mmol) of freshly distilled phenylacetylene in 2.1 mL of 1,2,4-trichlorobenzene was placed in a 10-mL glass ampule. The solution was degassed by two successive freeze (liquid nitrogen)–evacuate–thaw cycles. The ampule was sealed and placed in a 500-mL Paar bomb containing 75 mL of 1,2,4-trichlorobenzene in order to partially equalize the pressure inside and outside the ampule. The bomb was heated to 210 °C for 69 h. The bomb was cooled and the ampule was opened. Gas chromatography of the solution (240 °C, 5 ft × 0.375 in., 15% SE-30 on Chromosorb P) gave overlapping peaks of *m*- and *p*-terphenyls. Comparison of the peak shape with standard solutions of authentic samples indicated the ratio of meta to para was 2:1. The yield as determined by comparison with standard solutions by gas chromatography was 68.5%. The infrared spectrum of the sample collected by preparative gas chromatography indicated the presence of both *m*- and *p*-terphenyls.

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Polyphenylenes via Bis(2-pyrones) and Diethynylbenzenes. The Effect of *m*- and *p*-Phenylene Units in the Chain

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ABSTRACT: Polyphenylenes with varying degrees of meta and para catenation have been synthesized utilizing the Diels–Alder 4 + 2 cycloaddition reaction of bis(2-pyrone) monomers with diethynylbenzenes. The polyphenylenes are yellow to brown, insoluble, highly crystalline, and thermally stable. Increasing amounts of meta catenation lower the T_m and improve solubility.

The 4 + 2 cycloaddition reaction of diacetylenes with bis(diene) monomers such as bis(cyclopentadienes) or bis(pyrones) has been demonstrated to afford high molecular weight polyphenylenes.[1-10] In the step-growth Diels–Alder polymerization, the elimination of either carbon monoxide or carbon dioxide, depending on the bis(diene) system used, simultaneously generates a benzene ring in the polymer backbone and prevents reversibility of the initial adduct. The properties of these polyphenylenes are different, in some respects, from those of unsubstituted polyphenylenes prepared by other means. Polyphenylenes prepared either from benzene by a Friedel–Crafts reaction under oxidative conditions or the 1,4-polymerization of 1,3-cyclohexadiene followed by hydrogenation are brown to black, crystalline, and insoluble in any solvents.[8]

By contrast, the high molecular weight phenylated polyphenylenes obtained from Diels–Alder reactions of bis(cyclopentadienes) with diacetylenes are light yellow, amorphous, completely soluble in common organic solvents, and have good thermal stability. They are, however, subject to thermal degradation due to the loss of the pendant phenyl groups.[2,11] Unphenylated poly(*p*-phenylene) prepared by a Diels–Alder reaction of 5,5′-*p*-phenylenebis(2-pyrone) (1) with *p*-diethynylbenzene is yellow, insoluble in all solvents, highly crystalline, and thermally stable.[12] The unusually high solubility of the phenylated polyphenylenes can be attributed to either pendant phenyl substitution or to the presence of meta catenation (ca. 50%)[9] in the newly formed benzene ring.

Because of the differences in the physical properties of the various polyphenylenes, the synthesis of unphenylated polyphenylenes with varying amounts of meta catenation was of particular interest.

Monosubstituted bis(cyclopentadienone)[13] and bis(sulfone)[14] monomers are not suitable choices for the preparation of unphenylated polyphenylenes because of monomer unbalancing side reactions. Monosubstituted 2-pyrones, however, are stable monomers and react with acetylenes to afford benzene derivatives.[15] Furthermore, the catenation of the products of the reactions of acetylenes and monosubstituted 2-pyrones can be predicted by consideration of the net atomic charge distribution of the reactants and any secondary overlap of frontier molecular orbitals.[16,17]

Results and Discussion

There are two ways to introduce meta catenation into the backbone of the Diels–Alder polyphenylene. Either the monomers used must contain meta substitution prior to the Diels–Alder reaction or the reaction itself must produce a new meta catenated ring. The synthesis of a poly(*m*-phenylene) requires both meta-substituted monomers and the formation of a meta-catenated benzene ring during the cycloaddition reaction. Since the only variable is the position of attachment to the 2-pyrone ring, 4,4′- and/or 6,6′-bis(2-pyrone) monomers are required to prepare an all meta-catenated polymer. Unfortunately, 4-phenyl-2-pyrones react with phenylacetylenes

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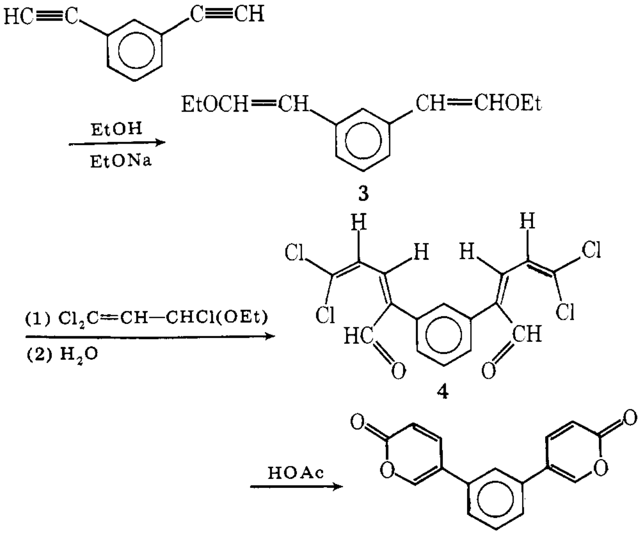
Table I
Polymerization Specifics

Reactant		Reaction conditions			Products			CH Anal.[c]		
Bis(pyrone)	Diethynylbenzene	Solv[a]	Temp °C	Time, h	Type[b]	Wt %	Color	C	H	Resid
Polymer 6										
(a) para	Meta	DCE	230	142	Film	70	Dark	91.9	4.7	
					Powder	25	brown	91.9	4.9	
(b) Para	Meta	TCB	230	142	Film	10	Light	91.9	4.8	
					Powder	90	yellow	89.4	4.8	1.04
(c) Para	Meta	TCB	300	93.5	Solid	100	Yellow brown	89.9	4.7	0.96
								90.5	4.7	0.79
(d) Meta	Para	DCE	230	146	Film	35	Dark brown	90.6	5.2	
					Powder	60		91.3	5.1	
(e) Meta	Para	NMP	205	22	Film	<5	Yellow			
					Powder	93		90.7	5.4	
Polymer 7										
(a) Meta	Meta	DCE	230	140	Powder	76	Brown	88.6	5.1	
(b) Meta	Meta	TCB	230	140	Powder[d]	87	Yellow brown 85.6	4.9		
(c) Meta	Meta	NMP	205	22	Film	20	Yellow brown			
					Powder	79	Yellow brown	90.5	5.4	

[a] DCE = 1,2-dichloroethane; TCB = 1,2,4-trichlorobenzene; NMP = *N*-methylpyrrolidinone. [b] Film was deposited on the walls of the reaction ampule. [c] Calculated for $(C_6H_4)_n$: C, 94.70; H, 5.30. [d] $[\eta] = 0.09$ dL/g, solvent = TCB, 25.1 °C.

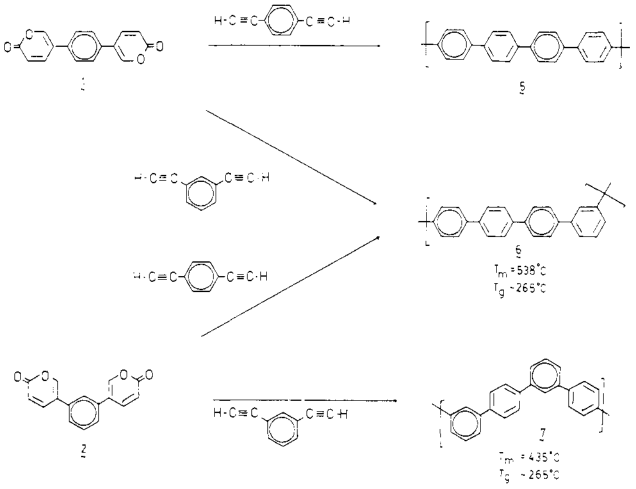
to give a mixture of isomers (m/p = 2:1) in low yield.[17] The 6-phenyl-2-pyrones not only afford low yields but some of the wrong isomer (o/m = 5.4:1).[17] Neither of these last two reactions is suitable for a polymerization and the only way to introduce meta catenation into polyphenylenes is by way of meta-substituted monomers.

The synthesis of 5,5′-*m*-phenylenebis(2-pyrone) (2) was achieved in a manner analogous to that previously reported for the corresponding para isomer.[12] The synthesis of *cis*, *cis*-β,β′-diethoxy-1,3-divinylbenzene (3) was accomplished by the base-catalyzed addition of ethanol to *m*-diethynylbenzene. The reaction of this vinyl ether with 1,1,3-trichloro-3-ethoxypropene[18,19] afforded a condensation product which was hydrolyzed to yield 2,2′-*m*-phenylenebis(5,5′-dichloropenta-2,4-dienal) (4). Cyclization to the pyrone was accomplished in refluxing acetic acid.



The use of combinations of 5,5′-*p*- or 5,5′-*m*-phenylenebis(2-pyrone) with *p*- or *m*-diethynylbenzene allows the preparation of unphenylated polyphenylenes with 0% (5),[7,10,12,20] 25% (6), and 50% (7) meta catenation (Scheme I). The only meta catenation found in the polymers is that introduced with monomer since the new benzene ring formed in the Diels–Alder reaction exhibits greater than 95% para catenation.[12,16,21] The polymerizations were carried out under a variety of conditions (Table I). Initially, the polymerizations were performed in 1,2-dichloroethane and in 1,2,4-trichlorobenzene at high temperatures (230 °C) as in the preparation of poly(*p*-phenylene).[12] However, incomplete solubility of the meta bis(pyrone) 2 was observed and the polymerization reaction was therefore not a homogeneous system. Two other solvents were found to dissolve this reactant completely even at room temperature: 1,1,2,2-tetrachloroethane and *N*-methylpyrrolidinone. Since tetrachloroethane readily decomposes at the polymerization temperature, it cannot be used at its boiling temperature (146 °C) to produce a high molecular weight polymer (intense IR carbonyl absorption in the product). *N*-Methylpyrrolidinone was therefore found to be the best solvent in which to carry out the polymerization. The yields in *N*-methyl are nearly quantitative and the polymer no longer shows a pyrone carbonyl absorption.

Scheme I
Unsubstituted Polyphenylenes



Polyphenylene 6, which contains a *m*-phenylene group every fourth phenylene unit (25% meta), was prepared by either the polycondensation of 5,5′-*p*-phenylenebis(2-pyrone) (1) with *m*-diethynylbenzene or of 5,5′-*m*-phenylenebis(2-pyrone) (2) with *p*-diethynylbenzene. Like poly(*p*-phenylene),[12] it is yellow, crystalline, and insoluble. This polymer, however, deposits as a film on the walls of the ampule during the course of the polymerization reaction; some powder precipitates also. Possibly the *m*-phenylene unit provides enough

Table II
C–H Out-of-Plane Deformation

Compd	Wave number, cm^{-1}	Compd	Wave number, cm^{-1}
5	800	*p*-Pentapheny[a]	826
p-Sexiphenyl[a]	812	*p*-Terphenyl[a]	837
6	815	**7**	840
p-Pentaphenyl[a]	818		

[a] Reported values.[24,25]

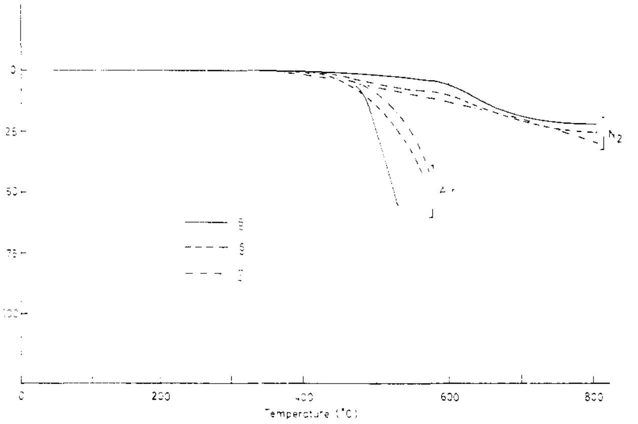


Figure 1. Thermal gravimetric analysis of polyphenylenes.

flexibility in the polymer chain to give added solubility, allowing the polymer to achieve a higher molecular weight before separating, and thereby producing a coherent film.

A polyphenylene containing alternating *m*- and *p*-phenylene rings (**7**) was synthesized from the reaction of 5,5′-*m*-phenylenebis(2-pyrone) (**2**) and *m*-diethynylbenzene. In most solvents, this polymer was obtained as a yellow brown powder. A portion (45%) of the polymer **7** prepared in 1,2,4-trichlorobenzene (**7b**) was successfully redissolved in the solvent, giving an intrinsic viscosity of 0.09 dL/g (25 °C).

In the preparation of polymer **6** in various solvents and **7** in *N*-methylpyrrolidinone, the formation of a dark brown film coating the walls of the glass polymerization tube was observed. This film was electrostatic and insoluble. The fact that a film was formed during the polymerization presumes the presence of a polymer with a higher molecular weight than that observed for the poly(*p*-phenylene).[12] The rest of the reaction product consisted of a yellow-brown precipitate. The ratio of yields between film and powder varied considerably with the nature of the solvent and the polymerization temperature, but in all cases, the overall yields are quantitative.

The λ_{max} (reflection) of the polyphenylenes containing some degree of meta catenation were in the range of 304 to 325 nm. Since the presence of meta catenation impedes the conjugation of more than four phenylene groups (polymer **6**) or three phenylene units (polymer **7**),[22] it was not possible to compare these values with those of the poly(*p*-phenylene) (340 nm)[12] and thereby obtain additional information about the molecular weight of these polymers using Kuhn's root law.[23]

The infrared spectrum of polymer **6** showed two strong absorptions at 785 and 820 cm^{-1} characteristic of the C–H out-of-plane deformations of the *m*- and *p*-phenylene moiety, respectively. The same observations were made at 785 and 840 cm^{-1} for polymer **7**. It is interesting to compare the frequency for the C–H out-of-plane deformation of the *p*-phenylene groups with the poly(*p*-phenylene) and observe the shift to higher wave numbers with decreasing degree of *p*-phenylation[9,24,25] (Table II). However, estimation of the amount of meta vs. para catenation in the polymer by comparing the infrared spectrum of the polymer with that of standard mixtures of *m*- and *p*-terphenyl was not possible because the bands broadened and shifted in the polymer spectrum causing an overlap of the CH deformation bands. A very strong absorption near 895 cm^{-1} due to the CH deformation of the isolated hydrogen in meta-substituted benzene was also observed for these new polyphenylenes.

All these polymers were found to be highly crystalline showing reproducible *d* spacings at 4.7, 3.85, and 3.2 Å for polymer **6** and at 4.8, 4.3, 3.8, and 3.25 Å for polymer **7**. A film of polymer **6** showed an additional diffraction at 7.5 Å. It was not possible to determine the percent crystallinity due to the absence of a reference compound. It is interesting to observe however, that the very intense diffraction at 19.8° recorded for *p*-terphenyl is also found for the polyphenylene having nearly 100% para catenation (Table III). In the polymers having lesser degrees of para catenation, this band becomes less evident. Similarly, diffractions at 23.2 and 20.7° found in *m*-terphenyl can be found in polyphenylene **7** but are not as distinctive in the 25% meta polymer **6**.

As expected, the new polyphenylenes showed excellent thermal stability (Figure 1). The TGA of a film of polymer **6** showed breaks at 500 °C in nitrogen with a weight loss of 10% at 640 °C and 50% at 800 °C and complete decomposition at 485 °C in air. The TGA of the powder sample of polymer **6** prepared in a better yield in 1,2,4-trichlorobenzene showed a break at 580 °C in nitrogen with a weight loss of 10% at 620

Table III
X-Ray Diffraction Angles

Compd	Angle, deg
2	29.4, 25.1, 18.1, 15.4, 12, 9.8, 8.25
p-Terphenyl	46.7, 39.8, 32.8, 19.8, 13, 4.5
m-Terphenyl	26, 23.2, 21, 20.7, 19

Polyphenylenes % para	Polyphenylenes % meta	Compd	Solv[a]	Angle, deg			
100	0	**5**	NMP				19.8
75	25	**6d** film	DCE		23		19.4
		6d solid	DCE		22.5	21.1	18.7
		6c solid	NMP	27.5	23		19
50	50	**7b** solid	TCB			21.65	
		7a solid	DCE			20	18.2
		7c solid	NMP	27	23.2	20.9	18.4
		7c film	NMP	27	23.2	20.9	18.5

[a] DCE = 1,2-dichloroethane; TCB = 1,2,4-trichlorobenzene; NMP = *N*-methylpyrrolidinone.

°C and 22% at 800 °C and a break at 480 °C in air. Polymer **7** with approximately 50% meta catenation showed a break at 575 °C in nitrogen with a weight loss of 25% at 800 °C while complete decomposition occurred at 550 °C in air.

The effect of para catenation in these polyphenylenes is evidenced in the crystalline transition temperatures as determined by differential scanning calorimetry (Scheme I). Poly(*p*-phenylene) has the highest crystalline transition temperature, evidently above its decomposition temperature. Increasing the portion of *m* units lowers T_m. The glass transition temperatures in these highly crystalline materials were observed on amorphous materials prepared by heating samples above T_m and then quenching in liquid nitrogen.

Experimental Section

The NMR spectra were measured with Varian A-60 and HA-100 instruments in deuteriochloroform. The infrared spectra were taken as KBr pellets or neat in the case of liquids on a Beckmann Model 20-A spectrometer. The ultraviolet spectra were obtained by diffuse reflectance spectroscopy for the polyphenylenes on a Beckmann DBG in a magnesium oxide matrix. X-ray scans were obtained in a powder camera using copper Kα radiation. Differential scanning calorimetry and thermal gravimetric analyses were carried out on Dupont 900 and 950 instruments. Intrinsic viscosities were measured with a Connon-Ubbelohde dilution viscometer at 25 °C. The mass spectra were obtained using a medium resolution Hitachi Perkin-Elmer RMU-6E spectrometer at an ionization potential of 70 eV.

The monomers *m*- and *p*-diethynylbenzene[26-28] and 5,5′-*p*-phenylenebis(2-pyrone)[12] were prepared as described.

***cis,cis*-β,β′-Diethoxy-1,3-divinylbenzene (3).** In a 200-mL glass ampule were placed 12.6 g of *meta*-diethynylbenzene together with a suspension of sodium ethoxide (from 5 g of sodium in 100 mL of previously dried ethanol). After evacuating and sealing, the ampule was placed in an oil bath and heated at 135 °C for 50 h. The mixture was shaken during the reaction. After cooling, the ampule was opened and the volatile material was removed under reduced pressure with a rotary evaporator. The residue was poured into 200 mL of water and extracted with ether. The extracts were washed with water and dried overnight over anhydrous magnesium sulfate and the ether was then removed by distillation to give 18.9 g of a viscous liquid. Distillation of the crude product gave 14.5 g (68%) of pure **3**: bp 144–148 °C (0.2 mm Hg); IR (neat) 1650 (C=C str), 1100 (COC str); NMR ($CDCl_3$) δ 7.6–6.9 (m, 4, phenyl), 6.00 (d, 2, J = 7 Hz, =CHO), 5.12 (d, 2, J = 7 Hz, -CH=), 3.72 (q, 4, J = 7 Hz, CH_2), 1.14 (t, 6, J = 7 Hz, CH_3). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.0; H, 8.3. Found: C, 77.2; H, 7.6.

2,2′-*m*-Phenylenebis(5,5′-dichloropenta-2,4-dienal) (4). To 0.12 g (2×10^{-4} mol) of anhydrous zinc chloride in 2 mL of dry ethyl acetate cooled to 0 °C in a flame-dried flask was added with stirring 11.9 g (0.063 mol) of 1,1,3-trichloro-3-ethoxypropene.[18,19] The mixture was stirred for 10 min, and 4.3 g of **3** (0.02 mol) was added dropwise over 20 min. The mixture was stirred for an additional 130 min at 0 °C, after which 0.5 g of sodium carbonate was added. After 30 min the reaction mixture was filtered using dry ether to facilitate the process. The volatile materials were removed by evaporation under reduced pressure. The resulting deep red viscous oil was then added dropwise to a boiling solution of 95 mL of concentrated hydrochloric acid in 200 mL of water over 30 min. After heating for a total of 1 h, the product solidified and after cooling was collected by filtration. In some cases, the solid did not appear and the solution was extracted with ether to yield the same product. The residue was recrystallized from toluene or acetone to afford 2.66 g (35.4%) of **4** as pale yellow crystals: mp 165 °C; IR (KBr) 1690 (C–O ald), 1615, 1582 (C–C conj str); NMR ($CDCl_3$) δ 9.83 (s, 2, CHO), 7.6–6.75 (m, 8, H vinyl and phenyl). Anal. Calcd for $C_{16}H_{10}Cl_4O_2$: C, 51.10; H, 2.70. Found: C, 60.5; H, 2.6.

5,5′-*m*-Phenylenebis(2-pyrone) (2). A solution of 0.25 g (0.55 mmol) of recrystallized **4** in 125 ml of glacial acetic acid containing 0.5 mL of water was heated at the reflux temperature for 7 h. The solvent was then removed by evaporation under reduced pressure and the residue was recrystallized from acetic acid: yield 0.20 g (87%) mp 243–245 °C; IR (KBr) 1745 (O=O pyrone); mass sp, 267 (M + 1), 266 (M), 265 (M − 1), loss of O, CO, CO_2, 2CO, peaks of phenyl, CO_2, CO. Anal. Calcd for $C_{16}H_{10}O_4$: C, 72.18; H, 3.76. Found: C, 72.0; H, 3.5.

Polyphenylenes 6 and 7. Polymerization Procedure. The polymerizations were performed in three different solvents that were distilled before use. Equimolar amounts (10^{-3} mol) of *m*- or *p*-5,5′-phenylenebis(2-pyrone) (**1** and **2**) and *m*- or *p*-diethynylbenzene were weighed into a glass ampule with 30 mL of solvent, degassed by three freeze–thaw cycles and then sealed under vacuum. The ampule was placed in a 500 mL Parr bomb with 100 mL of the reaction solvent inside the bomb in order to achieve partial equalization of pressure on the inside and outside of the ampule. The bomb was then sealed and heated to the desired temperature for the appropriate time (Table I). The bomb was then cooled, the ampule was opened, and the precipitated polymeric material was collected by filtration. The film was removed from the ampule walls and the polymers were washed separately by a Soxhlet extraction with methanol for 4 days, dried under vacuum at 80 °C for 24 h, and then characterized.

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