124 *Macromolecules* **1995,** *28,* 124−130

Diels−Alder Polymerization between Bis(cyclopentadienones) and Acetylenes. A Versatile Route to New Highly Aromatic Polymers

Uday Kumar and Thomas X. Neenan*

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

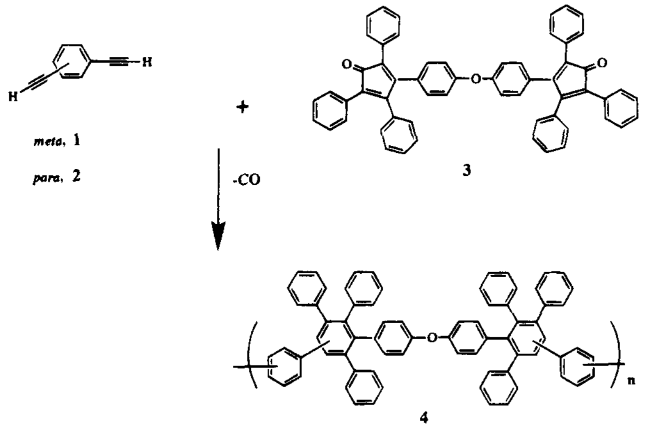
Received June 29, 1994; Revised Manuscript Received September 30, 1994⊗

ABSTRACT: New aromatic thermally stable polymers prepared by the Diels−Alder polymerization between diacetylenes and bis(cyclopentadienones) are described. The diacetylenes used were 1,3-diethynyl-5-(trimethylsilyl)benzene, 1,3-diethynyltetrafluorobenzene, 4,4′-diethynylbenzophenone, 2,5-diethnylthiophene, 1,3-bis[2-(methoxycarbonyl)ethynyl]benzene, 1,3-bis(1-bromoethynyl)benzene, and 1,3-bis[2-[(*N,N*-dimethylamino)carbonyl]ethynyl]benzene. Polymerization of these monomers with 4,4′-(oxy-*p*-phenylene)bis[2-(4-bromophenyl)-3-(3-methylphenyl)-5-phenylcyclopentadienone], 4,4′-(oxy-*p*-phenylene)bis[2,5-diphenyl-3-(3-methylphenyl)cyclopentadienone], or 4,4′-(oxy-*p*-phenylene)bis[2,3,5-tris(3-methylphenyl)cyclopentadienone] yielded polymers soluble in tetrahydrofuran, *p*-dioxane, cyclohexylbenzene, *N*-methylpyrrolidinone, toluene, xylene, chloroform, chlorobenzene, or *N,N*-dimethylformamide. The molecular weights of the polymers were strongly affected by the concentration of the reactants in the polymerization reaction. Size-exclusion chromatography of the polymers versus polystyrene standards yielded M_n's and M_w/M_n's from 5000 to 140 000 and from 1.4 to 4.2, respectively. The polymers had glass transition temperatures (T_g's) ranging from 245 to 270 °C and onsets of decomposition of 310−480 °C both in air and in argon. The polymers form strong, coherent optically transparent films in thicknesses of 1−7 μm and have potential as photodefinable organic dielectrics.

Introduction

The preparation of polymeric materials with combinations of desirable properties such as thermal stability, tractability, toughness, film-forming capabilities, and ease of preparation is an area of active research.[1,2] In our search for new materials as photodefinable organic dielectrics, we revisited the work of Stille and coworkers on the preparation of polymers by the Diel−Alder polymerization of diethynylbenzenes with bis(cyclopentadienones). This work,[3−9] reported in a series of papers between 1967 and 1972, centered on the copolymerization of *m*- or *p*-diethynylbenzene (**1** and **2**) with 3,3′-(oxy-*p*-phenylene)bis(2,4,5-triphenylcyclopentadienone) (**3**; Scheme 1) and yielded thermally stable, aromatic polymers with high glass transition (T_g) temperatures. High molecular weights were achieved because the reverse Diels−Alder reaction is prevented by the loss of carbon monoxide in the polymerization reaction. Of particular interest to us was the report of the unusually high solubility of these highly aromatic materials in common organic solvents (toluene, chloroform, etc.), due to the mixture of meta and para catenation achieved in the polymerization reaction.[10] Despite their attractive properties, materials such as **4** were virtually ignored after ~1976, due perhaps in part to the difficulty of preparing diethynylbenzenes by classical methods from the corresponding bismethyl ketones.[11] In light of the newer synthetic methods available for the preparation of aromatics acetylenes,[12−15] we chose to reexamine the synthetic utility of this polymerization reaction. We report here the potential of this polymerization reaction for the preparation of a broad class of new polymers and report the properties of the materials prepared. Specifically we show that a wide range of both terminal diethynyl aromatics may be used and that the efficiency of the polymerization reaction is relatively insensitive to the structure of the acetylene monomers. The materials prepared, though highly aromatic in structure, retain the solubility observed earlier by Stille and may have potential as organic dielectrics. We also report on our less successful efforts to polymerize internal acetylenes and our efforts to understand the difficulties with the latter systems.

Scheme 1



Results and Discussion

Monomer Syntheses. (a) Acetylenes. The structures of the terminal diethynyl aromatics used in this study are shown in Figure 1. Aromatic acetylenes are most easily prepared by the Pd/Cu-catalyzed coupling of (trimethylsilyl)acetylene with the corresponding aryl bromides or iodides, followed by the removal of the protecting trimethylsilyl group. We have previously reported the syntheses of monomer **5** by this method, starting from 1,3-dibromo-5-(trimethylsilyl)benzene,[16] in turn easily obtained by the monolithiation of 1,3,5-tribromobenzene followed by treatment with trimethylsilyl chloride. Monomer **6** was prepared according to our earlier procedure starting from commercially available 1,2,3,5-tetrafluorobenzene. Iodination of positions 4 and 6[17] was followed by subsequent replacement of

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⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1994.

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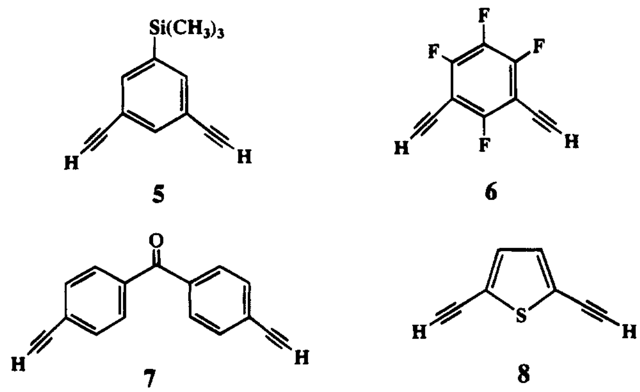
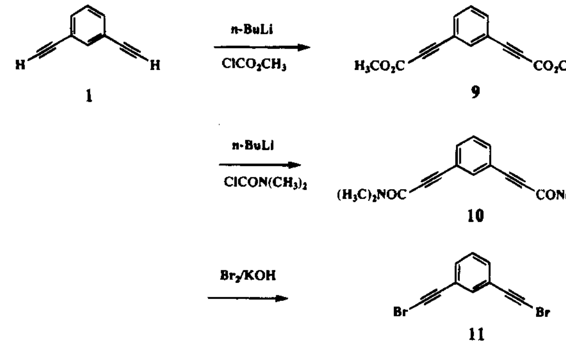


Figure 1. Structures of monomers **5**–**8**.

Scheme 2



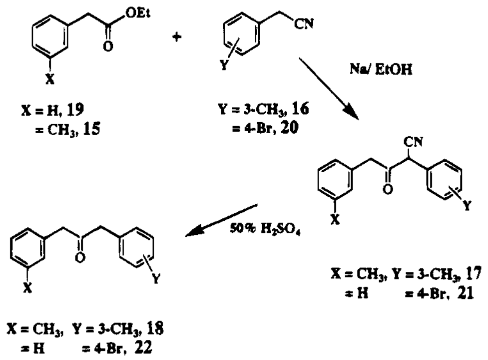
the iodides with acetylenes.[18] The synthesis of 4,4′-diethynylbenzophenone (**7**) was recently reported by Miller.[19] Monomer **8** has been reported by us[20] and others.[12]

The syntheses of the internal diethynyl aromatics are shown in Scheme 2. Commercially available 1,3-diethynylbenzene (**1**) was dilithiated and treated with methyl chloroformate or dimethylcarbamyl chloride to yield monomers **9** and **10**, respectively, in high yield as stable crystalline solids. Monomer **11** was prepared as a slightly unstable yellow solid by treating **1** with an excess of potassium hypobromite in water. Compound **11** was characterized by the loss of the acetylene hydrogen resonances at 3.11 ppm in the proton NMR spectrum and by the dramatic shift of the terminal acetylene carbon resonance in the ^{13}C NMR spectrum (from 82.3 to 50.9 ppm).

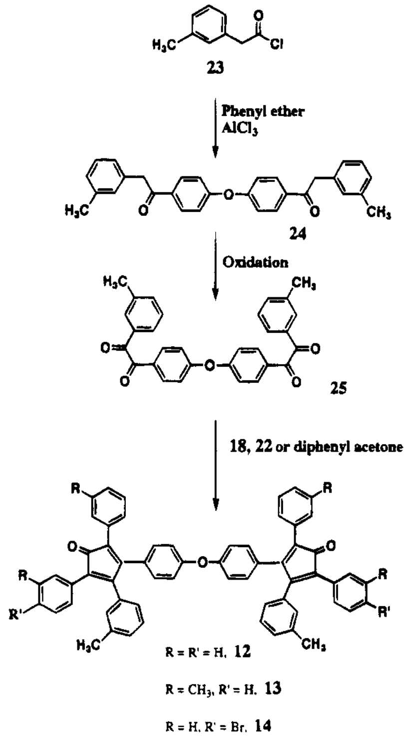
(b) Cyclopentadienones. The syntheses of the bis(cyclopentadienones) (**12**–**14**) were adapted from the procedure reported by Stille and Harris for the synthesis of **3**, involving the condensation of benzils with benzyl ketones.[21,22] We chose to prepare bis(cyclopentadienones) containing multiple methyl groups (**12** and **13**), because we have previously shown that copolymers of **12** or **13** with **1** could be easily imaged by cross-linking with photogenerated radicals and, further, that the efficiency of the cross-linking process was enhanced by the presence of methyl groups.[23] We chose to prepare the brominated bis(cyclopentadienone) **14** because the presence of bromides in the final polymers offered the potential for further elaboration of the polymers.

The synthesis of the necessary methylated and brominated benzyl ketones **18** and **22** is shown in Scheme 3. Claisen condensation between the ethyl ester of 3-tolylacetic acid (**15**) and 3-methylbenzyl cyanide (**16**) followed by *in situ* hydrolysis and decarboxylation of the α-cyano ketone (**17**) in 50% sulfuric acid yielded 1,3-bis(3-methylphenyl)-2-propanone (**18**). The synthesis of the brominated 2-propanone **22** followed an analogous route but started from the Claisen condensation of the ethyl ester of phenylacetic acid (**19**) and 4-bromobenzyl cyanide (**20**) followed by the decyanation of the intermediate α-cyano ketone **21**.

Scheme 3



Scheme 4



The Friedel–Crafts reaction of 3-tolylacetyl chloride (**23**) on diphenyl ether (Scheme 4) followed by oxidation of the intermediate bisacylated phenyl ether (**24**) produced 4,4′-bis[(3-methylphenyl)glyoxalyl]phenyl ether (**25**), after purification of the product by flash chromatography on silica gel. The ketones **18**, **19**, and 1,3-diphenylacetone were each condensed with **25** using a catalytic amount of potassium hydroxide to form the bis(cyclopentadienones) (**12**–**14**). The deep purple crystalline materials were purified by repeated crystallization from ethanol. Proton NMR spectra of the bis(cyclopentadienones) were complex, but in each case the ratio of aromatic to aliphatic protons was consistent with the postulated structure. Three distinct resonances of equal intensity were observed for the methyl groups of **13** (2.23, 2.26, and 2.10 ppm). The bis(cyclopentadienones) each showed a peak in the ^{13}C NMR spectrum at ~200 ppm, consistent with the presence of the carbonyl carbon of the cyclopentadienone rings. The presence of the carbonyl group was confirmed by the observation of a

Table 1

polymer	diacetylene	dienone	monomer concn (mol/L)[a]	rxn time (h)	yield (%)[b]	M_w ($\times 10^3$)	M_n ($\times 10^3$)	M_w/M_n
26a	**5**	**12**	0.288	30	99	38	25	1.5
26b	**5**	**12**	0.548	30	94	49	28	1.8
26c	**5**	**12**	0.449	30	98	72	39	1.8
27	**5**	**13**	0.541	24	91	56	35	1.6
28a	**6**	**12**	0.221	30	94	16	11	1.4
28b	**6**	**12**	0.342	30	89	97	40	2.4
28c	**6**	**12**	0.546	30	97	109	53	2.0
29a	**6**	**13**	0.353	24	84	350	140	2.5
29b	**6**	**13**	0.546	24	87	91	54	1.7
30a	**7**	**12**	0.106	30	87	77	33	2.3
30b	**7**	**12**	0.171	30	88	91	40	2.3
30c	**7**	**12**	0.372	30	92	185	47	3.9
30d	**7**	**12**	0.546	30	98	148	53	2.8
31a	**7**	**13**	0.176	30	93	185	53	3.5
31b	**7**	**13**	0.546	30	87	327	99	3.3
32	**8**	**12**	0.231	30	90	79	19	4.2
33a	**9**	**12**	0.323	30	94	42	19	2.2
33b	**9**	**12**	0.549	30	91	58	28	2.0
34a	**9**	**13**	0.546	26	97	42	26	1.6
34b	**9**	**13**	0.549	26	98	60	32	1.9
35a	**9**	**14**	0.216	24	82	27	14	1.9
35b	**9**	**14**	0.217	24	90	51	20	2.5
35c	**9**	**14**	0.482	24	83	86	32	2.7
36a	**10**	**12**	0.175	30	50	17	11	1.5
36b	**10**	**12**	0.342	30	94	19	12	1.6
36c	**10**	**12**	0.546	30	92	21	14	1.5
37a	**11**	**12**	0.261	26	82	10	5	1.9
37b	**11**	**12**	0.451	26	81	14	7	2.0

[a] All reactions were run on a 10 mmol scale (5 mmol each of diacetylene and dienone). [b] After one precipitation.

strong carbonyl stretching vibration for **12**–**14** at ~1720 cm^{-1} in the infrared spectrum.

Polymerization Reactions. The earlier polymerization procedure reported by Stille and Harris involved the Diels–Alder condensation between bis(cyclopentadienones) and diacetylenes in a Parr reactor at ~200 °C and at pressures of ~200 psi. We chose to carry out the polymerizations between acetylenes **5**–**11** and the bis(cyclopentadienones) **12**–**14** to form the polymers **26**–**37** in Schlenk tubes so that we could visually monitor the reaction. In a typical polymerization, a 1:1 molar mixture of **5** and **12** was prepared in cyclohexylbenzene in a sealed tube. The tube was degassed by a series of freeze–pump–thaw cycles, sealed, and immersed in a thermoregulated bath held at 200 °C. At the end of the reaction time (Table 1), the viscous polymer solution generally still had the magenta color characteristic of the cyclopentadienone moiety. The polymerization reaction was cooled, 50 mg of phenylacetylene was added, and the tube was resealed and heated for a further period to quench the polymerization reaction. A color change from magenta to yellow (generally within 15 min) served as an indication of reaction termination. Polymer **26** was recovered by dilution of the reaction mixture with toluene, followed by precipitation into acetone/hexanes. The polymer was purified by further precipitations, filtered, washed, and dried. Table 1 shows the compositions of all polymers prepared, and Tables 1 and 2 summarize the properties of the polymers.

Table 2. Physical Properties of Polymers 26–37

polymer	T_g (°C)	T_d^{10} (°C) in air[a]	T_d^{10} (°C) in argon[a]	[c]UV λ_{max} (a)
26a	280	522	534	
26b	280	525	533	
26c	280	514	527	256 (108.5)
27	255	346	467	
28a	260	508	543	
28b	*b*	492	540	
28c	285	490	534	
29a	*b*	370	399	250 (89.6)
29b	*b*	356	379	
30a	275	415	432	
30b	270	411	451	
30c	275	456	520	
30d	275	483	501	252 (86.2)
31a	*b*	383	410	254 (90.4)
31b	245	381	413	
32	255	515	527	328 (36.4)
33a	300	472	504	
33b	*b*	474	504	250 (90.9)
34a	250	361	418	244 (85.2)
34b	265	340	368	
35a	270	402	420	
35b	275	406	424	
35c	275	400	432	256 (98.6)
36a	290	433	476	
36b	285	431	465	
36c	290	422	477	250 (89.6)
37a	265	344	360	
37b	260	340	358	240 (75.6)

[a] Temperature measured by TGA at which polymer samples had lost 10% of their initial weight when heated at a rate of 10 °C/min in air or argon. Sample sizes of 3–4 mg were used. [b] These samples did not show any T_g by DSC. [c] The values in parentheses are the adsorptivity denoted by a.

Characterization of the Polymers. The polymers **26**–**37** are all white/tan fibrous materials which are readily soluble in a variety of solvents including tetrahydrofuran (THF), *p*-dioxane, cyclohexylbenzene, *N*-methylpyrrolidinone, toluene, xylene, chloroform, chlorobenzene, or *N*,*N*-dimethylformamide. Solutions of up to 25 wt % can be easily prepared, and the solutions are indefinitely stable to precipitation. The solubility is limited by solution viscosity and not by the inherent property of the polymer. Table 1 shows the strong dependence of the molecular weights of polyphenylenes **26** and **37** on monomer concentration. Typical of condensation polymerizations, an increase in monomer concentration results in an increase in the molecular weight and polydispersity (PD) of the polymers. We were surprised that polymers with molecular weights of 200 000 could be synthesized by this synthetic method; previous workers had reported molecular weights in the range of ~40 000–100 000.[4] The molecular weights of the polymers from the internal acetylenes (**9**–**11**) were lower, with the brominated diacetylenes **11** giving particularly low molecular weights. We attribute the lower molecular weights to the thermal instability of monomers **9**–**11** under the reaction conditions for polymerization. TGA analysis of **11** indicated that the monomer suffered an onset of weight loss at 60 °C, and reached 35% by 140 °C, at a heating rate of 10 °C/min under an atmosphere of argon. Any deviation from perfect stoichiometry in a condensation results in a dramatic decrease in molecular weights. A TGA analysis of monomer **9** under the same conditions showed an onset of decomposition at 160 °C, but with only a 3% weight loss by 200 °C. The enhanced thermal stability of **9** over **11** presumably contributes to the (modest) increase in molecular weight achieved with the former monomer.

Although the proton NMR spectra of the polymers were extremely complex, the ratio of aliphatic to aromatic protons generally agreed well with the structures of the constituent monomer units. In certain instances, individual features of monomer units, such as the trimethylsilyl protons of polymers containing **5**, were discernible and served as useful internal integration standards. A curious feature of polymers containing **9** was the observation of two separate sets of resonances for the methyl groups of the $CON(CH_3)_2$ moieties (2.3 ppm (4 protons) and 2.5–2.9 ppm (8 protons)), suggesting that hydrogens attached to the same carbon have the possibility to see vastly different microenvironments. The ^{13}C NMR spectra of the polymers were equally complex, but in all instances the resonance for the carbonyl carbon of the cyclopentadienone monomers at ~200 ppm disappeared, to be replaced by an increase in the complexity of the aromatic region due to the formation of the new (Diels–Alder produced) phenyl rings.

The polymers formed thick (1–7 μm) coherent films on a variety of substrates (silicon, quartz, aluminum oxide) and, despite their structural complexity, were optically transparent in the UV. Table 2 summerizes the UV data for polymers **26**–**37**. Most polymers show a maximum in absorbance in the UV spectrum at ~250 nm, the exception being polymers containing the thiophene nucleus **32**, with a λ_{max} at 328 nm. Of most interest to us were the low absorbances of the materials at 364 nm (typically ~0.015–0.025 absorbance units/μm), suggesting their utility as photodefinable organic dielectrics. Initial measurements of the dielectric properties of the polymers as 9-mm-thick films on aluminum confirmed that the polymers have dielectric constant values in the range of 2.6–2.9, comparing favorably with typical values of 3.0–3.5 for polyimides.

Most of the polymers exhibited a weak glass transition temperature (T_g) in the range 245–300 °C, with the T_g of any particular series of polymers of the same composition being independent of molecular weight (Table 2). A T_g for polymers containing the fluorinated monomer **6** was particularly difficult to detect and was only observed for two of the five polymers containing **6**. We have no explanation for this observation.

The thermal stabilities of the polymers in air and argon are summarized in Table 2. As expected, the thermal stabilities of the materials are higher in argon than in air, with a difference of ~25–50 °C in T_d^{10} (the temperature at which 10 wt % of the polymers were lost upon heating at 10 °C/min in air or argon) being typically observed. In general, the thermal stabilities of polymers containing **12** showed greater thermal stability than polymers containing **13**, due in part to the higher content of easily oxidizable methyl groups in **13**. Several of the polymers containing **13** showed weight gains of 3–4% in air at temperatures greater than 350 °C due to the oxidation of the pendent groups.

Experimental Section

Materials and Characterization. Phenyl ether, *m*-tolylacetic acid, 3-methylbenzyl cyanide, *N*,*N*-diethyl-4-nitrosoaniline, 1,3-diphenylacetone, ethyl phenylacetate, 4-bromophenylacetonitrile, methyl chloroformate, dimethylcarbamyl chloride, thionyl chloride, and anhydrous aluminum chloride were obtained from Aldrich Chemical Co. and used without further purification. 1,3-Bis[(trimethylsilyl)ethynyl]benzene was obtained from Farchan Laboratories (Gainesville, FL) and purified by flushing through a short column of silica with hexanes as eluent, followed by recrystallization from MeOH; mp 60–62 °C (lit.[20] mp 57–59 °C). Treatment of 1,3-bis[(trimethylsilyl)ethynyl]benzene with methanolic KOH afforded 1,3-diethynylbenzene **1**. 1,3-Diethynyl-5-(trimethylsilyl)benzene (**5**) and 1,3-diethynylthiophene (**8**) were prepared according to literature procedures.

Unless otherwise stated ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a Bruker AM 360 spectrometer and referenced to the solvent peak. IR and UV spectra were determined using Bio-Rad FTS-40 FTIR and HP 8452A diode array spectrophotometers, respectively. IR and UV spectra were measured in polymer films spun on sodium chloride and a quartz disk, respectively. A gel permeation chromatography (GPC) system equipped with a Waters Model 510 pump at a flow rate of 1.0 mL/min, and Waters Model 410 differential refractometer and Viscotek Model 100 differential viscometer detectors were used for molecular weight measurements on Polymer Laboratories PL-gel columns (particle size 5 mm) with THF as a mobile phase. Narrow molecular polystyrene standards were used to calibrate the GPC system. Elemental analyses were obtained from Robertson-Microlit Lab (Madison, NJ). Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were done on a Perkin-Elmer DSC 7/TGA 7 system. The glass transition temperatures were determined at a heating rate of 15 °C after annealing the samples to 300 °C. The peak of the exotherm determined by DSC (rate 10 °C) was taken as the melting point. Aluminum pans containing 5–10 mg of the sample were used. The temperature scale was calibrated using the melting points of indium and tin and is accurate to ±0.1 °C. TGA analysis was done in air and argon at a heating rate of 10 °C/min.

Synthesis of 1,3-Bis[2-(methoxycarbonyl)ethynyl]benzene (9). 1,3-Diethynylbenzene **1** (2.80 g, 22.2 mmol) was dissolved in 200 mL of dry THF under argon and cooled to −78 °C in a dry ice bath. A n-BuLi solution (22.5 mL of a 2.0 M solution in pentane (2.88 g, 44.9 mmol)) was then slowly added over a 30-min period. The resulting suspension of the dilithium salt of diethynylbenzene was stirred for 30 min at −78 °C, followed by the addition of methyl chloroformate (25 mL, 0.32 mol) over a period of 10 min. The resulting light yellow solution was stirred at −78 °C for 30 min and then slowly allowed to warm to room temperature. The reaction mixture was poured into water and extracted with a hexane/ether (2:1) mixture; the organic layer was washed with brine and dried over anhydrous $MgSO_4$. Purification by flash chromatography on a silica gel column using hexane/methylene chloride/ethyl acetate (25:4:1) as eluent gave 1,3-bis[2-(methoxycarbonyl)ethynyl]benzene (**9**) as a white solid (4.58 g, 85%). Mp: 94 °C. ^1H NMR: δ 7.73 (s, 1H), 7.60 (dd, 2H), 7.37 (m, 1H), 3.81 (s, 6H). ^{13}C NMR: δ 154.0 (−COO−), 136.8, 134.6, 129.0, 120.4 (aromatics), 84.2, 81.1 (triple bond), 52.9 ($-CH_3$). Elem anal. Calcd for $C_{14}H_{10}O_4$: C, 69.42; H, 4.16. Found: C, 69.38; H, 3.94.

1,3-Bis[2-[(*N,N*-dimethylamino)carbonyl]ethynyl]benzene (10). A solution of n-BuLi in pentane (18.3 mL of a 2 M solution, 36.5 mmol) was added to a cooled solution (−78 °C, dry ice/acetone) of 1,3-diethynylbenzene **1** (2.00 g, 15.9 mmol) in 170 mL of anhydrous THF, and the resulting white suspension of the dilithio salt of 1,3-diethynylbenzene was stirred at −78 °C for an additional 30 min. Dimethylcarbamyl chloride (17 mL, 23.2 g, 0.216 mol) was added over a 10-min period. Stirring at −78 °C was continued for a further 30 min, and the solution was allowed to warm to room temperature over a 5-h period. The reaction mixture was poured into cold water, and the resulting precipitate was filtered, washed with water, air dried, washed with diethyl ether, and dried in a vacuum oven to give 3.35 g (79%) of 1,3-bis[2-[(*N,N*-dimethylamino)carbonyl]ethynyl]benzene (**10**) as a white solid. ^{1}H NMR: δ 7.68 (s, 1H, aromatics), 7.54 (m, 2H, aromatics), 7.34 (m, 1H, aromatics), 3.26 (s, 3H, $-CH_3$), 3.00 (s, 3H, $-CH_3$). ^{13}C NMR: δ 152.8 (CON), 135.4, 133.8, 129.6, 120.6 (aromatics), 87.3, 82.5 (triple bond). Elem anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.11. Found: C, 71.45; H, 6.22; N, 10.03.

1,3-Bis(bromoethynyl)benzene (11). Bromine (4.5 mL, 13.96 g, 87.3 mmol) was slowly added to an ice cold solution of potassium hydroxide (15.5 g, 0.276 mol) in 40 mL of water. 1,3-Diethynylbenzene **1** (2.25 g, 17.8 mmol) was slowly added to the light yellow solution at 0 °C, accompanied by vigorous stirring. After stirring at 0 °C for 30 min, the reaction mixture was allowed to warm to room temperature and stirring was continued for 24 h in the dark. The resulting yellow suspension was poured into water and extracted with ether, and the organic layer was washed with brine and dried over anhydrous $MgSO_4$. The light yellow solid resulting after the removal of solvent was washed with cold hexane to give 4.70 g (92%) of pure 1,3-bis(bromoethynyl)benzene (**11**) (single spot on TLC). Mp: 67 °C. ^{1}H NMR: δ 7.40 (s, 1H, aromatics), 7.27 (d, J = 7.2 Hz, 2H, aromatics), 7.13 (m, 1H, aromatics). ^{13}C NMR: δ 135.3, 132.0, 128.4, 123.0 (aromatics), 79.0, 50.9 (triple bond). Elem anal. Calcd for $C_{10}H_4Br_2$: C, 42.30; H, 1.42; Br, 56.28. Found: C, 42.50; H, 1.36; Br, 55.98.

Synthesis of *m*-Tolylacetic Acid Ethyl Ester (15). To a solution of *m*-tolylacetic acid (24.9 g, 0.17 mol) in 250 mL of absolute ethanol was added 25 mL of concentrated sulfuric acid, and the solution was refluxed for 4 h. The reaction mixture was allowed to stand overnight and then poured into 1 L of crushed ice. The product was extracted with ether, and the organic layer was washed with water, a 10% sodium bicarbonate solution, and water and dried over $MgSO_4$. After removal of the ether, the residual oil was dried on a vacuum pump for 2 h to yield 27.85 g (93%) of *m*-tolylacetic acid ethyl ester (**15**). The material was used without further purification. ^{1}H NMR: δ 7.2 (m, 1H), 7.1 (m, 3H), 4.1 (q, 2H, $-OCH_2-$), 3.56 (s, 2H, $-CH_2CO-$), 2.33 (s, 3H, $-CH_3$), 1.2 (t, 3H, $-CH_2CH_3$). ^{13}C NMR: δ 171.7 ($-CO-$), 138.1, 134.0, 129.9, 128.4, 127.7, 126.2 (aromatics), 60.8 ($-OCH_2$), 41.3 ($-CH_2CO-$), 21.3 ($-CH_3$), 14.1 ($-CH_2CH_3$).

Synthesis of 1,3-bis(3-methylphenyl)-2-propanone (7). Sodium ethoxide was prepared in situ by dissolving 10.05 g (0.44 mol) of sodium in 200 mL of absolute ethanol. To this solution was added a mixture of **15** (47.5 g, 0.27 mol) and 3-methylbenzyl cyanide (**16**; 28.0 g, 0.21 mol), and the resulting solution was heated at reflux for 4 h. The reaction mixture was cooled, poured into ice cold water, and extracted with ether to remove any unreacted starting materials. The aqueous layer was then acidified with dilute HCl to pH 1 and extracted with ether. The ether extract was washed with water, 10% $NaHCO_3$, and again with water and dried over anhydrous $MgSO_4$. The solvent was removed to yield the α-cyano ketone (**17**) as a slightly impure yellow solid (38.0 g, 71%), which was used in the next step without further purification.

Compound **17** (38.0 g, 0.15 mol) was suspended in 50% sulfuric acid and refluxed for 5 h. The reaction mixture was poured into ice cold water and extracted with ether. The ether extract was washed with water, 10% $NaHCO_3$, and water and dried over $MgSO_4$. The solvent was removed, and the crude product was purified by flash chromatography on silica gel using petroleum ether/dichloromethane/ethyl acetate (20:5:1) as eluent to give 33.25 g (69% based on 3-methylbenzyl cyanide, **16**) of 1,3-bis(3-methylphenyl)-2-propanone (**18**). ^{1}H NMR: δ 7.2 (m, 2H, aromatics), 7.1 (d, 2H, aromatics), 7.0 (m, 4H, aromatics), 3.69 (s, 4H, $-CH_2-$), 2.34 (s, 6H, $-CH_3$). ^{13}C NMR: δ 205.9 ($-CO-$), 138.2, 133.8, 130.2, 128.5, 127.7, 126.5 (aromatics), 48.9 ($-CH_2-$), 21.2 ($-CH_3$). Elem anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.94; H, 7.85.

1-Phenyl-3-(4-bromophenyl)acetone (22). A solution of ethylphenyl acetate (**19**; 35.00 g, 0.123 mol) and 4-bromophenylacetonitrile (**20**; 35.00 g, 0.178 mol) in 60 mL of hot ethanol was added to a solution of sodium ethoxide (8.2 g, 0.356 mol of sodium metal in 210 mL of anhydrous ethanol) at room temperature. The resulting amber solution was refluxed for 4 h, cooled, poured into ice cold water, and extracted once with ether to remove the unreacted starting material. The aqueous layer was acidified with 10% HCl and extracted with ether, and the organic layer was washed with a 10% $NaHCO_3$ solution and brine and dried over anhydrous $MgSO_4$. The light yellow α-cyano ketone (**21**; 47.9 g) that resulted upon removal of the solvent was used in the next step without purification.

Compound **21** was suspended in 120 mL of 50% sulfuric acid and refluxed for 5 h. The resulting dark yellow solution was cooled and poured into ice cold water. The aqueous layer was extracted with ether, and the ether layer was washed with a 10% $NaHCO_3$ solution and brine and dried over anhydrous $MgSO_4$. Purification by flash chromatography on a silica gel column using petroleum ether/ethyl acetate (20:1) as eluent gave 36.49 g (71%) of 1-phenyl-3-(4-bromophenyl)acetone (**22**). Mp: 56 °C. ^{1}H NMR: δ 7.40 (d, J = 8.3 Hz, 2H), 7.32–7.26 (m, 3H), 7.15 (d, J = 6.5 Hz, 2H), 6.98 (d, J = 8.3 Hz, 2H), 3.71 (s, 2H, CH_2), 3.66 (s, 2H). ^{13}C NMR: δ 204.9 (CO), 133.7, 132.8, 131.7, 131.2, 129.4, 128.8, 127.1, 120.0 (aromatics), 49.4, 48.0 (CH_2). Elem anal. Calcd for $C_{15}H_{13}BrO$: C, 62.30; H, 4.53; Br, 27.63. Found: C, 62.21; H, 4.50; Br, 27.69.

Synthesis of 4,4′-Bis[(3-methylphenyl)acetyl]phenyl Ether (24). *m*-Tolylacetyl chloride (**23**) was prepared by refluxing a mixture of *m*-tolylacetic acid and thionyl chloride under argon for 3 h and removing the excess thionyl chloride on a rotary evaporator. A solution of **23** (51.96 g, 0.31 mol) and phenyl ether (22.95 g, 0.16 mol) in 100 mL of carbon disulfide was slowly added to an ice cold suspension of anhydrous aluminum chloride (41.5 g, 0.31 mol) and carbon disulfide (400 mL). The ensuing reaction mixture was stirred at room temperature for 2 h and then refluxed for 1.5 h. The flask was cooled in ice and the aluminum chloride complex decomposed by slow addition of 20% HCl followed by the addition of methylene chloride (200 mL). (Note: Rapid addition of the HCl solution will cause caking of the reaction mixture.) The organic layer was separated, washed with water, a 10% $NaHCO_3$ solution, and water again, and dried over $MgSO_4$. The crude product was purified by flash chromatography on silica gel using petroleum ether/methylene chloride/ethyl acetate (20:4:1) as eluent, yielding 34.1 g (58.2%) of **24**. Mp: 94 °C. ^{1}H NMR: δ 8.07 (d, 4H, aromatics), 7.26 (dd, 2H, aromatics), 7.06 (m, 10H, aromatics), 4.20 (s, 4H, $-CH_2-$), 2.31 (s, 6H, $-CH_3$). ^{13}C NMR: δ 196.2 ($-CO-$), 160.1, 138.4, 134.4, 132.4, 131.0, 130.0, 128.6, 127.7, 126.4, 118.8 (aromatics), 45.4 ($-CH_2-$), 21.4 ($-CH_3$). Elem anal. Calcd for $C_{30}H_{26}O_3$: C, 82.92; H, 6.03. Found: C, 82.36; H, 6.30.

Preparation of 4,4′-Bis[(3-methylphenyl)glyoxalyl]phenyl Ether (25). A suspension of **24** (26.60 g, 0.06 mol) and *N,N*-diethyl-4-nitrosoaniline (32.8 g, 0.18 mol) in 400 mL of anhydrous ethanol was refluxed for 6 h. The reaction mixture was cooled, 100 mL of 50% HCl was added, and the resulting solution was refluxed for an additional 1 h. Upon cooling, the reaction mixture was poured into a beaker containing 1000 mL of water and allowed to stand overnight. The dark brown precipitate was filtered and purified by flash chromatography on silica gel with petroleum ether/methylene chloride/ethyl acetate (15:4:1) as eluent to give 19.55 g (69%) of 4,4′-bis[(3-methylphenyl)glyoxalyl]phenyl ether (**25**). ^{1}H NMR: δ 8.0 (d, 4H, aromatics), 7.7 (d, 4H, aromatics), 7.4 (dd, 4H, aromatics), 7.1 (d, 4H, aromatics), 2.39 (s, 6H, $-CH_3$). ^{13}C NMR: δ 194.5, 192.9 ($-CO-$), 161.1, 139.0, 135.8, 132.9, 132.5, 130.2, 129.1, 128.9, 127.2, 119.3 (aromatics), 21.3 ($-CH_3$). Elem anal. Calcd for $C_{30}H_{22}O_5$: C, 77.90; H, 4.79. Found: C, 77.62; H, 4.67.

Preparation of 4,4′-(Oxy-*p*-phenylene)bis[2,5-diphenyl-3-(3-methylphenyl)cyclopentadienone] (12). A solution of **25** (12.0 g, 26 mmol) and 1,3-diphenylacetone (10.9 g, 52 mmol) in 700 mL of absolute ethanol was brought to near boiling. A solution of potassium hydroxide (1.0 g) in 20 mL of water was then added and the resulting dark purple solution refluxed for 45 min. The reaction mixture was cooled, and the dark purple precipitate was filtered, washed with ethanol, and recrystallized twice from ethanol containing 5% toluene to give 12.55 g (60%) of 4,4′-(oxy-*p*-phenylene)bis[2,5-diphenyl-3-(3-methylphenyl)cyclopentadienone]. Mp: 268 °C. ^{1}H NMR: δ 7.2 (m, 20H, aromatics), 7.0 (m, 4H, aromatics), 6.9 (d, 4H, aromatics), 6.7 (m, 8H, aromatics), 2.1 (s, 6H, $-CH_3$). ^{13}C NMR: δ 200.2 ($-CO-$), 156.7, 154.2, 153.7, 137.5, 132.9, 131.2, 130.8, 130.7, 130.1, 129.9, 129.2, 128.3, 128.1, 127.9, 127.8, 127.4, 126.5, 125.2, 125.0, 118.2 (aromatics), 21.3 ($-CH_3$). Elem anal. Calcd for $C_{60}H_{42}O_3$: C, 88.48; H, 4.96. Found: C, 89.08; H, 5.22.

Preparation of 4,4′-(Oxy-*p*-phenylene)bis[2,3,5-tris(3-methylphenyl)cyclopentadienone] (13). Aldol condensation of **18** and **25** similar to the preparation of **12** gave 4,4′-(oxy-*p*-phenylene)bis[2,3,5-tris(3-methylphenyl)cyclopentadienone] (**13**) in 58% yield. Mp: 192 °C. ^{1}H NMR: δ 7.0–7.1 (m, 20H, aromatics), 6.9 (d, 4H, aromatics), 6.7 (m, 8H, aromatics), (2.23, 2.26, two closely spaced singlets, 12H, $-CH_3$), 2.1 (s, 6H, $-CH_3$). ^{13}C NMR: δ 200.4 ($-CO-$), 156.8, 154.0, 153.6, 137.5, 137.4, 133.0, 131.2, 130.8, 130.7, 130.6, 129.9, 129.2, 128.5, 128.2, 127.9, 127.8, 127.8, 127.1, 126.5, 125.2, 125.1, 118.2 (aromatics), 21.4, 21.3 ($-CH_3$). Elem anal. Calcd for $C_{64}H_{50}O_3$: C, 88.65; H, 5.81. Found: C, 88.96; H, 5.87.

4,4′-(Oxy-*p*-phenylene)bis[2-(4-bromophenyl)-3-(3-methylphenyl)-5-phenylcyclopentadienone] (14). A solution of 4,4′-bis[(3-methylphenyl)glyoxalyl]phenyl ether (**25**; 8.23 g, 17.8 mmol) and 1-phenyl-3-(4-bromophenyl)acetone (**22**; 10.80 g, 37.4 mmol) in 350 mL of absolute ethanol was brought to near boiling. A solution of potassium hydroxide (1.0 g) in 15 mL of water was then added and the resulting dark purple solution refluxed for 45 min. The reaction mixture was cooled, and the dark purple precipitate was filtered, washed with ethanol, and recrystallized twice from ethanol/toluene (1:1) to give 4.05 g (23.5%) of 4,4′-(oxy-*p*-phenylene)bis[2-(4-bromophenyl)-3-(3-methylphenyl)-5-phenylcyclopentadienone] (**14**) (one spot by TLC). Mp: 301 °C. ^{1}H NMR: δ 7.40–7.00 (m, 26H, aromatics), 6.90–6.65 (m, 14H, aromatics), 2.17 (s, 6H, CH_3). ^{13}C NMR: δ 199.8 (CO), 157.0, 156.8, 156.7, 154.8, 154.3, 154.1, 153.7, 137.7, 137.6, 132.7, 131.6, 131.3, 131.2, 131.1, 130.6, 130.5, 130.1, 129.9, 129.7, 129.6, 129.5, 129.4, 128.1, 128.0, 127.9, 127.6, 126.5, 126.3, 125.4, 125.2, 124.0, 123.8, 121.8, 118.4, 118.2 (aromatics), 21.3 (CH_3). Elem. anal. Calcd for $C_{60}H_{40}Br_2O_3$: C, 74.38; H, 4.16; Br, 16.50. Found: C, 74.06; H, 4.23; Br, 16.66.

Polymer Synthesis. A representative polymer synthesis is as follows: A 20-mL Schlenk tube was charged with a suspension of 4,4-(oxy-*p*-phenylene)bis[2,5-diphenyl-3-(3-methylphenyl)cyclopentadienone] (**12**; 1.50 g, 1.85 mmol) and cyclohexylbenzene (8.25 mL). To this mixture was added 366 mg (1.85 mmol) of the diacetylene **5**, giving an initial total concentration of reactants in the solvent of 0.449 mol/L. The reaction mixture was degassed by a series of three freeze–pump–thaw techniques. The Schlenk tube was then purged with argon, sealed, and placed in an oil bath at 200 °C for 40 h. The tube was cooled and opened (CAUTION! CO pressure). To the viscous magenta solution was added 50 mg of phenylacetylene; the tube was degassed for a second time and stirred at 200 °C for a further 3 h. The magenta color was discharged within 30 min. The clear viscous yellow liquid was cooled, diluted with toluene, and precipitated into hexane/acetone (3:1). Polymer **26c** was purified by dissolving it in toluene, reprecipitating into hexane/acetone (3:1), filtering, and drying in a vacuum pump at 70 °C for 24 h. The properties of **26c** and other polymers are given below or summarized in Tables 1 and 2.

Polymer Characterization. Polymer 26a. Calcd for $C_{71}H_{56}OSi$: C, 89.45; H, 5.91; Si, 2.94. Found: C, 88.78; H, 6.15; Si, 3.05.

Polymer 26b. Calcd for $C_{71}H_{56}OSi$: C, 89.45; H, 5.91; Si, 2.94. Found: C, 89.38; H, 5.66; Si, 2.87.

Polymer 26c. ^{1}H NMR: δ 7.35 (s, 2H, aromatics), 7.0–7.25 (m, 10H, aromatics), 7.0–6.5 (m, 23H, aromatics), 6.4–6.25 (m, 4H, aromatics), 1.95 (two overlapping singlets, 6H, CH_3), −0.08 (s, 9H, $SiCH_3$). ^{13}C NMR: δ 155.0–155.2, 141.0–125.5, 117.1 (aromatics), 21.1 (CH_3), −1.4 ($SiCH_3$). IR (cm^{-1}): 1605, 1506. Calcd for $C_{71}H_{56}OSi$: C, 89.45; H, 5.92; Si, 2.94. Found: C, 89.17; H, 5.94; Si, 2.82.

Polymer 27. IR (cm^{-1}): 1603, 1504. Calcd for $C_{75}H_{64}OSi$: C, 89.24; H, 6.39; Si, 2.78. Found: C, 89.07; H, 6.25; Si, 2.91.

Polymer 28a. Calcd for $C_{68}H_{44}F_4O$: C, 85.69; H, 4.65; F, 7.97. Found: C, 85.86; H, 4.89; F, 7.31.

Polymer 28b. ^{1}H NMR: δ 7.41 (s, 1H, aromatics), 7.3–6.4 (m, 33H, aromatics), 6.4–6.15 (m, 4H, aromatics), 2.0 (two overlapping singlets, 6H, CH_3). ^{13}C NMR: δ 155.9–154.8, 152.7, 149.8, 148.1, 145.8, 141.5–126.1, 117.3, 117.1, 115.5, 115.2 (aromatics), 21.1, 21.0 (CH_3). IR (cm^{-1}): 1600, 1504, 1476. Calcd for $C_{68}H_{44}F_4O$: C, 85.69; H, 4.65; F, 7.97. Found: C, 85.38; H, 4.76; F, 7.95.

Polymer 28c. Calcd for $C_{68}H_{44}F_4O$: C, 85.69; H, 4.65; F, 7.97. Found: C, 85.45; H, 4.41; F, 7.90.

Polymer 29a. Calcd for $C_{72}H_{52}F_4O$: C, 85.69; H, 5.19; F, 7.53. Found: C, 84.39; H, 4.89; F, 7.31.

Polymer 29b. ^{1}H NMR: δ 7.2–6.45 (m, 30H, aromatics), 6.4–6.1 (m, 4H, aromatics), 2.35–2.15 (m, 6H, CH_3), 2.15–1.7 (12H, CH_3). ^{13}C NMR: δ 155.3, 155.0, 152.6, 148.3, 145.8, 142.0–126.0, 117.3, 115.6, 115.4 (aromatics), 21.3–20.8 (CH_3). IR (cm^{-1}): 1603, 1503, 1476. Calcd for $C_{72}H_{52}F_4O$: C, 85.69; H, 5.19; F, 7.53. Found: C, 85.48; H, 4.89; F, 7.30.

Polymer 30a. Calcd for $C_{75}H_{52}O_2$: C, 91.43; H, 5.32. Found: C, 90.25; H, 5.05.

Polymer 30b. Calcd for $C_{75}H_{52}O_2$: C, 91.43; H, 5.32. Found: C, 90.41; H, 5.02.

Polymer 30c. Calcd for $C_{75}H_{52}O_2$: C, 91.43; H, 5.32. Found: C, 90.37; H, 5.69.

Polymer 30d. ^{1}H NMR: δ 7.55 (two overlapping singlets, 6H, aromatics), 7.35–7.05 (m, 14H, aromatics), 7.0–6.0 (22H, aromatics), 6.45–6.25 (4H, aromatics), 2.00 (d, 6H). ^{13}C NMR: δ 196.2 (CO), 155.4–154.8, 146.0, 142.2–125.9, 117.4, 117.1 (aromatics), 21.1 (CH_3). IR (cm^{-1}): 1664, 1604, 1502. Calcd for $C_{75}H_{52}O_2$: C, 91.43; H, 5.32. Found: C, 91.01; H, 5.16.

Polymer 31a. Calcd for $C_{79}H_{60}O_2$: C, 91.12; H, 5.80. Found: C, 90.67; H, 5.76.

Polymer 31b. ^{1}H NMR: δ 7.55 (s, 6H, aromatics), 7.26 (s, 4H, aromatics), 7.15–6.9 (m, 8H, aromatics), 6.9–6.5 (m, 20H, aromatics), 6.5–6.25 (4H, aromatics), 2.25 (two overlapping doublets, 6H, CH_3), 2.0 (s, 12H, CH_3). ^{13}C NMR: δ 196.3 (CO), 155.5–154.8, 146.2, 142.2–126.0, 117.4–117.1 (aromatics), 21.3, 21.1 (CH_3). IR (cm^{-1}): 1665, 1604, 1501. Calcd for $C_{79}H_{60}O_2$: C, 91.12; H, 5.80. Found: C, 90.96; H, 5.56.

Polymer 32. ^{1}H NMR: δ 7.62 (s, 2H, aromatics), 7.17 (s, 11H, aromatics), 7.05 (s, 6H, aromatics), 6.94 (s, 4H, aromatics), 6.9–6.5 (m, 12H, aromatics), 6.4–6.2 (m, 5H, aromatics), 1.99 (two overlapping singlets, 6H, CH_3). ^{13}C NMR: δ 155.8–155.6, 143.2–126.1, 117.3, 117.0 (aromatics), 21.0 (CH_3). IR (cm^{-1}): 1599, 1501. Calcd for $C_{66}H_{46}SO$: C, 89.35; H, 5.23; S, 3.61. Found: C, 88.64; H, 5.76; S, 3.59.

Polymer 33a. Calcd for $C_{72}H_{52}O_5$: C, 86.72; H, 5.26. Found: C, 85.97; H, 5.20.

Polymer 33b. ^{1}H NMR: δ 7.3–6.4 (m, 34H, aromatics), 6.2 (s, 6H, aromatics), 3.25 (s, 5H, CO_2CH_3), 3.1 (m, 1H, CO_2CH_3), 2.0 (s, 6H, CH_3). ^{13}C NMR: δ 169.2, 169.0 (CO), 155.1–154.8, 142.6–125.5, 117.0 (aromatics), 51.7, 51.6 (CO_2CH_3), 21.0 (CH_3). IR (cm^{-1}): 1737, 1601, 1502. Calcd for $C_{72}H_{52}O_5$: C, 86.72; H, 5.26. Found: C, 86.36; H, 5.26.

Polymer 34a. ^{1}H NMR: δ 7.2–6.3 (m, 32H, aromatics), 6.2 (s, 4H, aromatics), 3.4–3.0 (m, 6H, CO_2CH_3), 2.3–1.8 (m, 18H, CH_3). ^{13}C NMR: δ 169.3 (CO), 155.0, 142.6–126.0, 116.9 (aromatics), 51.6 ($CO_{\infty}CH_3$), 21.2 (CH_3). IR (cm^{-1}): 1738, 1603, 1504. Calcd for $C_{76}H_{60}O_5$: C, 86.66; H, 5.74. Found: C, 86.62; H, 5.50.

Polymer 34b. Calcd for $C_{76}H_{60}O_5$: C, 86.66; H, 5.74. Found: C, 86.26; H, 5.73.

Polymer 35a. Calcd for $C_{68}H_{46}Br_2O$: C, 78.61; H, 4.46; Br, 15.38. Found: C, 78.37; H, 4.56; Br, 14.89.

Polymer 35b. Calcd for $C_{68}H_{46}Br_2O$: C, 78.61; H, 4.46; Br, 15.38. Found: C, 78.37; H, 4.56; Br, 14.89.

Polymer 35c. ^{1}H NMR: δ 7.5–7.25 (m, 3H, aromatics), 7.25–6.45 (m, 33H, aromatics), 6.45–6.2 (m, 4H, aromatics), 2.0 (m, 6H). ^{13}C NMR: δ 156.0–154.0, 141.4–126.2, 120.5–117.2 (aromatics), 21.1 (CH_3). IR (cm^{-1}): 1600, 1503. Calcd for $C_{68}H_{46}Br_2O$: C, 78.61; H, 4.46; Br, 15.38. Found: C, 78.28; H, 3.78; Br, 15.10.

Polymer 36a. Calcd for $C_{74}H_{58}N_2O_3$: C, 86.86; H, 5.71; N, 2.74. Found: C, 85.50; H, 5.97; N, 2.50.

Polymer 36b. Calcd for $C_{74}H_{58}N_2O_3$: C, 86.86; H, 5.71; N, 2.74. Found: C, 86.14; H, 5.66; N, 2.47.

Polymer 36c. ^{1}H NMR: δ 7.5–6.0 (m, 40H, aromatics), 2.9–2.5 (m, 8H, NCH_3), 2.3 (s, 4H, aromatics), 1.9 (s, 6H, CH_3). ^{13}C NMR: δ 169.5, 169.2 (CO), 154.8, 142.2–126.5, 117.0 (aromatics), 38.3, 33.9, 33.5 (NCH_3), 21.0 (CH_3). IR (cm^{-1}): 1647, 1601, 1501. Calcd for $C_{74}H_{58}N_2O_3$: C, 86.86; H, 5.71; N, 2.74. Found: C, 85.53; H, 5.49; N, 2.59.

Polymer 37a. Calcd for $C_{68}H_{46}Br_2O$: C, 78.61; H, 4.46; Br, 15.38. Found: C, 78.25; H, 4.47; Br, 14.37.

Polymer 37b. ^{1}H NMR: δ 7.5–6.4 (m, 37H, aromatics), 6.3–6.1 (m, 3H, aromatics), 4.47 (m, 0.3H, aromatics), 2.30 (m, 1H, CH_3), 2.2–1.8 (m, 5H). ^{13}C NMR: δ 205.9 (CO), 176.9, 174.7, 155.0, 142.0–124.4, 119.3–116.0 (aromatics), 41.3, 63.0, 57.2, 56.8, 21.5–21.0 (aliphatics). IR (cm^{-1}): 1706, 1600, 1501. Calcd for $C_{68}H_{46}Br_2O$: C, 78.61; H, 4.46; Br, 15.38. Found: C, 78.76; H, 4.45; Br, 14.02.

Conclusion

Diels–Alder polymerization between diacetylenes and bis(cyclopentadienones) first developed by Stille and coworkers is a useful and flexible method to prepare highly aromatic, tractable polymers. Both internal and terminal diacetylenes may be used in the polymerization reaction though much lower molecular weights are obtained from internal acetylenes. The polymers prepared have high thermal stability and low dielectric constants and form coherent films on a variety of substrates. These properties, together with the low optical density of the polymers, suggest the possible use of these materials as photodefinable organic dielectrics.

Acknowledgment. We thank Dr. Timothy M. Miller for helpful discussions.

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