had been washed with methanol and dried. The stirred mixture was heated to about 75° while a benzene–methanol azeotrope was collected (bp 58°). The mixture was maintained at this temperature for 24 hr, then filtered and concentrated *in vacuo* to give a white crystalline product which was washed with ethanol and dried to give 1445 g (74%) of IVa. The bischloride was dissolved in hot ethanol and slowly precipitated into cold water to give IVa, mp 95–96°.

Anal. Calcd for $C_9H_{14}Cl_2O_4$: Cl, 27.58. Found: Cl, 27.30.

Poly[2,4,8,10-tetraoxaspiro[5.5]undecan-3,9-ylene-9-(methylenethiomethylene)] (IIa). In a 12-l. resin pot equipped with a mechanical stirrer, gas inlet tube, and thermocouple were mixed 1003 g (7.5 mol) of sodium sulfide flake, 1931 g (7.5 mol) of bischloride IVa, and 6 l. of DMSO. The mixture was stirred under nitrogen, then heated to 75–80°. When the exothermic reaction began, the external heat source was removed. The temperature reached 120–125° within 5 min and remained in this range for 20–25 min. During this time, the mixture became very viscous. It was cooled to room temperature and left overnight. The resultant solid mass was cut into pieces and washed with two 5-gal. portions of water in a Cowles dissolver to give a finely divided white polymer which was washed with 2 gal. of 95% ethanol and dried *in vacuo* to give 1500 g (92%) of polymer IIa, inherent viscosity 1.1 (0.5% chloroform solution at 30°).

Anal. Calcd for $C_9H_{14}O_4S$: C, 49.53; H, 6.49; S, 14.69. Found: C, 49.26; H, 6.38; S. 14.63.

3,9-Bis(*N*,*N*-dimethyldithiocarbamyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (IVb). To 28.6 g (0.2 mol) of sodium *N*,*N*-dimethyldithiocarbamate in 100 ml of DMSO (distilled over calcium hydride) was added 25.7 g (9.1 mol) of bischloride IVa. The mixture was heated at 95–100° for 3 hr under nitrogen, then cooled and poured into 1 l. of water to give 37.1 g (87%) of IVb as a white powder, mp 198–205°. The adduct was recrystallized twice from benzene to give needles, mp 209–210°.

Anal. Calcd for $C_{15}H_{26}N_2O_4S$: C, 42.23; H, 6.14; N, 6.57. Found: C, 42.20; H, 6.30; N, 6.47.

3,9-Bismercaptomethyl-2,4,8,10-tetraoxaspiro[5.5]undecane (IVc). To 25 g (0.059 mol) of IVb in a 500-ml round-bottomed flask was added 170 ml of DMSO, 50 ml of water, and 25 g (0.63 mol) of sodium hydroxide pellets. The mixture was magnetically stirred, flushed with nitrogen, and heated between 90 and 115° for 18 hr. It was cooled and poured into 500 ml of water, then carefully neutralized with concentrated HCl to pH 4–5. A white precipitate which formed was separated on a filter and then dissolved in methylene chloride. This solution was washed with water, dried over anhydrous magnesium sulfate, filtered, and concentrated *in vacuo* to give 12 g (83%) of the bismercaptan IVc. Two recrystallizations from cyclohexane gave white needles, mp 84–87°. Distillation *in vacuo* gave a white solid, mp 87–89° (bp 148–152° (0.1 mm)). The molecular weight was found by vapor pressure osmometry to be 250.

Anal. Calcd for $C_9H_{16}O_4S_2$: C, 42.83; H, 6.39; S, 25.41. Found: C, 43.0; H, 6.35; S, 25.70.

3,9-Bis(1-chloroethyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (Va). To 55 g (0.6 mol) of α-chloropropionaldehyde (bp 86°) were added 40.8 g (0.3 mol) of pentaerythritol, 2 g of *p*-toluenesulfonic acid monohydrate, and 350 ml of benzene. The stirred mixture was heated to 75° for 2 hr as a water–benzene azeotrope was collected (10 ml). After the cooled solution was filtered, it was concentrated *in vacuo* to give 60 g of a white solid. This material was dissolved in methylene chloride. The solution was washed with dilute sodium carbonate solution and water then dried over anhydrous magnesium sulfate. It was filtered and concentrated to give 56 g (66%) of bischloride. Recrystallization from 95% ethanol gave white crystals, mp 85–89°.

Anal. Calcd for $C_{11}H_{18}Cl_2O_4$: C, 46.33; H, 6.36. Found: C, 46.0; H, 6.17.

Poly[2,4,8,10-tetraoxaspiro[5.5]undecan-3,9-ylene-9-(ethylidenethioethylidene)] (IIIb). To 10 g (0.035 mol) of bischloride Va were added 4.6 g (0.035 mol) of sodium sulfide flake and 40 ml of DMSO. The mixture was stirred and heated under nitrogen to 150° for about 2 hr. After cooling, the solution was poured into 1 l. of water and the resultant off-white powder was collected on a filter, washed with additional water and 95% ethanol, and dried *in vacuo* to give 6 g (70%) of low molecular weight polymer, mp 90–100°. The molecular weight by vapor phase osmometry was 1300–1400.

Anal. Calcd for $C_{11}H_{18}O_4S$: S, 13.0. Found: S, 12.4.

Acknowledgment. The molding characteristics and mechanical properties of the spiroacetal polymer were determined by Mr. M. Hudak and Mr. L. Cech.

Poly(*p*-phenylene). The Reaction of 5,5′-*p*-Phenylenebis-2-pyrone with *p*-Diethynylbenzene[1]

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ABSTRACT: The reaction of 5,5′-*p*-phenylenebis-2-pyrone with *p*-diethynylbenzene in solution at 200–300° produces poly(*p*-phenylene) *via* a Diels–Alder reaction followed by the elimination of carbon dioxide. In the formation of the new phenylene ring as a result of the cycloaddition reaction, predominant para catenation is predicted on the basis that the reaction of 2-phenylpyrone with phenylacetylene affords ~90% *p*-terphenyl (~10% meta isomer). The poly(*p*-phenylene) is yellow (λ_{max} 340 nm), insoluble in all solvents, highly crystalline, and thermally stable. Its sulfonation affords a soluble polymer which has an intrinsic viscosity of 0.14–0.23.

High molecular weight phenylated polyphenylenes obtained from the 1,4-cycloaddition reaction of biscyclopentadienones or bispyrones with bisacetylenes[2-6] have properties which are quite different from those of unsubstituted polyphenylenes prepared by other methods. The phenylated

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(1) For a preliminary account of this research, see J. K. Stille and Y. Gilliams, *Macromolecules*, 4, 515 (1971).

(2) (a) J. K. Stille, F. W. Harris, R. O. Rakutis, and H. Mukamal *J. Polym. Sci., Part B*, 4, 791 (1966); (b) H. Mukamal, F. W. Harris, and J. K. Stille, *ibid., Part A-1*, 5, 2721 (1967).

(3) C. L. Schilling, Jr., J. A. Reed, and J. K. Stille, *Macromolecules*, 2, 85 (1969).

(4) J. K. Stille and G. Noren, *J. Polym. Sci., Part B*, 7, 525 (1969).

(5) J. K. Stille, *J. Macromol. Sci., Chem.*, 3, 1043 (1969).

(6) J. K. Stille, F. W. Harris, H. Mukamal, R. O. Rakutis, C. L. Schilling, G. K. Noren, and J. A. Reed, *Advan. Chem. Ser.*, **No. 91**, 625 (1969).

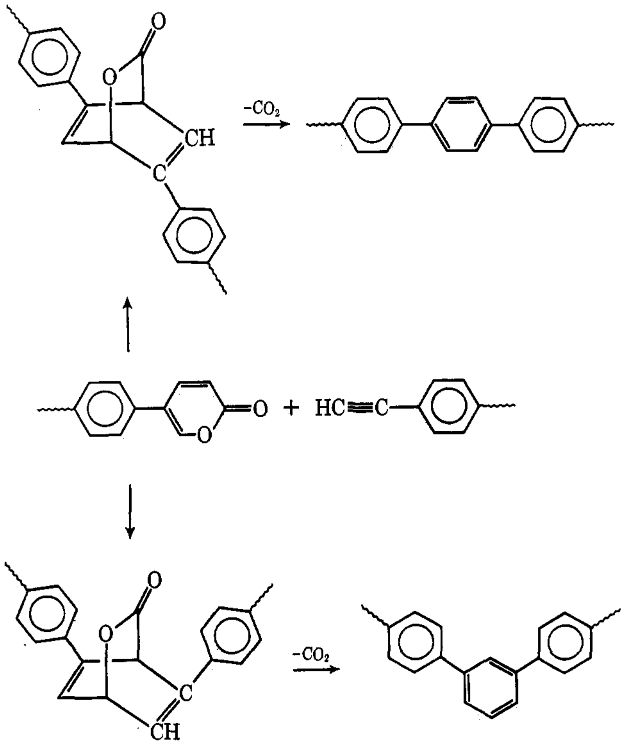
polyphenylene in which the phenylated rings have a 1:1 para to meta catenation ratio and have number-average molecular weights of 40,000–100,000, are light yellow, amorphous, and completely soluble in common organic solvents (benzene, chloroform, etc.) in concentrations of up to 10 wt %.

By contrast, those polyphenylenes prepared either from benzene by a Friedel–Crafts reaction under oxidative conditions or the 1,4 polymerization of 1,3-cyclohexadiene followed by dehydrogenation are brown to black, crystalline, and insoluble in any solvents.[7] Because of these differences in the physical properties of the two kinds of polyphenylenes, the synthesis of an unphenylated polyphenylene by a Diels–Alder route was of particular interest.

Results and Discussion

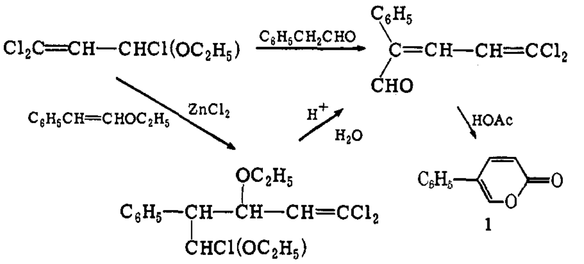
Biscyclopentadienone monomers are not suitable choices for the preparation of unphenylated polyphenylenes because the mono-substituted cyclopentadienones required are too reaction to be purified, undergoing a self-cycloaddition readily at ambient temperatures.[8] Monosubstituted α-pyrones, however, are stable monomers and react with acetylenes to afford benzene derivatives.[9]

In order to prepare a linear, unphenylated poly(*p*-phenylene), the reaction of 5,5′-*p*-phenylenebis-2-pyrone with *p*-diethynylbenzene was chosen. During polymerization, the step-growth reaction which affords the new phenylene ring can take place, depending on the direction of the addition, to afford either or both meta and para catenation.



In order to determine the amount of each type of catenation, a study of the model reaction of 5-phenyl-2-pyrone with phenylacetylene was carried out. The synthesis of 5-phenylpyrone (1) was effected by the reaction of phenylacetaldehyde with 1,1,3-trichloro-3-ethoxypropene to afford 5,5-dichloro-2-phenylpenta-2,4-dienal; cyclization was accomplished with heating in acetic acid. Alternatively, **1** was obtained through the zinc chloride catalyzed addition of 1,1,3-trichloro-3-ethoxypropene to styryl ethyl ether followed by hydrolysis and cyclization (Scheme I).

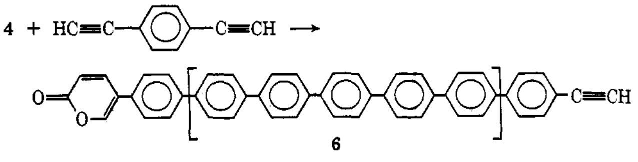
Scheme I



The reaction of 5-phenyl-2-pyrone[13] (1) with phenylacetylene at 230° in 1,2,4-trichlorobenzene gave both *p*- and *m*-terphenyl in a 9:1 ratio, as shown by glpc in comparison with authentic samples. The para isomer, in fact, was the one predicted by the extended Hückel MO calculations of the net charge distribution of the reactants.[10] Since the formation of the para isomer is preferred in the model reaction, this catenation would be expected to take place predominantly in polymerization.

The preparation of 5,5′-*p*-phenylenebis-2-pyrone was also accomplished by the two synthetic pathways employed in the preparation of **1** (Scheme II). The synthesis of *p*-phenylenebis-3,5-dimethylpyrazoylacetamide (**2**) was accomplished by the reaction of 2,2′-*p*-phenylenebisacetyl chloride with 3,5-dimethylpyrazole. Lithium aluminum hydride reduction of **2** gave only low yields (<30%) of *p*-phenylenebisacetaldehyde (**3**). Reaction of the bisaldehyde **3** with 1,1,3-trichloro-3-ethoxypropene under acidic conditions followed by cyclization afforded 5,5′-*p*-phenylenebis-2-pyrone (**4**). Since the bisaldehyde **3** was difficult to synthesize reproducibly in large quantities, a second synthetic method for the bispyrone which proved to be more practical was effected. The base-catalyzed addition of ethanol to *p*-diethynylbenzene afforded *cis,cis*-β,-β′-diethoxy-1,4-divinylbenzene (**5**). The reaction of **5** with 1,1,3-trichloro-3-ethoxypropene followed by hydrolysis and cyclization also gave the bispyrone **4** in good yields.

The polymerization reaction of **4** with *p*-diethynylbenzene was carried out under a variety of reaction conditions (Table I) to give quantitative yields of poly(*p*-phenylene) (**6**) which



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was yellow, insoluble in all solvents, and highly crystalline, showing d spacings at 4.60, 3.95, and 3.22 Å, characteristic of *p*-quaterphenyl[11] and the poly(*p*-phenylenes) obtained from 1,3-cyclohexadiene[12] and benzene.[13] The absence of first- or second-order transitions below 500° was shown by dsc. Generally, to obtain higher molecular weight polymers in 1,2,4-trichlorobenzene, high temperatures and long reaction times

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(7) For a review of the synthesis and properties of polyphenylenes, see G. K. Noren and J. K. Stille, *J. Polym. Sci., Part D*, **5**, 385 (1971).

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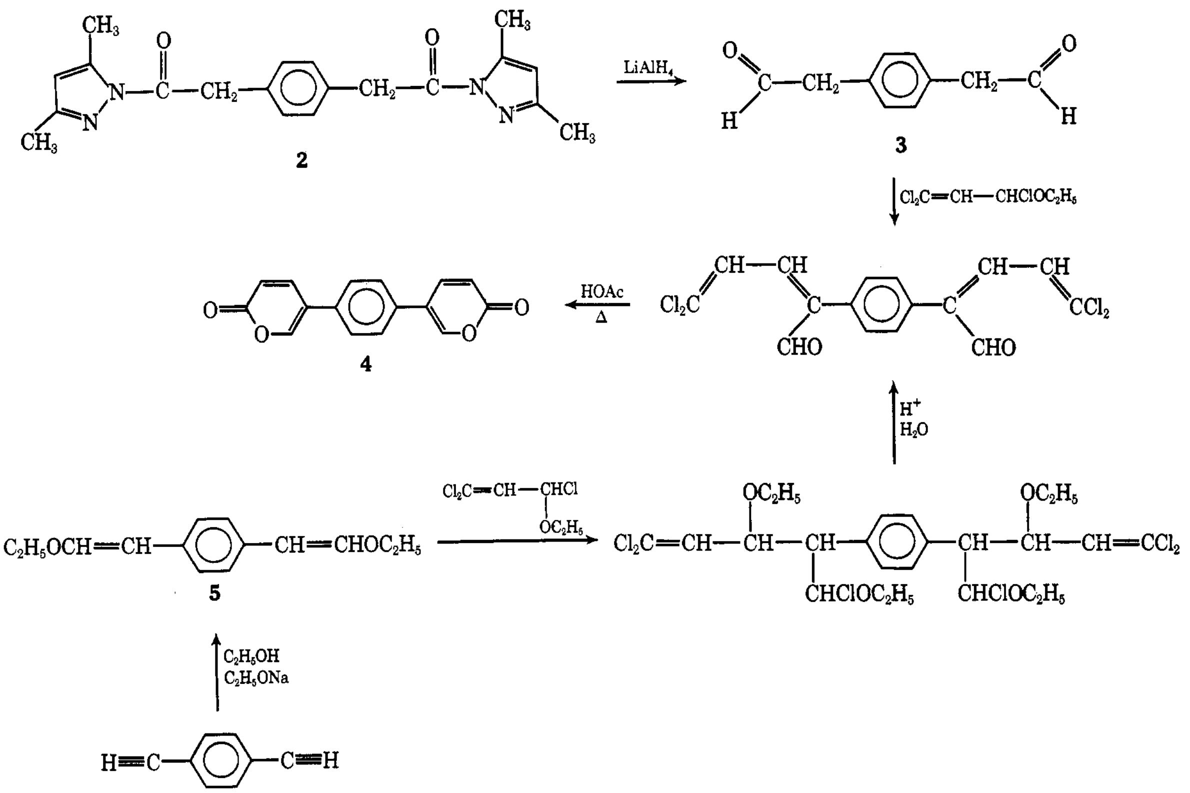
TABLE I
SYNTHESIS OF POLY(*p*-PHENYLENE)

Solvent	Temp, °C	Time, hr	Polymer color	Sulfonated poly(*p*-phenylene): % sol. in 60:40 acetone–water	[η][b]	[η][c]	Mol wt (combust anal.)
α-Chloronaphthalene	230	130	Light yellow[a]				
1,2,4-Trichlorobenzene	230	130	Yellow	>90	0.05		
1,2,4-Trichlorobenzene	300	72	Dark yellow	80	0.12	0.075	>1000
1,2-Dichloroethane	230	140	Dark yellow	55	0.23	0.14	>1000

[a] Low molecular weight. [b] Intrinsic viscosities in 60:40 acetone–water. [c] Intrinsic viscosities with salt (1%) added to the acetone–water solution.

SCHEME II



were necessary, while in 1,2-dichloroethane a lower reaction temperature could be employed. It is quite unlikely that during the course of this polymerization side reactions, particularly those which might occur with *p*-diethynylbenzene, alter the polymer structure, since *p*-diethynylbenzene reacts with biscyclopentadienones under these same reaction conditions to afford high molecular weight ($\bar{M}_n$ = 150,000) phenylated polyphenylenes.[2,14]

These poly(*p*-phenylenes) were extremely difficult to burn in obtaining elemental analyses. The lower limit of molecular weights as determined by carbon analyses, however, was an undecaphenyl (**6**, n = 2, $\bar{M}_n$ = 1012). The infrared spectra showed only a very weak carbonyl absorption (pyrone and/or carboxylic acid) at 1720 cm^{-1} and a strong CH out-of-plane deformation (two adjacent hydrogens) characteristic of the *p*-phenylene moiety at 798–800 cm^{-1}, depending on the individual polymer sample (Figure 1).

Although the model reaction of **1** with phenylacetylene yielded a 9:1 product ratio of *p*- to *m*-terphenyl, this same ratio of *p*- to *m*-phenylene units in the polymer may not be present in the rings formed from the cycloaddition reaction. It has been pointed out,[13,15] that an increasing degree of para-phenylation leads to a shift to lower wavelengths of the C–H out-of-plane deformation frequency characteristic of two adjacent hydrogens. Thus, this frequency in the polymer now falls at the same place as that characteristic of the deformation frequency of three adjacent hydrogens found in a *m*-phenylene unit. However, the infrared spectrum of the poly(*p*-phenylene) (Figure 1) shows virtually an absence of any maximum near 890 cm^{-1} for the CH deformation of the isolated hydrogen also present in meta-substituted benzenes. Although it would be difficult to measure the extent of any meta catenation by this infrared spectrum, a higher para to meta ratio than indicated by the model reaction may be present in the polymer as a result of different electronic and/or steric effects.

In contrast to those poly(*p*-phenylenes) prepared from benzene or 1,3-cyclohexadiene, the poly(*p*-phenylene) (**6**) prepared by the Diels–Alder reaction of the bispyrone (**4**) with *p*-diethynylbenzene showed a λ_{max}(refl) of 340 nm, in agreement

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(14) J. K. Stille and G. K. Noren, *Macromolecules*, **5**, 49 (1972).

(15) P. Kovacic and L. C. Hsu, *J. Polym. Sci., Part A*, **4**, 5 (1966); *p*-quaterphenyl, *p*-pentaphenyl, and *p*-sexiphenyl show maxima at 825, 818, and 812 cm^{-1}, respectively.

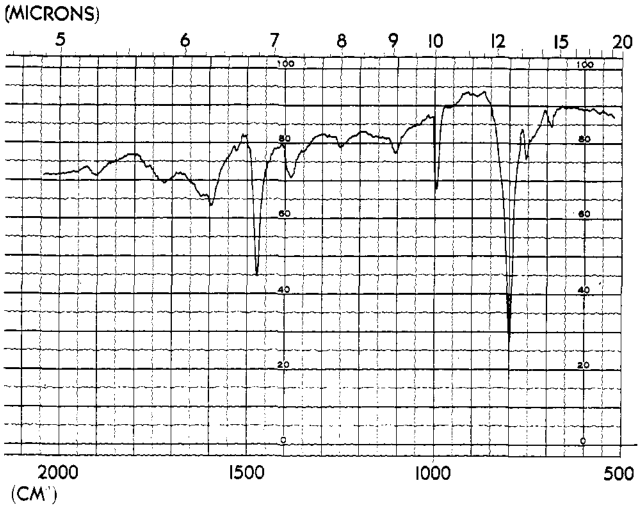

Figure 1. Infrared spectrum of poly(*p*-phenylene).

with the theoretical value of a high molecular weight poly(*p*-phenylene).[7] The λ_{max} for poly(*p*-phenylene) calculated by Kuhn's root law[16] is 343.8 nm, while calculations using other equations in combination with experimental data obtained from oligomeric phenyls show that λ_{max} approaches a limiting value of 339 nm as the degree of polymerization becomes infinite.[17-20] Although the phenylated polyphenylenes were light yellow and showed broad maxima near 340 nm, these polymers might be expected to exhibit a low λ_{max}, since the pendant phenyl groups would offer steric hindrance to the coplanar excited state. Experimental values as high as 395 nm have been reported,[15] however, for polyphenylenes prepared from benzene; some of this absorption[15,21] may be attributed to para quinoid-type linkages.

In order to obtain a soluble polymer, the sulfonation of some of the poly(*p*-phenylene) samples was carried out in sulfuric acid at 250° for 120 hr. With this procedure,[22] the polymer was not appreciably cross-linked, and one sulfonic acid group was introduced for every phenylene unit. The sulfonated polymers were partially to nearly completely soluble in a mixture of acetone and water (60:40); the degree of solubility appeared to depend on the polymerization conditions, the higher molecular weight polymers affording less soluble sulfonated poly(*p*-phenylene). Measurement of the intrinsic viscosities of the sulfonated poly(*p*-phenylenes) in the acetone–water solvent revealed a slight polyelectrolyte effect; addition of salt to the solvent provided a linear inherent viscosity–concentration relationship.

The poly(*p*-phenylenes) (**6**), as expected, showed excellent thermal stability (Figure 2). In comparison, the phenylated polyphenylenes had a break in the tga at 550° in air and decomposed rapidly, and under a nitrogen atmosphere they lost about 30–35% of their weight rather sharply at the same temperature; we had attributed this to the loss of some of the pendant phenyl groups.[2] The tga analysis of poly(*p*-phenylene) reinforces this interpretation in that, although a similar decomposition (tga 530°) of **6** in air is observed, under nitrogen, **6** loses 10% of its weight at 650° and only 20% at 800°.

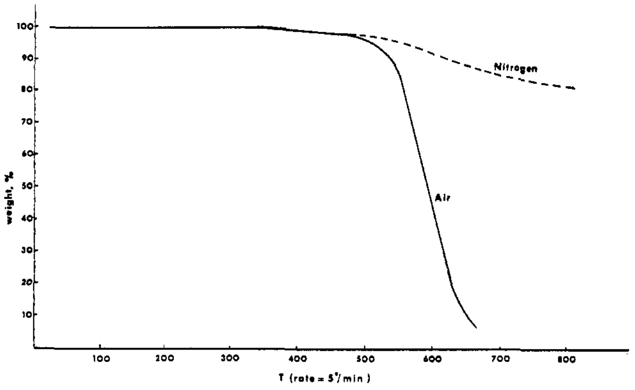

Figure 2. Thermal gravimetric analysis of poly(*p*-phenylene).

Experimental Section

The melting points were determined in a capillary tube on a Mel-Temp melting point apparatus. The nmr spectra were measured with Varian A-60 and HA-100 instruments in deuteriochloroform. The infrared spectra were taken as Nujol mulls, KBr pellets, or neat in the case of liquids on Perkin-Elmer Models 21 and 421. The ultraviolet spectrum in the case of the poly(*p*-phenylenes) was obtained by diffuse reflectance spectroscopy (drs) on a Beckman DBG in a KBr matrix. X-Ray scans were obtained on a powder camera using Cu Kα radiation. Differential scanning calorimetry and thermal gravimetric analyses were carried out on Du Pont 900 and 950 instruments. Intrinsic viscosities were measured with a Cannon-Ubbeholde dilution viscometer at 25°.

5-Phenyl-2-pyrone (1) from Phenylacetaldehyde. This reaction was carried out using a procedure described for similar condensations.[23,24] To a solution of 15 g (0.124 mol) phenylacetaldehyde in 20 ml of glacial acetic acid cooled in an ice bath was added a cooled mixture of 28 g (0.148 mol) of 1,1,3-trichloro-3-ethoxypropene[23,25] in 30 ml of glacial acetic acid. To this mixture was added 3 g of water. The reaction mixture which quickly turned dark red and separated into two layers was kept for 48 hr in a refrigerator. The mixture was then poured into ice–water and the yellow oil was extracted with ether. The ether extract was washed with sodium bicarbonate and water and dried over sodium sulfate. The ether was removed by distillation. (Distillation of the product under reduced pressure results in rearrangement.) Purification was accomplished by dissolving the residue in hexane and cooling to −78° to precipitate a solid; the solvent was decanted at −78°. This was repeated twice more with the solvent, and the hexane was distilled under reduced pressure to afford 26 g (92%) of a yellow oil, 5,5-dichloro-2-phenyl-2,4-pentadienal: ir (neat) 2831 and 2716 (aldehyde C—H), 1687 cm^{-1} (aldehyde C═O); nmr ($CDCl_3$) δ 9.66 (s, 1, CHO), 7.21 (d, 2, *J* = 12 Hz, Cl_2C═CH–), 6.71 (d, 1, *J* = 12 Hz, –C*H*═C—CHO(C_6H_5)).

Anal. Calcd for $C_{11}H_8Cl_2O$: C, 58.17; H, 3.54. Found: C, 58.04; H, 2.92.

A solution of 26 g (0.115 mol) 5,5-dichloro-2-phenyl-2,4-pentadienal in 300 ml of glacial acetic acid was heated to the reflux temperature for 8 hr. The solution was cooled and poured into ice–water, and the resulting mixture was extracted with ether. The ether layer was washed with sodium bicarbonate and water and dried over sodium sulfate. The ether was removed and the residual dark oil was dissolved in heptane–benzene (9:1); this solution was treated with charcoal at the reflux temperature and filtered. On cooling, 4 g (20%) of yellow needles was obtained: mp 68–69°; ir (KBr) 1720 (C═O), 1640 and 1628 cm^{-1} (C═C); nmr ($CDCl_3$) δ 7.66 (s, 1, ═CH—O–), 7.45 (d, 1, *J* = 10 Hz, ═CH—CO–), 6.4 (d, 1, *J* = 10 Hz, –C*H*═CH–).

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(25) M. Julia and J. Bullot, *Bull. Soc. Chim. Fr.*, 1828 (1959).

Anal. Calcd for $C_{11}H_8O_2$: C, 76.73; H, 4.68. Found: C, 76.66; H, 4.66.

5-Phenyl-2-pyrone (1) from β-Ethoxystyrene. This reaction was carried out by using a procedure described for a similar addition to ethyl vinyl ether.[26] To a slurry of 0.06 g of dry zinc chloride in 1 ml of dry ethyl acetate was added 13 g (0.069 mol) of 1,1,3-trichloro-3-ethoxypropene.[23,25] The solution was cooled to 0° and 10.3 g (0.069 mol) of β-ethoxystyrene[27] was added slowly such that the temperature did not rise above 0°. After stirring for 1 hr, 0.4 g of sodium carbonate was added and the solution was stirred for another 20 min. To this mixture was added 100 ml of ether and the slurry was filtered; the ether was distilled and 200 ml of water and 40 ml of concentrated hydrochloric acid were added. The mixture was steam distilled and the distillate was extracted with chloroform. The chloroform extract was washed with water and dried over calcium chloride. The chloroform was distilled to afford a yellow oil which was dissolved in 20 ml of glacial acetic acid and heated to the reflux temperature for 8 hr. The solution was cooled and poured into ice–water. The resulting oil was extracted with ether and the ether extract was washed with a sodium bicarbonate solution and water and dried over sodium sulfate. The ether was removed by distillation and the residue was purified as described above to give 1.32 g (11%) of yellow needles of product, mp 67–68°.

Terphenyl. The Reaction of 1 with Phenylacetylene. A solution of 0.8850 g (5.145 mmol) of 5-phenyl-2-pyrone and 0.5247 g (5.145 mmol) of phenylacetylene in 25 ml of 1,2,4-trichlorobenzene was placed in a 50-ml glass ampoule. The solution was degassed on a vacuum line by three successive freeze(−198°)–evacuate–thaw cycles; the ampoule was sealed and placed in a 500-ml Parr bomb containing 100 ml of 1,2,4-trichlorbenzene. The bomb was sealed and heated to 230° for 60 hr. The ampoule was cooled and opened, and the solution was injected into a gas chromatograph (5% SE 30, 5 ft at 175°) to determine the ratio of *p*-:*m*-terphenyl, which was 9:1. Comparison was made with standard solutions of authentic samples. The solvent was removed from the remainder of the solution under reduced pressure and the crude product was recrystallized from methanol. The ir spectrum of the recrystallized material showed a very strong absorption at 805 cm^{-1} (CH def, 2 adj H), corresponding to 1,4 substitution in the benzene ring, but gave no evidence of the presence of *m*-terphenyl.

5,5′-*p*-Phenylenebis-2-pyrone (4) from *p*-Phenylenebisacetaldehyde (3). *p*-Phenylenebis-3,5-dimethylpyrazoylacetamide (2). To a solution of 8.3 g (0.85 mol) of 3,5-dimethylpyrazole in 100 ml of benzene containing 11.5 ml of dry pyridine at 0° was added 10 g (0.043 mol) of *p*-phenylenebisacetyl chloride, which had been obtained from the acid by reaction with thionyl chloride.[28] The reaction mixture was stirred for 1 hr at 0°, during which time the pyridine hydrochloride precipitated. The mixture was stirred overnight at 25° and was then poured into 200 ml of 2 *N* hydrochloric acid. The precipitate was filtered and the benzene layer was separated, washed with water, and dried over calcium chloride. The benzene was distilled and the solid residue was combined with the first precipitate. Recrystallization from benzene gave 14.2 g (95%) of bisamide **2**: mp 177–180° (lit.[29] 198–202°); ir (KBr) 1715 (C=O), 1370 and 1350 cm^{-1} (C—N); nmr δ 7.32 (s, 4, phenyl H), 5.97 (s, 2, 4-H pyrazole ring), 4.41 (s, 4, CH_2–), 2.50 (s, 6, 5-CH_3), 2.25 (s, 6, 3-CH_3).

Anal. Calcd for $C_{20}H_{22}N_4O_2$: C, 68.55; H, 6.32; N, 15.99. Found: C, 68.69; H, 6.60; N, 15.64.

***p*-Phenylenebisacetaldehyde (3).**[29] To a solution of 40 g (0.115 mol) of the bisamide **2** in 4 l. of dry tetrahydrofuran at 0° was added 3.8 g (0.1 mol) of lithium aluminum hydride. The mixture was stirred at 0° for 20 hr, during which time it became green and gel-like. The mixture was then poured into 10 l. of 2 *N* hydrochloric acid. The product was extracted with ether and the ether was dried over sodium sulfate. The ether was distilled to afford a tacky residue which was taken up in hot benzene. On cooling, the benzene solution deposited an impurity; the benzene was removed from the filtrate to afford 5.6 g of impure dialdehyde **3**: ir 1725 cm^{-1} (C=O); nmr ($CDCl_3$) δ 9.58 (s, CHO), 7.07 (s, phenyl H), 3.67 (s, CH_2).

2,2′-*p*-Phenylenebis-5,5-dichloropenta-2,4-dienal. A solution of 3 g of crude oil containing *p*-phenylenebisacetaldehyde (**3**) in 10 ml of glacial acetic acid was cooled to 0° and added to a solution of 9.5 g (0.05 mol) of 1,1,3-trichloro-3-ethoxypropene[23,25] in 10 ml of glacial acetic acid at 0°, and 2 ml of water was added. The reaction mixture became clear red and was placed in the refrigerator for 48 hr; after 24 hr, a solid precipitated. The light yellow solid was filtered to yield 1.1 g (2.5% with respect to the bisamide) of product, which was recrystallized from benzene: mp 155–157°; ir 1690 cm^{-1} (C=O).

Anal. Calcd for $C_{16}H_{10}Cl_4O_2$: C, 51.10; H, 2.68. Found: C, 52.38; H, 3.03.

5,5′-*p*-Phenylenebis-2-pyrone (4). A solution of 1 g (2.66 mmol) of 2,2′-*p*-phenylenebis-5,5-dichloropenta-2,4-dienal in 40 ml of glacial acetic acid was heated to the reflux temperature for 20 hr. The solution was cooled and the black-brown solid obtained was filtered to yield 0.6 g of crude product, which was sublimed at 240° under reduced pressure (<0.1 mm) and recrystallized from 1,2,4-trichlorobenzene to yield 0.1 g (14%) of pure **4**: mp 308–310°; ir 1720 cm^{-1} (C=O).

Anal. Calcd for $C_{16}H_{10}O_4$: C, 72.17; H, 3.78. Found: C, 72.40; H, 3.75.

5,5′-*p*-Phenylenebis-2-pyrone (4) from *cis,cis*-β,β′-Diethoxy-1,4-divinylbenzene (5). An ampoule containing 10 g (0.08 mol) of *p*-diethynylbenzene[30] and 100 ml of a 20% ethanolic sodium ethoxide solution (prepared from 7 g of sodium and 100 ml of dry ethanol) was cooled to −198°, evacuated, sealed, and then heated in an oil bath at 150° for 48 hr. The ampoule was then cooled and opened, and the contents were poured into 300 ml of cold water. The mixture was extracted with ether and the ether was washed twice with a silver nitrate solution (1 g of silver nitrate, 12.5 g of water, 12.5 g of ethanol) in order to remove any unreacted acetylene-containing compounds. The ether layer was washed with water and dried over sodium sulfate and the ether was then removed by distillation. The crude yellow oil was distilled twice through a short path to yield 16.3 g (94%) of **5**: bp 130° (0.35 mm); ir (neat) 1645 (C=C str), 1088 (C—O—C str), 847 cm^{-1} (C—H wag, 2 adj H); nmr ($CDCl_3$) δ 7.50 (s, 4, phenyl H), 6.31 (d, 2, J = 7 Hz, –CH=*CH*—O–), 5.12 (d, 2, J = 7 Hz, –*CH*=CH—O–), 3.82 (q, 4, J = 7 Hz, CH_3—CH_2—O–), 1.25 (t, 6, J = 7 Hz, CH_3—CH_2—O–).

2,2′-*p*-Phenylenebis-5,5-dichloropenta-2,4-dienal. To a solution of 40 g (0.21 mol) of 1,1,3-trichloro-3-ethyoxypropene[23,25] and 1 g of dry zinc chloride in 5 ml of dry ethyl acetate stirred and cooled to 0° was added dropwise 17.5 g (0.08 mol) of *cis,cis*-β,β′-diethoxy-1,4-divinylbenzene (**5**) while keeping the temperature at 0°. The solution turned dark red and became viscous. After stirring the reaction mixture for 1 hr, 2.5 g of sodium carbonate was added; stirring was continued for an additional 30 min, then 2 ml of ether was added and the reaction mixture was filtered. The ether and unreacted 1,1,3-trichloro-3-ethoxypropene were distilled under reduced pressure to leave the crude red oily reaction product. This crude product, 47 g, was stirred with a solution of 90 ml of concentrated hydrochloric acid in 300 ml of water at 50° for 1 hr. The reaction mixture was cooled and extracted with ether. The ether layer was washed with water, dried over sodium sulfate, and distilled to yield a light yellow oil which usually was not purified further. When a yellow solid was obtained, some purification could be effected by recrystallization from benzene, to yield 27.7 g (82%) of 2,2′-*p*-phenylenebis-5,5-dichloropenta-2,4-dienal, mp 155–157°.

5,5′-*p*-Phenylenebis-2-pyrone (4). A solution of 27 g (0.072 mol) of 2,2′-*p*-phenylenebis-5,5-dichloropenta-2,4-dienal in 400 ml of glacial acetic acid was heated to the reflux temperature for 20 hr.

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On cooling, a dark brown product precipitated which was filtered and dried to yield 14 g (75%) of crude **4**. Purification was carried out by sublimation at 240° (10^{-2} mm) and subsequent recrystallization from 1,2,4-trichlorobenzene to yield 2.2 g (11%) of **4**, mp 310–312°.

Poly(*p*-phenylene) (6). Polymerization Procedure. Equimolar amounts of the 5,5′-*p*-phenylenebis-2-pyrone (**4**) and *p*-diethynylbenzene were weighed into a glass ampoule along with enough solvent (1,2,4-trichlorobenzene, α-chloronaphthylene, or 1,2-dichloroethane) to obtain a solution about 1.5 wt % in total monomer. (Typically, 1 mmol of each monomer in 30 ml of solvent was employed.) The reaction mixture was then degassed on a vacuum line by three freeze(−198°)–evacuate–thaw cycles, and the ampoule was sealed *in vacuo*. The ampoule was placed in a 500-ml Parr bomb with 100 ml of the reaction solvent, and the bomb was sealed and heated to the desired temperature for the desired reaction time (Table I). The bomb was then cooled and opened; the polymer in each case had precipitated. The contents of the ampoule were poured into methanol and the resulting precipitate was filtered. The polymers were dried under reduced pressure at 80° for 24 hr: ir 800 cm^{-1} (CH def, 2 adj H); $\lambda_{\max}$(refl) 340 nm.

Anal. Calcd for $C_{79}H_{52}O_2$ (**6**, $n = 2$): C, 91.59. Found: C, 91.11, 91.20 (two different samples).

Sulfonation of Poly(*p*-phenylene).[22] To 30 ml of concentrated sulfuric acid heated to 250° under a constant stream of nitrogen was added 0.2 g of the poly(*p*-phenylene) sample to be sulfonated. The mixture was stirred under these conditions for 120 hr. The black reaction mixture was then cooled and poured into ice–water, and the polymer was separated by centrifugation. The polymer was washed with water several times and dried under reduced pressure: ir 1150 and 1015 (sulfonic acid), 875 (CH def, isolated), 815 cm^{-1} (CH def, 2 adj H).

Anal. Calcd for 92% $(C_6H_4SO_3)_n$, 8% $(C_6H_4)_n$: C, 50.0. Found: C, 50.2.

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Calculations on the Unperturbed Dimensions of Polypropylenes

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ABSTRACT: Using the matrix method of Flory the unperturbed dimensions $\langle r_0^2\rangle nl^2$ and their temperature coefficients have been evaluated as function of tacticity for polypropylene. The model parameters have been varied systematically within reasonable limits to fit the experimental results. The minimum positions of the rotational bond angles probably do not deviate more than 5° from planar trans and from symetrically staggered gauche, respectively. Entropy contributions to the free energies of the rotational isomers are discussed with respect to the influence on the temperature coefficient.

For linear polymers the unperturbed dimensions and their temperature coefficients can be evaluated with the rotational isomeric state model.[1] Energies and rotation angles of the prefered conformations can be taken from semiempirical energy calculations.[2,3] Neglecting some details of such calculations, Flory and coworkers[4] have proposed a three-state model, which should describe all vinyl polymers. Therefore, this model seems to be especially suitable for an extension to vinyl copolymers.[5] Such an approach has to be based on parameters of the corresponding homopolymers.

In this paper parameters are reported which describe the experimental data on polypropylenes. These have been found by studying the influences of the variables on the unperturbed dimensions. The exactness of the free energies of the rotational isomeric states, required for a good fit with experiment, may be estimated from the influence of a variation of the corresponding parameter values. Furthermore, entropy contributions to the free energies of the isomeric states are discussed with regard to their influence on the temperature coefficients of the unperturbed dimensions.

Theory

According to Flory, *et al.*,[4] the free energy of a chain conformation is expressed as a sum, where each term is dependent on *one* bond rotational angle only (first-order interactions) or on two consecutive bonds (second-order interactions). The three isomeric states of a bond are shown in Figure 1. A mirror reflection of the diagrams inverts the asymetric center and reverses the sign of the rotation angle, whereas the interaction energy is not altered. Therefore each diagram represents two states of different asymmetric center with a rotation angle of the same absolute value but with opposite sign.

The first-order free energies of the states are taken relative to the gauche (g) state. (In Figure 1 their statistical weights are put in parentheses.) In the trans state, CH_3 instead of CH_2 is syn with respect to CH. Therefore, it is expected that η may be a little lower than unity, partly due to the increased restriction of internal rotation for the methyl group. For $\bar{g}$ CH is syn to CH_3 as well as to CH_2. This corresponds to $\tau < \eta$.

Second-order interactions involve essential steric overlapping of groups separated by four bonds, *i.e.*, CH, CH_2, and CH_3. Calculations on *n*-pentane[2,3] indicate that this overlapping yields two minima, which are separated by a low

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