 Å) columns (Column Resolution, Inc., San Jose, CA) in line with a Wyatt Technology (Santa Barbara, CA) DAWN DSP-F laser photometer and a Wyatt Optilab 903 interferometric refractometer. Measurements were made at a wavelength of 688 nm. Refractive index increments for polymers **8** and **14** were measured with an Otsuka Electronics RM-102 differential refractometer at 688 nm.

3,4-Bis(*p*-bromophenyl)-2,5-dimethyl-4-hydroxycyclopent-2-en-1-one (1). In a 1 L round-bottomed flask, 28.0 g (76.1 mmol) of 4,4′-dibromobenzil was combined with 56 mL of 3-pentanone, 1 mL of a 33% aqueous KOH solution, and 350 μL of ethanol. The flask was hand-shaken for 10 min, during which time the yellow paste became a fluid suspension. A stir bar was added, and the flask was equipped with a reflux condenser. The reaction was then stirred overnight in a 65 °C oil bath. The resulting tan solution was then poured into 200 mL of water and extracted into 200 mL of diethyl ether. The water layer was washed with 2 × 100 mL of ether, and the organic layers were combined, washed with 1 × 100 mL of brine, and dried over $MgSO_4$. Removal of the solvent with a rotary evaporator resulted in a yellow oil. This was heated to 70 °C under vacuum for 8 h in a Kugelrohr apparatus to remove residual 3-pentanone. A 30.8 g (70.4 mmol, 92.5% yield based on purity) quantity of 3,4-bis(*p*-bromophenyl)-2,5-dimethyl-4-hydroxycyclopent-2-en-1-one (**1**) was isolated in 99% purity (as determined by NMR) as a yellowish resin. For characterization purposes, 600 mg of the product mixture was chromatographed on silica (20% ethyl acetate in petroleum ether) to yield, upon distillation in a bulb to bulb apparatus (120 °C oven temperature, dynamic 5 mTorr vacuum), 239 mg of the major isomer as a white, crystalline solid, and 151 mg of the minor isomer as a yellowish resin (65% total recovery). Major isomer: mp 174−176 °C; IR (neat) 1696, 3447 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.20 (d, $J = 7.4$ Hz, 3H), 1.96 (s, 3H), 2.23 (s, 1H), 2.65 (q, $J = 7.4$ Hz, 1H), 7.16−7.27 (m, 4H), 7.38−7.44 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.3, 10.0, 55.5, 82.2, 121.1, 123.6, 126.8, 130.6, 131.6, 132.1, 138.1, 142.6, 165.5, 208.6, one resonance not resolved. Anal. Calcd for $C_{19}H_{16}Br_2O_2$: C, 52.32; H, 3.70. Found: C, 52.26; H, 3.52. Minor isomer: IR (neat) 1693, 3436 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.72 (d, $J = 7.2$ Hz, 3H), 2.00 (s, 3H), 2.33 (s, 1H), 2.88 (q, $J = 7.3$ Hz, 1H), 7.01 (dm, $J_d = 8.6$ Hz, 2H), 7.15 (br d, $J = 7.4$ Hz, 2H), 7.43−7.53 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.8, 10.3, 56.0, 84.5, 122.0, 123.9, 127.4, 130.5, 131.4, 131.8, 132.0, 140.2, 164.4, 206.0, one resonance not resolved. Anal. Calcd for $C_{19}H_{16}Br_2O_2$: C, 52.32; H, 3.70. Found: C, 52.14; H, 3.49.

3,4-Bis(*p*-bromophenyl)-2,5-dimethylcyclopent-2-en-1-one (2). A 500 mL round-bottomed flask was charged with 30.0 g (68.1 mmol assuming 99% purity) of **1**, 2.00 mL (15.2 mmol) of 57% aqueous hyrdiodic acid, 3.90 g (0.126 mol) of red phosphorus, and 100 mL of acetic acid. The flask was equipped with a stir bar and reflux condenser, and the reaction was brought to reflux for 1 h. The resulting brownish-red suspension was filtered hot through a medium frit into 200 mL of 10% aqueous $NaHSO_3$. The filtrate turned white and cloudy upon contact with the solution. This mixture was then extracted into 3 × 200 mL of diethyl ether. The organic layers were combined, washed with 1 × 200 mL of brine, and dried over $MgSO_4$. Removal of the solvent with a rotary evaporator resulted in the isolation of 28.1 g (65.5 mmol based on purity, 96% yield) of 3,4-bis(*p*-bromophenyl)-2,5-dimethylcyclopent-2-en-1-one (**2**) as an off-white resin (98% pure by NMR) that was a mixture of two isomers. For characterization purposes, 500 mg of the product mixture was chromatographed on silica (10% ethyl acetate in petroleum ether) to yield, upon distillation in a bulb to bulb apparatus (120 °C oven temperature, dynamic 5 mTorr vacuum), 323 mg of the major isomer and 53 mg of the minor isomer, both as colorless resins (75% total recovery). Major isomer: IR (neat) 1698 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.33 (d, $J = 7.3$ Hz, 3H), 2.00 (d, $J = 2.0$ Hz, 3H), 2.34 (qd, $J_q = 7.4$ Hz, $J_d = 3.0$ Hz, 1H), 3.91 (m, 1H), 6.93 (d, $J = 8.4$ Hz, 2H), 7.16 (d, $J = 8.6$ Hz, 2H), 7.33 (d, $J = 8.3$ Hz, 2H), 7.45 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.1, 15.0, 51.2, 55.6, 120.7, 123.4, 129.2, 129.7, 131.7, 132.0, 133.7, 137.5, 140.7, 164.8, 209.9. Anal. Calcd for $C_{19}H_{16}Br_2O$: C, 54.31; H, 3.84. Found: C, 54.30; H, 3.99. Minor isomer: IR (neat) 1699 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.75 (d, $J = 7.5$ Hz, 3H), 2.05 (d, $J = 1.7$ Hz, 3H), 2.90 (quint, $J = 7.4$ Hz, 1H), 4.51 (dd, $J = 7.2$ Hz, 1.7 Hz, 1H), 6.94 (br d, $J = 7.7$ Hz, 2H), 7.22 (d, $J = 8.6$ Hz, 2H), 7.34 (d, $J = 8.6$ Hz, 2H), 7.46 (d, $J = 8.7$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.2, 12.4, 45.1, 51.8, 121.0, 123.5, 129.6, 130.4, 131.7, 131.8, 134.2, 137.7, 137.9, 164.3, 210.6. Anal. Calcd for $C_{19}H_{16}Br_2O$: C, 54.31; H, 3.84. Found: C, 54.26; H, 3.96.

3,4-Bis(*p*-bromophenyl)-2,5-dimethylcyclopent-2-en-1-ol (3). A 500 mL three-necked flask equipped with a stir bar and thermometer was charged with 27.0 g (63.0 mmol assuming 98% purity) of **2**, 25.5 g (68.4 mmol) of cerium chloride heptahydrate, and 250 mL of absolute ethanol. The mixture was stirred until almost all of the reactants were dissolved, resulting in a slightly cloudy yellow solution. It was then chilled to 0 °C in an ice/brine bath and 2.60 g (68.7 mmol) of $NaBH_4$ was added at a rate so that the temperature did not exceed 5 °C. A white precipitate gradually formed, and hydrogen gas was evolved as the reaction was allowed to warm to room temperature overnight. The solid was filtered off and recrystallized from absolute ethanol to yield 5.43 g (12.9 mmol, 20% recovery) of a pure isomer of **3** as a white solid. The remaining filtrates were combined, poured into 500 mL of water, and extracted into 3 × 300 mL of diethyl ether. The ether layers were combined, washed with 1 × 200 mL of brine, and dried over $MgSO_4$. Removal of the solvent with a rotary evaporator resulted in the recovery of 20.4 g (*ca.* 48.3 mmol) of 3,4-bis(*p*-bromophenyl)-2,5-dimethylcyclopent-2-en-1-ol (**3**) as a colorless resin that was a complex mixture of isomers, the purity of which could not be determined due to its complicated NMR spectrum. Pure isomer: mp (ethanol) 198−199 °C; IR (neat) 3179 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.13 (d, $J = 7.1$ Hz, 3H), 1.41 (d, $J = 7.1$ Hz, 1H), 1.97 (d, $J = 2.1$ Hz, 3H), 2.11 (sext, $J = 7.0$ Hz, 1H), 3.88 (dt, $J_d = 7.3$ Hz, $J_t = 1.9$ Hz, 1H), 4.61 (t, $J = 6.6$ Hz, 1H), 6.88 (d, $J = 8.4$ Hz, 2H), 6.96 (d, $J = 8.5$ Hz, 2H), 7.28 (d, $J = 6.9$ Hz, 2H), 7.32 (d, $J = 6.8$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.3, 13.3, 47.9, 59.5, 81.2, 120.0, 120.2, 120.6, 129.7, 129.9, 131.1, 131.5, 139.4, 140.9, 142.2. Anal. Calcd for $C_{19}H_{18}Br_2O$: C, 54.06; H, 4.30. Found: C, 53.89; H, 4.37.

Diethyl 5,6-Bis(*p*-bromophenyl)-1,4-dimethyl[2.2.1]-bicyclohepta-2,5-diene-2,3-dicarboxylate (5). A 20.4 g (*ca.* 48.3 mmol) amount of the crude mixture of isomers of **3** was placed in a 1 L round-bottomed flask along with 50 mL of concentrated HCl, 500 mL of methanol, and a stir bar. The mixture was brought to reflux, at which point it became homogeneous, and stirred at reflux for 1 h. The reaction was then allowed to cool, causing the oiling out of a yellow liquid, and was concentrated to *ca.* 100 mL with a rotary evaporator. The resulting mixture was then extracted into 500 mL of diethyl ether. The layers were separated, and the organic phase was washed with saturated aqueous $NaHCO_3$ until no more carbon dioxide was evolved. It was then rinsed with 1 × 100 mL of brine, dried over $MgSO_4$, and the solvent was removed with a rotary evaporator to yield an orange resin. This was cracked at 160 °C under a 5 mTorr dynamic vacuum in a bulb to bulb apparatus to yield 18.7 g (*ca.* 34.6 mmol based on purity) of 2,3-bis(*p*-bromophenyl)-1,4-dimethylcyclopentadiene (**4**) as a colorless resin that yellowed upon standing. This material was *ca*. 75% pure as estimated by ^{1}H NMR and could not be purified further due to its instability: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.94 (s, 6H), 3.02 (s, 2H), 6.73 (d, $J = 8.5$ Hz, 4H), 7.26 (d, $J = 8.5$ Hz, 4H).

All 18.7 g of **4** was dissolved in 100 mL of THF in a 250 mL round-bottomed flask equipped with a stir bar. Then 10.0 g (58.8 mmol) of diethyl acetylenedicarboxylate was added via pipet, and the flask was fitted with a reflux condenser. After 2 days of stirring at reflux, the solvent was removed with a rotary evaporator to yield a yellow-orange viscous oil. This was chromatographed on silica with 10% ethyl acetate in petroleum ether to yield 12.5 g (*ca*. 90% pure estimated by ^{1}H NMR, 19.6 mmol, *ca*. 40% yield from **3**) of diethyl 5,6-bis(*p*-bromophenyl)-1,4-dimethyl[2.2.1]bicyclohepta-2,5-diene-2,3-dicarboxylate (**5**) as a slightly yellowish resin.

Analytically pure material was obtained by saponification to form **6** (*vide infra*), which once purified was reesterified back to **5**: 5.10 g (9.07 mmol) of **6** was dissolved in 100 mL of deionized water, and 10% aqueous HCl was added (causing the precipitation of the free acid) until the solution was acidic to litmus paper. The mixture was then extracted into ether (3 × 200 mL), after which the organic phases were combined, rinsed with 1 × 100 mL of brine, and dried over $MgSO_4$. Removal of the solvent with a rotary evaporator resulted in the isolation of the free acid, which was then stirred at reflux for 24 h in 250 mL of absolute ethanol saturated with HCl. The reaction was neutralized with saturated aqueous $NaHCO_3$ and extracted into 500 mL of diethyl ether. The phases were separated, and the aqueous layer was washed with 2 × 100 mL of ether. The organic layers were pooled, rinsed with 1 × 200 mL of brine, and dried over $MgSO_4$. After removal of the solvent with a rotary evaporator, chromatography of the residue on silica eluted with 12.5% ethyl acetate in petroleum ether yielded 4.83 g (8.41 mmol, 92.7% yield) of diethyl 5,6-bis(*p*-bromophenyl)-1,4-dimethyl[2.2.1]bicyclohepta-2,5-diene-2,3-dicarboxylate (**5**) as a colorless resin: IR (neat) 1706 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.26 (t, $J = 7.1$ Hz, 6H), 1.43 (s, 6H), 2.33 (d, $J = 7.0$ Hz, 1H), 2.41 (d, $J = 6.9$ Hz, 1H), 4.25 (q, $J = 7.1$ Hz, 4H), 6.95 (d, $J = 8.5$ Hz, 4H), 7.34 (d, $J = 8.5$ Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 15.1, 60.9, 61.0, 79.4, 121.1, 130.1, 131.1, 134.1, 153.3, 154.0, 165.2. Anal. Calcd for $C_{27}H_{26}Br_2O_4$: C, 56.45; H, 4.53. Found: C, 56.50; H, 4.65. MS (FAB): *m/z* 574.

Disodium 5,6-Bis(*p*-bromophenyl)-1,4-dimethyl[2.2.1]-bicyclohepta-2,5-diene-2,3-dicarboxylate (6). A 9.52 g sample of 90% pure **5** (14.9 mmol) was dissolved in 200 mL of absolute ethanol in a 500 mL round-bottomed flask equipped with a stir bar. A suspension of 3.8 g (95 mmol) in 50 mL of ethanol was added, and the reaction was brought to reflux for 2 h, or until no **5** remained as determined by thin layer chromatography (10% ethyl acetate in petroleum ether). The reaction was concentrated to *ca*. 50 mL with a rotary evaporator and acidified with 10% aqueous HCl, resulting in the precipitation of the free acid. This was extracted into 3 × 100 mL of ether, after which the organic phases were pooled, rinsed with 1 × 100 mL of brine, and dried over $MgSO_4$. After removal of the solvent with a rotary evaporator, the residue was redissolved in absolute ethanol and titrated to the phenolphthalein endpoint with 10% aqueous NaOH. The solvent was again removed with a rotary evaporator, and the resulting solid was recrystallized from deionized water until colorless. The white flakes were isolated via filtration and lyophilized from HPLC-grade water to yield 5.10 g (9.07 mmol, 60.9% yield) of disodium 5,6-bis(*p*-bromophenyl)-1,4-dimethyl-[2.2.1]bicyclohepta-2,5-diene-2,3-dicarboxylate (**6**) as a white powder. IR (KBr) 1560 cm^{-1}; ^{1}H NMR (200 MHz, D_2O) δ 1.35 (s, 6H), 2.25 (m, 2H), 7.08 (d, $J = 8.5$ Hz, 4H), 7.39 (d, $J = 8.5$ Hz, 4H); ^{13}C NMR (75 MHz, D_2O) δ 14.8, 60.0, 78.9, 119.6, 130.4, 130.5, 135.4, 151.7, 153.3, 174.9; Anal. Calcd for $C_{23}H_{16}Br_2Na_2O_4$: C, 49.14; H, 2.87. Found: C, 48.75; H, 3.00.

1-Bromo-4-(1,3,2-dioxaborolan-2-yl)benzene (11). The following procedure was performed on a vacuum line using standard air-sensitive techniques: 7.17 g (30.4 mmol) of freshly sublimed 1,4-dibromobenzene was dissolved in 150 mL of dry ether in a 500 mL argon-purged Schlenk flask equipped with a stir bar. The flask was cooled to −78 °C in an acetone/dry ice bath, after which 12.2 mL (30.4 mmol) of a 2.5 M *n*-butyllitihium solution in hexanes was added dropwise via syringe. The reaction was allowed to warm to 0 °C, during which time a separate argon-purged 500 mL Schlenk flask was charged with 20.4 mL (91.2 mmol) of boron triisopropoxide and 150 mL of dry ether. This flask was then chilled to −78 °C, and the lithium reagent solution was added via cannula. The reaction was allowed to warm to ambient temperature, during which time it gradually turned cloudy. After stirring for 3 h, it was poured into 50 mL of concentrated HCl in 200 mL of ice. The mixture was allowed to stir until all of the ice melted. The layers were separated, and the aqueous phase was washed with 2 × 100 mL of ether. The ether layers were pooled, washed with 1 × 100 mL of brine, and dried over $MgSO_4$. Removal of the solvent with a rotary evaporator produced a yellow solid, which was then combined with 2.2 mL of 1,3-propanediol and 250 mL of benzene in a 500 mL round-bottomed flask. To this was added a stir bar, and the flask was equipped with a Dean/Stark trap and reflux condenser. The mixture was allowed to reflux overnight, after which the solvent was removed with a rotary evaporator. The resulting oil was distilled at 90 °C under a dynamic 5 mTorr vacuum in a bulb to bulb apparatus to yield, after a brief forerun, 6.52 g (27.0 mmol, 89.0% yield) of 1-bromo-4-(1,3,2-dioxaborolan-2-yl)benzene (**11**) as a clear liquid, which solidified upon standing: mp 52−53 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.05 (quin, $J = 5.4$ Hz, 2H), 4.15 (t, $J = 5.4$ Hz, 4H), 7.47 (d, $J = 8.2$ Hz, 2H), 7.62 (d, $J = 8.2$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.3, 62.0, 125.4, 130.7, 135.3, one resonance not resolved. Anal. Calcd for $C_9H_{10}BBrO_2$: C, 44.87; H, 4.18. Found: C, 44.88; H, 4.06.

Diethyl 5,6-Bis(*p*-bromophenyl)[2.2.1]bicyclohept-2-ene-2,3-dicarboxylate (13). The following procedure was performed on a vacuum line using standard air-sensitive techniques. A 200 mL Schlenk flask was charged with 19.0 g (67.2 mmol) of *p*-iodobromobenzene, 17.5 g (74.0 mmol) of diethyl [2.2.1]bicyclohepta-2,5-diene-2,3-dicarboxylate (**12**), 4.07 (16.9 mmol) of **11**, and 18 mL of THF. A separate 100 mL Schlenk flask was charged with 5.8 g (35 mmol) of potassium carbonate sesquihydrate and 35 mL of HPLC-grade water. Both of these flasks were thoroughly degassed via several freeze−pump−thaw cycles and transferred via cannula to an argon-purged 250 mL Schlenk flask charged with 181.5 mg (0.350 mmol of Pd) of the chloroform adduct of tris(dibenzylideneacetone)dipalladium(0), 212.8 mg (0.700 mmol) of tris(*o*-tolyl)phosphine, and a stir bar. Under an argon backflow, the flask was fitted with a purged-out reflux condenser equipped with a gas-flow adapter, and the reaction was refluxed under argon for 12 h. The resulting mixture was poured into 200 mL of diethyl ether, the layers were separated, and the aqueous phase was washed with 2 × 50 mL of ether. The organic layers were pooled, rinsed with 1 × 50 mL of brine, and dried over $MgSO_4$. After removal of the solvent with a rotary evaporator, the crude product was heated under dynamic 5 mTorr vacuum at 70 °C in a Kugelrohr apparatus to distill away unreacted *p*-iodobromobenzene and **12**. The residue was chromatographed on silica with a solvent gradient from 5% to 15% ethyl acetate in petroleum ether, resulting in an orange oil that solidified under vacuum. Repeated recrystallization from absolute ethanol resulted in a colorless solid that was then lyophilized from benzene to yield 2.28 g (4.16 mmol, 24.6% yield) of diethyl 5,6-bis(*p*-bromophenyl)[2.2.1]-bicyclohept-2-ene-2,3-dicarboxylate (**23**) as a white powder: mp 145−148 °C; IR (neat) 1712 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.32 (t, $J = 7.1$ Hz, 6H), 2.07 (d, $J = 9.7$ Hz, 1H), 2.30 (d, $J = 9.7$ Hz, 1H), 3.46 (dd, $J = 5.4$ Hz, 1.2 Hz, 4H), 4.27 (q, $J = 7.1$ Hz, 4H), 6.74 (d, $J = 8.5$ Hz, 4H), 7.17 (d, $J = 8.4$ Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 44.9, 48.3, 50.4, 61.2, 119.9, 130.2, 130.9, 139.7, 146.6, 164.5. Anal. Calcd for $C_{25}H_{24}Br_2O_4$: C, 54.77; H, 4.41. Found: C, 54.97; H, 4.61. Since analogous syntheses[19,20] resulted in the formation of predominantly *exo* isomers, **13** is most likely the *exo* isomer as well. However, we have not performed experiments to confirm this.

Attempted Polymerization of 6 with 7. (a) Using Phosphine-Based Catalysts. The following procedure was performed on a vacuum line using standard air-sensitive techniques. In a typical example, a reaction tube with a side arm and Teflon stopcock was charged with 4.60 mL (0.432 mmol) of a tetramethylurea stock solution 0.0940 M in both **6** and **7**, 10.2 mL (1.24 mmol) of an aqueous stock solution 0.122 M in $NaHCO_3$, and a stir bar. The mixture was then degassed via three (or until completely degassed) freeze−pump−thaw cycles, after which the tube was back-filled with argon and 500 μL (0.0095 mmol, *ca.* 1%) of a degassed methanol stock solution 0.019 M in bis[(sodiophenyl-4-sulfonyl)diphenylphosphine]-[4-(methylcarboxy)phenyl]palladium(II) iodide[24] was added via syringe. The reaction was then degassed once more, back-filled with argon, sealed, and allowed to stir in a 60 °C oil bath. The reaction started out as a milky suspension that noticeably yellowed with time. After 2 days, it was a homogeneous yellow solution. The polymerization was allowed to stir at 60 °C for 10 days, after which it was opened to air and poured into 30 mL of 5% aqueous HCl. The resulting solid mass was filtered off, dissolved in THF and reprecipitated twice more, resulting in the recovery of 106.2 mg (0.208 mmol, 48.2%) of a yellow filmy solid. The material adhered to GPC columns, preventing molecular weight determination, but analysis by ^{1}H NMR showed a complicated spectrum with sharp peaks overlapped with broad resonances, indicative of oligomer formation. As a result, the material was not purified or characterized further. Other attempts at polymerization varying the catalyst concentration (from 0.2% to 1.0%) and temperature of reaction (50, 60, and 70 °C) produced identical results.

(b) Utilizing "Ligandless" Catalyst Methodology. An identical procedure was followed with the substitution of 100 μL (0.0017 mmol Pd, *ca.* 0.2%) of a degassed THF stock solution 0.0174 M (in Pd) in the benzene adduct of tris(dibenzylideneacetone)dipalladium(0) for the phosphine-based catalyst stock solution above. The reaction never turned homogeneous and, consequently, was not worked up.

Polymerization of 5 with 7. The following procedure was performed on a vacuum line using standard air-sensitive techniques. A 50 mL ampule was charged with 1.0306 g (1.7945 mmol) of analytically pure **5**, 577.8 mg (1.795 mmol) of **7**, 1.483 g (8.97 mmol) of potassium carbonate sesquihydrate, 9 mL of HPLC-grade water, 7 mL of THF, and a stir bar. The mixture was degassed via three (or until completely degassed) freeze−pump−thaw cycles and back-filled with argon. Then 900 μL (0.072 mmol) of a degassed THF stock solution 80 mM in tris(*o*-tolyl)phosphine and 900 μL (0.036 mmol Pd, *ca.* 1%) of a degassed THF stock solution 40 mM (in Pd) in the benzene adduct of tris(dibenzylideneacetone)dipalladium(0) were added via syringe. The reaction was degassed once more, sealed under vacuum, and allowed to stir in a 65 °C oil bath. The mixture started out as a biphasic mixture, the organic phase being a bright yellow color, and the aqueous phase a milky white. After 24 h, the aqueous phase was clear and the organic layer was a dingy-green color and was slightly viscous. The polymerization was allowed to stir at 65 °C for 1 week, by which time it had become a triphasic mixture, the aqueous layer being clear, the top layer being a light green, and a viscous middle phase being a dark green color. The ampule was opened to air, the phases were separated, and the aqueous layer was washed with 2 × 15 mL of CH_2Cl_2. The organic phases were combined and dried over $MgSO_4$, and the solvent was removed with a rotary evaporator, leaving behind a green film. This was dissolved in 10 mL of THF and precipitated into 40 mL of methanol acidified with concentrated HCl. The resulting suspension was centrifuged, the supernatant was decanted off, and the residual solid was redissolved in CH_2Cl_2. It was then reprecipitated into acid-free methanol, centrifuged, and isolated as before. This process was repeated until the supernatant was no longer acidic. The polymer was then dissolved in CH_2Cl_2 and precipitated into hexanes to remove any residual grease. After isolation via centrifugation, the resulting material was dissolved in benzene and lyophilized to yield 971 mg (1.71 mmol, 95.5% yield) of polymer **8** as a spongy yellow solid: $M_n = 34\,000 \pm 2300$; $M_w = 59\,300 \pm 1000$; PDI = 1.75 ± 0.12; IR (KBr) 1712 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.31 (t, $J = 6.9$ Hz, 6H), 1.53 (s, 6H), 2.44 (br, 2H), 4.28 (q, $J = 6.9$ Hz, 4H), 7.24 (d, $J = 7.9$ Hz, 4H), 7.51 (d, $J = 7.9$ Hz, 4H), 7.64 (s, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 15.5, 60.9, 61.2, 79.9, 126.4, 127.2, 129.1, 134.8, 138.8, 139.4, 139.7, 153.5, 154.3, 165.5. Anal. Calcd for $C_{39}H_{34}O_4$: C, 82.66; H, 6.05. Found: C, 82.46; H, 5.88. Refractive index increment (THF, 25.6 °C, 688 nm): 0.255 mL/g.

Polymerization of 13 with 7. The following procedure was performed on a vacuum line using standard air-sensitive techniques. A 20 mL sealable ampule was charged with 1.25 mL (0.297 mmol) of a THF stock solution 0.2376 M in both **13** and **7**, 245 mg (1.49 mmol) of potassium carbonate sesquihydrate, 1.5 mL of HPLC-grade water, and a stir bar. The mixture was degassed via three (or until completely degassed) freeze−pump−thaw cycles and back-filled with argon. Then 230 μL (0.006 mmol) of a degassed THF stock solution 25.8 mM in tris(*o*-tolyl)phosphine and 230 μL (0.003 mmol Pd, *ca.* 0.5%) of a degassed THF stock solution 12.9 mM (in Pd) in the benzene adduct of tris(dibenzylideneacetone)dipalladium(0) were added via syringe. The reaction was degassed once more, sealed under vacuum, and allowed to stir in a 65 °C oil bath. After 15 min the polymerization was mixture of two homogeneous phases, but after 30 min, a precipitate had started to form. The reaction was allowed to stir at 65 °C for 10 days, after which the ampule was opened to air, the phases were separated, and the aqueous layer was washed with 2 × 15 mL of CH_2Cl_2. The polymer was isolated as described for **8**, and the resulting material was dissolved in benzene and lyophilized to yield 142.0 mg (0.263 mmol, 88.4% yield) of polymer **14** as a spongy pale-yellow solid. The molecular weight distribution was polymodal, but the overall molecular weight averages (as determined by tandem GPC−LS) were $M_n = 75\,500 \pm 800$ and $M_w = 114\,100 \pm 1300$. IR (KBr): 1713 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.33 (t, $J = 7.2$ Hz, 6H), 2.11 (br, 1H), 2.48 (br, 1H), 3.58 (br s, 4H), 4.28 (q, $J = 7.1$ Hz, 4H), 6.97 (d, $J = 7.1$ Hz, 4H), 7.28 (d, $J = 7.0$ Hz, 4H), 7.48−7.57 (br, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2, 45.2, 48.7, 50.7, 61.1, 126.2, 127.1, 129.2, 137.9, 139.3, 139.5, 140.3, 146.9, 164.7. Anal. Calcd for $C_{37}H_{32}O_4$: C, 82.20; H, 5.97. Found: C, 81.62; H, 5.91; ash, 0.2. Refractive index increment (THF, 25.0 °C, 688 nm): 0.211 mL/g.

Thermolysis of Polymer 8. A 50 mL round-bottomed flask was charged with 151.2 mg (0.267 mmol) of **8**. This was placed under 5 mTorr dynamic vacuum in a Kugelrohr apparatus. The oven was heated to 300 °C for 2 h, during which time the polymer darkened to an earthy brown color, and a clear liquid distilled into the collection bulb. The apparatus was allowed to cool, and 93.8 mg (62.0% weight retention) of the solid and 49.1 mg (32.5% by weight) of the liquid were recovered. The distillate was dissolved in 5 mL of diethyl ether, and 25 μL of this solution was diluted to 10 mL with ether. This final solution was analyzed by GC−MS (Supporting Information), revealing that approximately 90% of the thermolysis produced the alkyne functionality in the polymer backbone and 10% yielded the cyclopentadiene moiety (see text). The thermolyzed polymer was found to be insoluble in chloroform, toluene, and hot 1-chloronaphthalene but was analyzed by IR, Raman spectroscopy, solid state ^{13}C NMR, and elemental analysis: IR (KBr) 810 (vs), 1003 (m), 1485 (m) cm^{-1}; Raman (neat) 2215 cm^{-1}; ^{13}C NMR (75 MHz, solid state) δ 13.7 (very weak), 91.1 (very weak), 126.3, 138.7. Anal. Calcd for 90% $C_{26}H_{16}$ and 10% $C_{31}H_{24}$: C, 94.97; H, 5.03; Found: C, 91.29; H, 4.99; ash, 0.45. The low carbon value is most likely due to the incomplete thermolysis.

Thermolysis of Polymer 14. A 50 mL round-bottomed flask was charged with 252.1 mg (0.466 mmol) of **14**. This was placed under 5 mTorr dynamic vacuum in a Kugelrohr apparatus. The oven was heated to 300 °C for 1 h, during which time the polymer darkened to a tannish-brown color, and a clear liquid, which darkened upon standing, distilled into the collection bulb. The apparatus was allowed to cool, and 148.6 mg (58.9% weight retention) of the solid and 90.8 mg (36.0% by weight) of the liquid were recovered. The distillate was dissolved in 5 mL of diethyl ether, and 25 μL of this solution was diluted to 10 mL with ether. This final solution was analyzed by GC−MS (Supporting Information), which suggested that the desired retro-Diels−Alder reaction was the primary thermolytic pathway. The thermolyzed polymer was found to be insoluble in chloroform, toluene, and hot 1-chloronaphthalene but was analyzed by IR and elemental analysis: IR (KBr) 813 (vs), 963 (w), 1002 (m), 1110 (w), 1384 (w), 1486 (s) cm^{-1}. Anal. Calcd for $C_{26}H_{18}$: C, 94.14; H, 5.86. Found: C, 93.42; H, 5.36; ash, 0.3.

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Supporting Information Available: IR and NMR spectra and GC–MS analysis for **8** and TGA and GC–MS analysis of **14** (5 pages). Ordering information is given on any current mashead page.

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