Organic Polymers from Condensations of Cyclopentadienyl and Indenyl Dinucleophiles with Carbon Dielectrophiles

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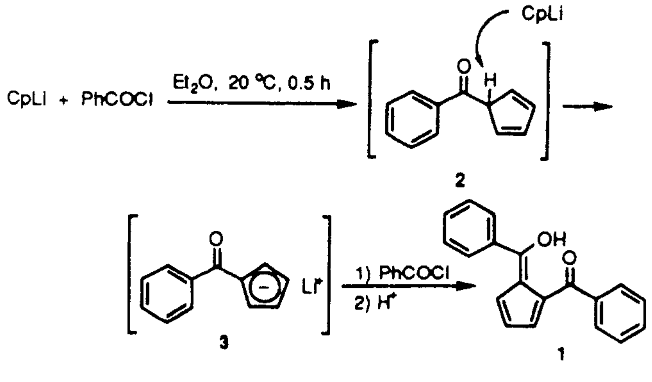
ABSTRACT: Condensations of carbon dinucleophiles with carbon dielectrophiles produce a new class of condensation oligomers. Model condensations of sodium cyclopentadienide (CpNa) in the presence of NEt_3 with 2 equiv of benzoyl chloride and phthalic anhydride yield 1,2-substituted fulvene enols cleanly and in excellent yields. Condensations of CpNa with dianhydrides (PMDA, BTDA) and diacid chlorides in the presence of NEt_3 afford oligomeric and polymeric materials that are soluble in organic solvents. Some polymers cast high-quality films from solution. Heat treatment of the condensation polymers obtained from CpNa and PMDA or BTDA causes thermosetting and renders the polymers insoluble. Polymers derived from CpNa can be readily hydrogenated by means of a Rh catalyst.

This paper describes reactions of carbon dinucleophiles with carbon dielectrophiles that produce a new class of condensation oligomers.[1] We have found several examples of this type of condensation oligomerization and believe that this synthetic strategy is generally applicable. Although many polymers are obtained from condensation reactions between dinucleophiles (e.g., diamines and diols) and dielectrophiles (e.g., dianhydrides and diacid chlorides), we are unaware of examples of polymers formed in condensation reactions between *carbon* dinucleophiles and dielectrophiles. The backbones of such polymers should have useful stability toward hydrolysis. Some of these polymers contain a high degree of residual functionality and can be chemically modified after polymerization.

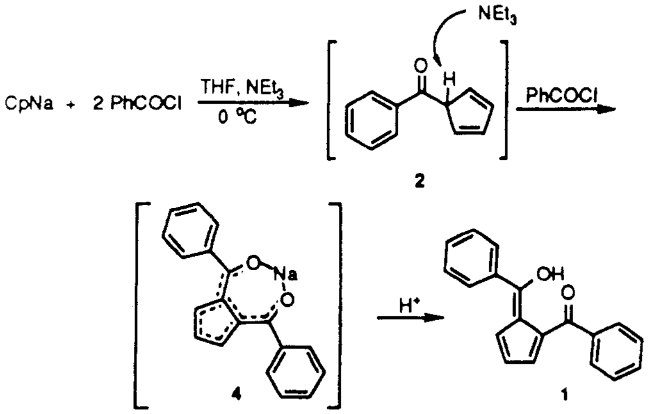
These polymerizations were presaged by the known reactivity of Cp^- toward carboxylic acid halides and anhydrides. Treatment of an ethereal suspension of CpLi with benzoyl chloride has been reported to form the 1,2-substituted fulvene enol, 1-benzoyl-6-hydroxy-6-phenylfulvene (1), in up to 50% yield.[2-5] The mechanism proposed involves a reaction of 1 equiv of CpLi to form intermediate ketone 2. Removal of the acidic proton of the benzoyl cyclopentadiene by a second 1 equiv of CpLi[6] forms the anion 3, which then attacks a second 1 equiv of benzoyl chloride. A yield of 50% for this reaction actually represents a quantitative conversion, since half of the added CpLi is consumed in the deprotonation of 2.

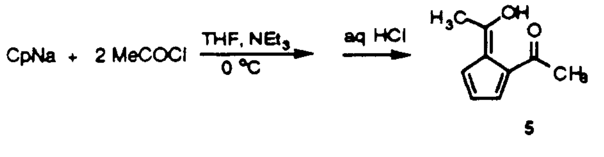


In this reaction Cp^- acts as latent dinucleophile. It occurred to us that this latent reactivity might be useful in a polymerization reaction. Indeed, polymeric materials are formed in reactions of Cp^- with dielectrophiles such as dianhydrides and diacid chlorides. In this paper we describe the details of our studies of related model reactions and of oligomerization and polymerization reactions involving condensations of carbon dinucleophiles with carbon dielectrophiles.

Results and Discussion

We began our studies by considering a model of the polymerization reaction. We treated benzoyl chloride with 0.5 equiv of CpNa in the presence of triethylamine, reasoning that if it were possible to obtain 1 in high yield using added base to deprotonate 2, thereby minimizing the depletion of Cp^- via protonation by 2, then this reaction sequence might be applicable to a condensation polymerization. Indeed, when we slowly added a solution of CpNa in THF to a solution of benzoyl chloride at 0 °C, we obtained 1 in >95% isolated yield. We detected no 1,3- or 1,4-substituted products. This observation confirmed a report[5] that suggested that the dibenzoyl derivative was stabilized by the formation of the resonance-stabilized sodium enolate salt 4. Similarly, we found that treatment of CpNa with acetyl chloride affords the fulvene enol 5 in excellent yield.





Treatment of phthalic anhydride with CpNa in the presence of triethylamine afforded 6. To simplify its characterization we converted 6 to the diester 7, using diazomethane, in an overall yield of >90%. Again, no 1,3-

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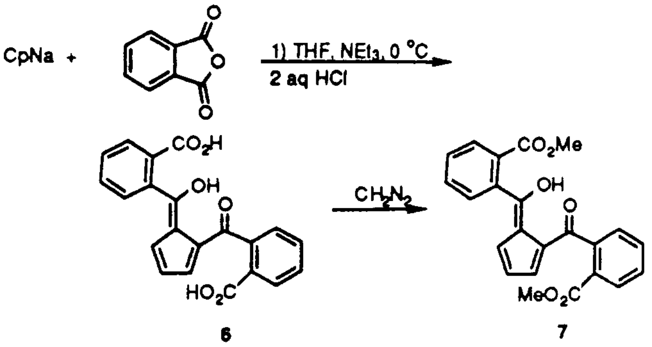
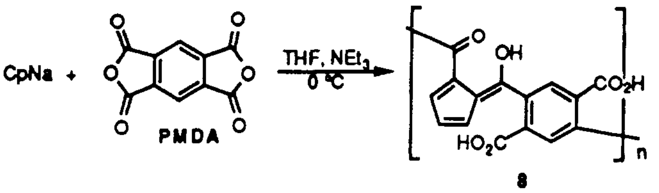
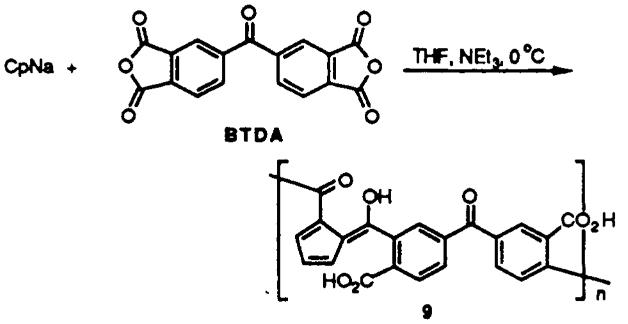


or 1,4-substituted products were detected. The large downfield ^{1}H NMR signal of the internally hydrogen-bonded enolic proton at δ 15.1 is diagnostic of this structure.[2-5]

Encouraged by the results of the studies of model systems with monofunctional electrophiles such as carboxylic acids and anhydrides, we next added CpNa to the dielectrophiles PMDA (1,2,4,5-benzenetetracarboxylic dianhydride, or pyromellitic dianhydride) and BTDA (benzophenonetetracarboxylic dianhydride) under similar conditions. Both dianhydrides produced oligomeric solids, formulated as structures 8 and 9, in high yields. The structures assigned are consistent with the results of the model reactions (vide supra) and with the ^{13}C NMR spectrum of 8.





We have considered the possibility of generating Cp$^-$ in situ by adding a nonnucleophilic base sufficiently strong to deprotonate cyclopentadiene in the presence of PMDA or BTDA. Survey experiments employing NaH, NEt$_3$, and DABCO, respectively, with equimolar mixtures of cyclopentadiene and PMDA in THF generated no oligomeric or polymeric materials.

The oligomeric materials obtained from CpNa and the dianhydrides (PMDA and BTDA) were soluble in many organic solvents, including THF, acetone, ethanol, and ethyl acetate. Deeply-colored transparent films of these polymers could be cast from solutions onto glass and other substrates, and fibers having lengths >1 m could be pulled from concentrated solutions. Films and fibers of polymer 9 were generally superior to those obtained from polymer 8, presumably owing to the greater flexibility of the BTDA-derived segment. Because of the carboxylic acid moieties present in the oligomers, they were also soluble in water at pH > 8. The addition of HCl to aqueous solutions caused these polymers to precipitate.

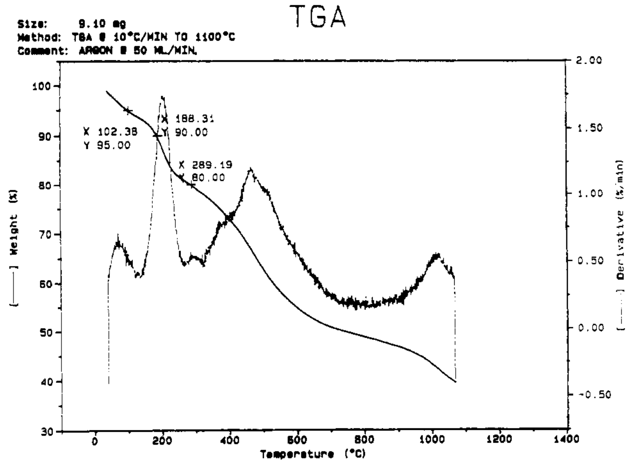


Figure 1. DTA trace of polymer formed in condensations of CpNa with PMDA.

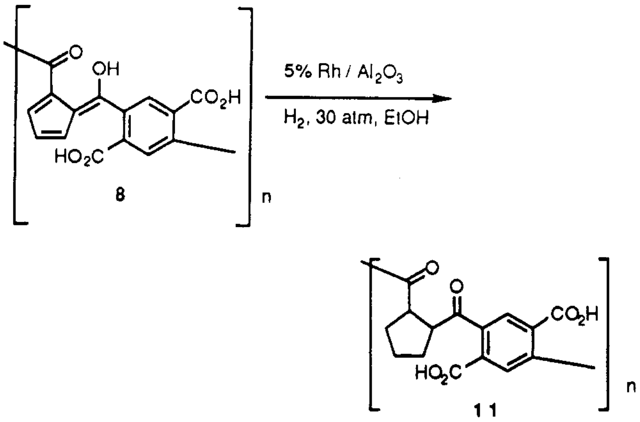
Heating solution-cast films of oligomers 8 and 9 to >150 °C resulted in curing or thermosetting behavior. After heating, the films remained intact—simply darkening somewhat—and were significantly sturdier and no longer soluble in organic solvents or aqueous acid or base. Thermal analysis (DSC, TGA) of 8 indicated that curing occurred in a stepwise manner (see Figure 1). Polymer 8 lost weight in successive stages but retained >50% of its mass on heating to 800 °C in argon. The IR spectra of free-standing films before and after curing at 150 °C suggest the formation of anhydride cross-linkages (ν_{CO} = 1860, 1780, and 1720 cm^{-1}). More extensive changes must occur in curing to account for the loss of weight, but we have not identified the species eliminated during curing.

The molecular weight distributions of these oligomers were approximated by size-exclusion chromatography (SEC) in THF solution, based on polystyrene standards. The chromatogram revealed a relatively broad, triphasic distribution, as is expected for typical products of condensation polymerizations. This analysis indicates that the molecular weight of 8 was apparently low. As is usually the case with SEC, the values obtained were relative to polystyrene and significant errors in absolute values can result. In order to obtain an independent approximation of the molecular weight of 8, we dialyzed the ammonium salt of polymer 8—obtained by treating it with aqueous NH$_4$OH—versus distilled water. A conventional dialysis membrane was used with a cutoff of 16 000. No material passed through the membrane, indicating that the polymeric molecules in solution were probably larger than protein molecules of molecular weight of ca. 16 000. This indication of high molecular weight may, however, be complicated by association of the polyanions in solution.

We also ran the reaction of CpNa with PMDA using NaH as the base. This produced oligomer that was similar to polymer 8 made using NEt$_3$ but of slightly higher molecular weight (GPC). The oligomer was film-forming and somewhat less intensely colored. Experiments in which we added the PMDA to CpNa (reverse addition) produced low molecular weight oligomers in significantly lower yields. Very rapid addition of CpNa to PMDA also afforded oligomers in somewhat lower yield. Additions of CpNa to PMDA at room temperature and at −78 °C, respectively, produced low yields of 8 that were contaminated by unreacted starting monomers and their byproducts (pyromellitic acid, dicyclopentadiene). Heating the polymerization mixture to reflux temperature for several hours after it had slowly warmed from 0 °C to room temperature did not yield polymer of higher molecular weight.

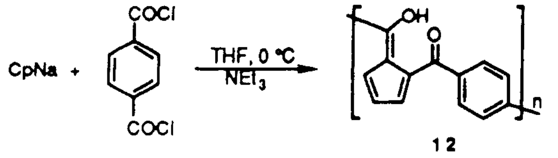
We performed experiments in which the trielectrophile 1,3,5-benzenetricarboxylic acid chloride (**10**) was included as a minor component. As little as 0.13 equiv of **10** was sufficient to produce an intractable polymer. When the proportion of **10** was decreased to 0.01 equiv, a viscous material was obtained that was only partially soluble in THF.

Polymer **8** could be catalytically hydrogenated to form **11** using 5% rhodium on alumina catalyst under 30 atm of H_2. The color of the oligomer diminished in intensity upon hydrogenation, presumably because of the interruption of the extended conjugation of the unsaturated structure of polymer **8**. IR and NMR analyses indicated that only the cyclopentadiene ring of **8** was hydrogenated: ^{13}C NMR signals (20 °C, D_2O, pD 9) assigned to the cyclopentadiene segment at δ 136.8, 128.9, 126.8, and 126.4 disappeared on hydrogenation and were replaced by signals at δ 27.9, 30.2, and 44.6 (cyclopentyl).



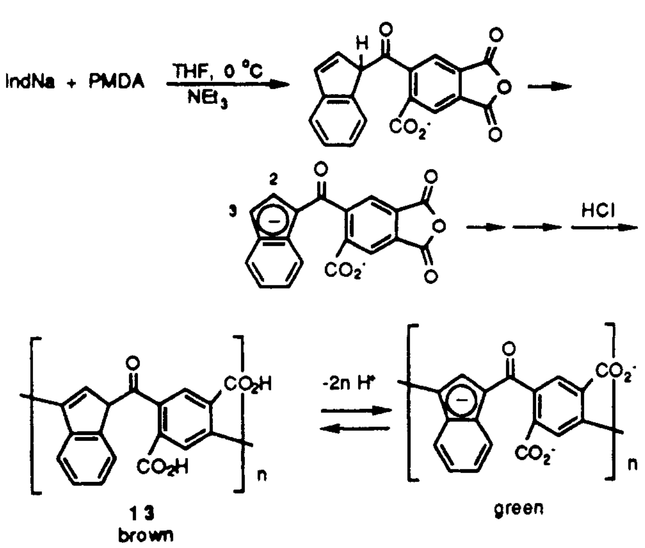
Dicarboxylic acid chlorides—dielectrophiles commonly used in the synthesis of nylons and polyesters—also afforded polymers when we added carbon dinucleophiles to them. For example, terephthaloyl chloride reacted immediately at 0 °C when treated with CpNa to form **12**.

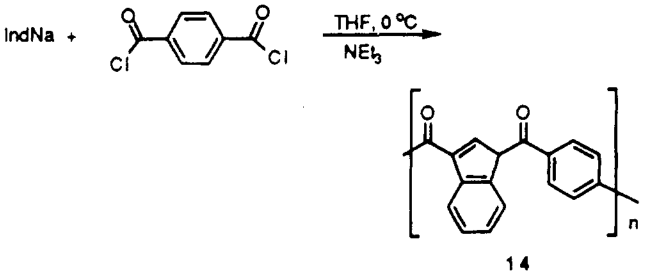
Toward the end of the addition of CpNa to terephthaloyl chloride, polymer **12** precipitated from the THF solution as a maroon suspension. This material was much less soluble than products obtained from dianhydride dielectrophiles. Polymer **12** was partially soluble in hot THF, CH_2Cl_2, and toluene. Films cast from these solvents were of relatively low quality owing to partial precipitation of solid polymer as the cast solutions concentrated.



Condensations of IndNa (Ind$^-$ = indenyl) with PMDA also afforded oligomers. This reaction is of interest because it demonstrates that Ind$^-$ can also act as a latent dinucleophile. The expected structure of oligomer **13** has a 1,3-pattern of substitution of the five-membered ring.[7] Treatment of **13** with aqueous base (pH > 8) resulted in the formation of a vivid green solution, which reverted reversibly to orange–brown when acidified.

In contrast to the poorly-soluble polymer **12** that was formed from the reaction of CpNa with terephthaloyl chloride, polymer **14** that resulted from the addition of IndNa to terephthaloyl chloride was very soluble in THF, acetone, etc. This bright-orange solution was noticeably more viscous than solutions of polymer **9** prepared with CpNa and PMDA, and high-quality orange films could be cast from solution.





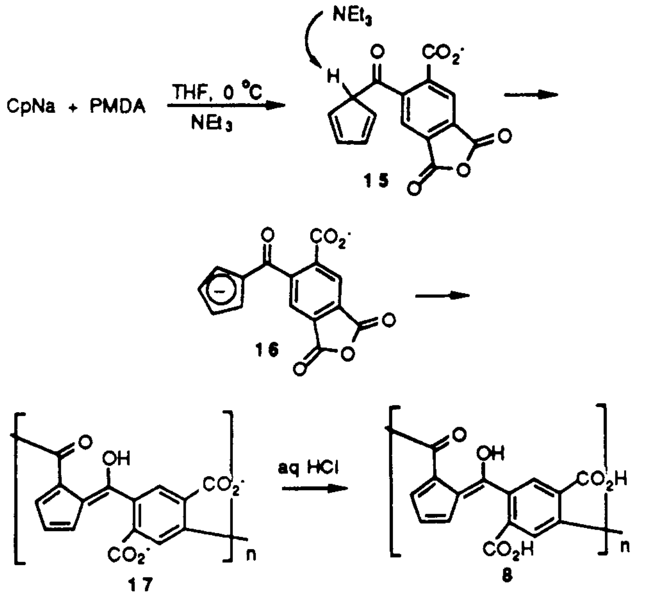
A substantial fraction of the polymers used in large scale are synthesized by reactions of nitrogen- or oxygen-containing dinucleophiles (diamines or diols) with dicarboxylic acids or derivatives of them (anhydrides, acid halides, esters, isocyanates). These polymerizations are successful primarily because the per-step yields of the condensation reactions are high.[8,9] It is generally agreed that any strategy aimed at forming new condensation polymers of reasonably high degrees of polymerization must be based on high-yield condensation steps.

Carbon nucleophiles, like oxygen and nitrogen nucleophiles, can react with certain dielectrophiles such as dianhydrides, diacid chlorides, etc., in excellent yields. We were surprised to discover that there are no reported examples of condensation polymerization reactions of carbon dinucleophiles.

We report herein reactions of the carbon-centered latent dinucleophiles, cyclopentadienide anion and indenyl anion, with a variety of difunctional carbonyl compounds that lead to oligomers and polymers.

Our model studies of high-yield coupling reactions—between CpNa and benzoyl chloride or phthalic anhydride to form **1** and **5**, respectively—encouraged us to run polymerization condensations with dianhydrides and diacid chlorides that are commonly used to form polyimides and polyamides. Reactions between CpNa and PMDA, BTDA, etc., produced oligomeric and polymeric materials in excellent yields.

We envision the condensation of CpNa with PMDA to occur with the initial formation of the transitory intermediate **15** which is then deprotonated by triethylamine to generate **16**. Because it has both nucleophilic and electrophilic functionalities present, species **16** can react further to ultimately form oligomeric polyanion **17**. ^{13}C NMR spectroscopic data indicate that the product has para carboxylate groups, and the structure is so indicated.



Some meta isomer is probably also present. The protonated form, oligomer 8, can be isolated in near quantitative yield as a dark orange–brown solid after treatment of the reaction mixture with aqueous HCl. Oligomer 8 is soluble in THF, ethyl acetate, alcohols, and other organic solvents. It is insoluble in water at pH 7 but dissolves readily as the polyanion 17 at pH > 8.

This class of oligomers and polymers has attractive physical properties. Because most of these oligomers are soluble in water and in organic solvents, they should be easily processed. Although they are of relatively low molecular weight, several can be cast from solution to form thin, optically clear films. The oligomers derived from CpNa and PMDA or BTDA are thermosets, becoming insoluble when thermally cured.

Many polymers such as polyimides, PEEK, poly(phenyl sulfide), poly(phenyl carbonate), etc., that have a high proportion of aromatic units in their backbones have useful combinations of high thermal stability and strength but may be difficult to process.[10] In contrast, the structures of these polymers can be tailored to impart both stability and processability. They also have residual functionality that makes possible postpolymerization modification and cross-linking chemistry.

Experimental Section

General Procedures. THF was distilled under argon from deep-violet solutions of sodium–benzophenone. CpNa was prepared from Na and cyclopentadiene by a standard procedure.[11] Indene, high-purity 1,2,4,5-benzenetetracarboxylic dianhydride (PMDA), 1,3,5-benzenetricarboxylic acid chloride, terephthaloyl chloride, sodium hydride, and 5% Rh on alumina were used as received from Aldrich Chemical Co. We sublimed a sample of this PMDA for comparison and did not detect significant differences in the molecular weights of the oligomers produced. Benzophenonetetracarboxylic dianhydride (BTDA) was used as received from Gulf Specialty Chemicals. Triethylamine was distilled from calcium hydride under nitrogen and stored over molecular sieves. Diazomethane[12] was prepared using a literature procedure.

NMR spectra were obtained at 300 MHz on Bruker instruments. Chemical shifts are reported in ppm relative to residual solvent protons referenced to TMS. Size-exclusion chromatography was performed on a Waters HPLC equipped with a PL gel column. Thermal analyses (DSC, TGA) were performed on a Du Pont 9900 thermal analysis instrument.

Moisture-sensitive solid components were weighed in a Vacuum Atmospheres or Braun MB-150 glovebox under N_2. All reactions were run under dry argon using standard Schlenk-tube techniques.

Model Reactions. 1-Benzoyl-6-hydroxy-6-phenylfulvene (1). CpNa (2.50 g, 28.4 mmol) dissolved in THF (ca. 50 mL) and triethylamine (8.3 mL, 60 mmol) was added dropwise at 0 °C with stirring to a solution of benzoyl chloride (57 mmol, 6.6 mL) in 100 mL of THF. During the addition the solution turned orange. After overnight stirring, the mixture was added to ca. 200 g of ice containing 5 mL of concentrated HCl and extracted with ether. The ether solution was dried with anhydrous magnesium sulfate and filtered, and the solvent was removed by rotary evaporation. Compound 1 was obtained as a violet–orange crystalline solid (>95%). Mp: 103 °C (lit.[2] mp 102–103 °C). ^{1}H NMR (20 °C, acetone-d_6): δ 7.6 (m, 10 H, Ph), 6.7 (d, 2 H, H_b), 6.25 (t, 1 H, H_a).

Reaction of CpNa with Phthalic Anhydride To Form 6. A solution of phthalic anhydride (2.00 g, 6.75 mmol) in 100 mL of THF and triethylamine (2 mL) was cooled in an ice bath under argon. CpNa (2.0 M, 1.7 mL, 3.4 mmol) was added dropwise via a pressure-equalizing addition funnel. Immediately upon addition of the first drop, the solution turned yellow and became successively darker yellow during the addition. The mixture became amber-colored as it slowly warmed to room temperature overnight. It was then added to 300 mL of dilute aqueous acetic acid, extracted with ether, washed with water, and dried over anhydrous sodium sulfate. A crude sample of 6 was isolated by quenching with aqueous HCl. IR (KBr, cm^{-1}): 3080–2880, 1850, 1700, 1600, 1470, 1360, 1240, 1100, 890, 710, 540. ^{1}H NMR (acetone-d_6, 20 °C): δ 15.1 (s, 1 H, OH), 7.71 (m, 8 H, ArH), 6.84 (d, 2 H, C_5H), 6.35 (t, 1 H, C_5H). ^{13}C NMR (D_2O, pD 9, 20 °C): δ 146, 139, 138, 130, 129, 128, 127, 125. ^{13}C NMR (acetone-d_6, 20 °C): δ 157.2, 13.3, 125.6, 125.0, 122.9, 119.4, 61.2.

Treatment of 6 with Diazomethane To Form 7. An ethereal solution of diazomethane, prepared from *N*-nitrosomethylurea,[12] was gradually added to the product solution (from the reaction of CpNa with phthalic anhydride) until nitrogen evolution ceased. The reaction was quenched with glacial acetic acid and washed with saturated sodium bicarbonate and then water. TLC indicated that a yellow spot could be separated from more polar material upon elution with 30/70 acetone/pentane. Compound 7 was obtained as a crystalline orange–yellow solid (>95%). Mp: 197 °C. ^{1}H NMR ($CDCl_3$, 20 °C): δ 7.58 (m, 8 H, ArH), 6.81 (d, 2 H, C_5H), 6.31 (t, 1 H, C_5H), 3.77 (s, 6 H, CO_2Me). IR (KBr, cm^{-1}): 3430, 3060, 2950, 1770, 1720, 1685, 1680, 1470, 1430, 1280, 1190, 1120, 1070, 1030, 950, 740, 690. Anal. Calcd for $C_{23}H_{18}O_6$: C, 70.76; H, 4.65. Found: C, 69.88; H, 4.89.

Polymers from CpNa. Condensation of CpNa with PMDA To Form Oligomer 8. In a typical synthesis, sublimed 1,2,4,5-benzenetetracarboxylic dianhydride (PMDA; 2.7 g, 12 mmol) dissolved in 100 mL of THF was treated with NEt_3 (2 mL, 15 mmol) and cooled to 0 °C. Cyclopentadienylsodium (CpNa; 2.15 M in THF, 5.8 mL, 12 mmol) was added over 0.5 h. After overnight stirring and warming to ambient temperature, the dark-brown solution was added to 300 mL of 0.25 M aqueous HCl and stirred until the oligomer agglomerated. The aqueous solution was decanted, and the oligomer was dissolved in THF and dried over anhydrous sodium sulfate. Residual THF was removed by rotary evaporation. The oligomer was ground to a fine powder, washed with 500 mL of water in 100-mL portions, and dried over P_2O_5 at 110 °C (<10^{-2} Torr). This procedure yielded 2.8 g (87%) of 8 as a dark-brown granular solid. ^{13}C NMR (D_2O, pH 9, 20 °C): δ 176.7, 156.2, 138.3, 137.9, 136.8, 133.1, 128.9, 127.5, 127.4, 126.8, 136.4, 126.1. IR (film cast on NaCl, cm^{-1}): 2960, 2880, 1780, 1720, 1490, 1400, 1250, 1110, 1040, 870, 790. Anal. Calcd for $C_{15}H_8O_6$: C, 63.39; H, 2.84. Found: C, 63.55; H, 2.69. The ammonium salt of 8 could be obtained by treating it with aqueous NH_4OH, and films could be cast from these solutions. IR (film on AgCl, cm^{-1}): 2960, 1780, 1720, 1580, 1470, 1360, 1250, 1010, 790.

Heat Treatment of Oligomer 8. Films of oligomer 8 cast on glass microscope slides were heated in air to 115 °C for 1 h in a laboratory gravity oven. The films darkened considerably upon heating and became insoluble in organic solvents and aqueous base. Free-standing films of cured 8 could be floated off the slides by soaking them in distilled water. IR (film on NaCl, cm^{-1}): 3080, 2960, 1860, 1780, 1720, 1615, 1360, 1230, 900, 30.

Catalytic Hydrogenation of 8 To Form 11. A 0.5-g sample of 8 dissolved in 50 mL of 5:1 ethyl alcohol/glacial acetic acid was treated with 20 mg of 5% Rh on alumina, pressurized to 30 atm with H_2, and stirred magnetically at room temperature for 20 h. ^{13}C NMR signals (20 °C, D_2O, pH 9) assigned to the cyclopentadiene segment at δ 136.8, 128.8, 126.8 and 126.4 disappeared on hydrogenation and were replaced by signals at δ 27.9, 30.2, and 44.6 (cyclopentyl). IR (film on NaCl, cm^{-1}): 3440, 2960, 2880, 2600, 1780, 1720, 1620, 1560, 1490, 1430, 1240, 1110, 1040, 870, 780. This procedure produced **11** in near-quantitative yield.

Polymerization Reaction between CpNa and BTDA To Form Oligomer 9. Benzophenonetetracarboxylic dianhydride (BTDA; 7.00 g, 21.7 mmol) was added to 200 mL of THF containing 25 mL of NEt_3, the solution was cooled in an ice bath, and CpNa (2.0 M in THF, 11 mL) was added dropwise via a pressure-equalizing addition funnel. During the addition the solution darkened significantly until it was black–orange. The ice bath was removed, and the solution was warmed to room temperature. A very dark orange solution was obtained. This solution was quenched by adding it to ca. 300 g of ice containing 5 mL of concentrated HCl. The addition of diethyl ether caused the polymer to precipitate and adhere to the inside of a separatory funnel. The polymer was dissolved in THF and dried over anhydrous sodium sulfate, and the solvent was removed by rotary evaporation. The orange–brown polymer **9** (7.8 g) had excellent film-forming properties, and very long fibers could be pulled from concentrated solution. The polymer was soluble in THF, acetone, alcohols, and ethyl acetate, as well as in aqueous base. IR (film on NaCl, cm^{-1}): 3080, 2980, 1870, 1790, 1740, 1680, 1620, 1500, 1240, 915, 725. Anal. Calcd for $C_{22}H_{12}O_7$: C, 68.04; H, 3.11. Found: C, 66.33; H, 3.22.

Condensations with 1,3,5-Benzenetricarboxylic Acid Chloride. PMDA (3.02 g, 13.9 mmol) dissolved in THF (ca. 200 mL) and 1,3,5-benzenetricarboxylic acid chloride (0.050 equiv, 0.69 mmol, 180 mg) and sodium hydride (excess, 60% dispersion in mineral oil) were treated with CpNa (1 equiv, 2.0 M, 14 mmol, 7.0 mL) dropwise at 0 °C. During the addition the solution turned deep orange–brown. After stirring overnight and warming to room temperature the mixture was poured over ca. 400 g of ice containing 4 mL of concentrated HCl. The aqueous phase was then decanted from the agglomerated polymer. The polymer was dissolved in THF, the solution was dried over anhydrous sodium sulfate, and THF was removed by rotary evaporation and subjected to high vacuum ($<10^{-3}$ Torr). This procedure afforded 2.8 g of polymer that was partially soluble in THF. The THF solutions were noticeably viscous. Films could be cast from THF solution.

Condensation of CpNa with Terephthaloyl Chloride To Form 12. Terephthaloyl chloride (97%, 3.2 g, 15 mmol) dissolved in ca. 100 mL of THF was treated with triethylamine (3.2 mL, 23 mmol). This solution was cooled to 0 °C, and CpNa (2.0 M, 7.6 mL) was added dropwise. During the addition the solution turned bright orange, and toward the end an orange precipitate formed. After overnight stirring and warming, the mixture was poured over 300 g of ice containing ca. 5 mL of concentrated HCl. The mixture was stirred until the polymer agglomerated. The polymer was extracted into THF, dried over anhydrous sodium sulfate, and filtered, and the solvent was removed by rotary evaporation. Polymer **12** (3.2 g) was isolated as an orange powder. This material was soluble in THF, from which soluble, high-quality orange films could be cast. Anal. Calcd for $C_{13}H_8O_2$: C, 79.58; H, 4.11. Found: C, 79.46; H, 5.86.

Polymerization Reaction between Indenylsodium and PMDA To Form 13. PMDA (2.00 g, 9.16 mmol) in 100 mL of THF was cooled in an ice bath, and triethylamine (3 mL) was added. Indenylsodium (51 mL, 0.18 M, 9.2 mmol) was added dropwise via a pressure-equalizing addition funnel. An immediate reaction occurred with the formation of a deep orange–black solution. After overnight stirring the solution was a deep orange. It was quenched with 100 mL of aqueous HCl and stirred until the polymer agglomerated. The polymer was dissolved in acetone, dried over anhydrous sodium sulfate, and filtered and the solvents were removed by rotary evaporation. Polymer **13** (2.2 g) was obtained as a deep-orange material that was soluble in acetone, THF, and alcohols. High-quality films could be cast from THF, and fibers could be pulled from concentrated solution. Treatment of **13** with 1 M aqueous NaOH resulted in the formation of deep-green solutions that cast deep-green films. Anal. Calcd for $C_{18}H_9O_5$: C, 70.82; H, 2.97. Found: C, 69.36; H, 3.63.

Polymerization Reaction between Indenylsodium and Terephthaloyl Chloride To Form 14. Terephthaloyl chloride (1.00 g, 4.93 mmol) in ca. 100 mL of THF was cooled in an ice bath, and 1.5 mL of triethylamine was added. Indenylsodium (14 mL, 0.18 M, 2.5) was added dropwise, and an immediate reaction ensued, with the solution gradually darkening. After overnight stirring the solution was deep orange–brown. It was quenched with 100 mL of aqueous HCl and stirred until the polymer agglomerated. It was redissolved in THF, dried over anhydrous sodium sulfate, and filtered, and the solvent was evaporated. Polymer **14** was obtained as a granular orange solid that formed viscous solutions and cast high-quality films.

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References and Notes

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