Diels–Alder Polymerizations. IV. Polymers Containing Short Phenylene Blocks Connected by Alkylene Units[1,2]

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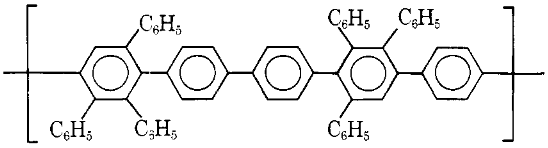
ABSTRACT: A series of polymers containing short blocks of phenylated phenylene units connected by alkylene chains have been prepared by the Diels–Alder reaction of *m*- or *p*-diethynylbenzene with tetraarylated biscyclopentadienones. Biscyclopentadienones connected by three, four, six, ten, and fourteen methylenes were employed. All of the polymers were colorless, soluble in common organic solvents, and formed clear films from chloroform or toluene solutions. The thermal gravimetric analyses (TGA) of the methylene-connected polyphenylenes demonstrated a surprisingly good thermal stability; in nitrogen, the major TGA break for all the polymers occurred between 465 and 485°. In air, the thermal stability ranged from 430 to 520°. The polymers had number-average molecular weights of 30,000–60,000.

Although the Diels–Alder reaction has been established as a useful synthetic organic reaction, and high yields of adduct can be obtained in many instances, there are few reported syntheses of polymers which employ it as a step-growth reaction.[4] In only a few reported cases have high molecular weight polymers been obtained in this reaction. The most successful polymerizations carried out through the use of the Diels–Alder step-growth reaction have been those which engage a cyclopentadienone,[5] 2-pyrone,[6,7] or thiophene dioxide[8] as the diene portion.

In a previous paper,[9] the synthesis of high molecular weight polyphenylenes through the Diels–Alder step-growth reaction of diethynylbenzenes (A–A type double dienophiles) with biscyclopentadienones (B–B type double dienes) was reported. The quantitative yields, high molecular weights, and the novelty of the polymer structures which could be obtained by the reaction, made the investigation of further polymer syntheses from this step-growth polymerization particularly attractive. The most interesting polymer synthesized from this reaction was a phenylated polyphenylene (**1**) which had a high molecular weight (M_n = 40,000), was white, was 100% soluble in toluene at 25° to the extent of 15 wt %, and showed a major break in thermal gravimetric analysis at 550°. The properties of this polyphenylene clearly are different than those prepared by other methods.[10–12]



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Through this Diels–Alder reaction it was also possible to synthesize polymers containing the phenylene block structure (**1**) separated by alkylene chains of varying length. We were particularly interested in the properties which such a polymer might possess. In theory, this synthesis could be accomplished through the use of an aliphatic straight chain α,ω-diyne as the dienophilic A–A monomer, or a bistetracyclone B–B diene containing the cyclopentadienone moieties separated by methylene units. Because it was learned early in this study that the reaction of α,ω-diynes was not suitable synthetically, at least, for the preparation of high molecular weight polymers, the problem was approached from the synthesis and polymerization of the alkylene–biscyclopentadienone monomers.

Discussion

A. Monomers. An excellent route to the synthesis of tetraarylated cyclopentadienones is the base-catalyzed condensation of benzils with benzyl ketones;[13] many bistetracyclones have been synthesized by this method.[14,15]

Figure 1 outlines the reaction paths selected for the synthesis of the methylene-connected bistetracyclones. The bistetracyclones with three, four, and six methylene units (Figure 1: **2**, **3**, and **4**, respectively) have been reported previously.[15] The bistetracyclones connected by ten and fourteen methylene units (Figure 1: **5** and **6**, respectively) were synthesized essentially by the same basic reactions as the lower homologs, with the exception of the reactions employed for the synthesis of the α,ω-diphenylalkanes.

In this series, an increasing number of methylene

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(2) For a previous report of this work, see J. K. Stille, F. W. Harris, R. O. Rakutis, and H. Mukamal, *J. Polym. Sci., Part B*, **4**, 791 (1966).

(3) Dunlop Research Center Fellow, 1966–1967.

(4) J. K. Stille, *Fortschr. Hochpolym. Forsch.*, **3**, 48 (1961).

(5) E. A. Kraimen, U. S. Patent 2,890,206 (June 9, 1959).

(6) S. W. Chow, U. S. Patent 3,074,915 (Jan 22, 1963).

(7) E. A. Kraimen, U. S. Patent 2,890,207 (June 9, 1959).

(8) S. W. Chow and J. M. Whelan, U. S. Patent 2,971,944 (Feb 14, 1961).

(9) H. Mukamal, F. W. Harris, and J. K. Stille, *J. Polym. Sci., Part A-1*, **5**, 2721 (1967).

(10) P. E. Cassidy, C. S. Marvel, and S. Ray, *ibid., Part A*, **3**, 1553 (1965), and references cited therein.

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(14) M. A. Ogliaruso, L. A. Shadoff, and E. I. Becker, *J. Org. Chem.*, **28**, 2725 (1963).

(15) M. A. Ogliaruso and E. I. Becker, *ibid.*, **30**, 3354 (1965).

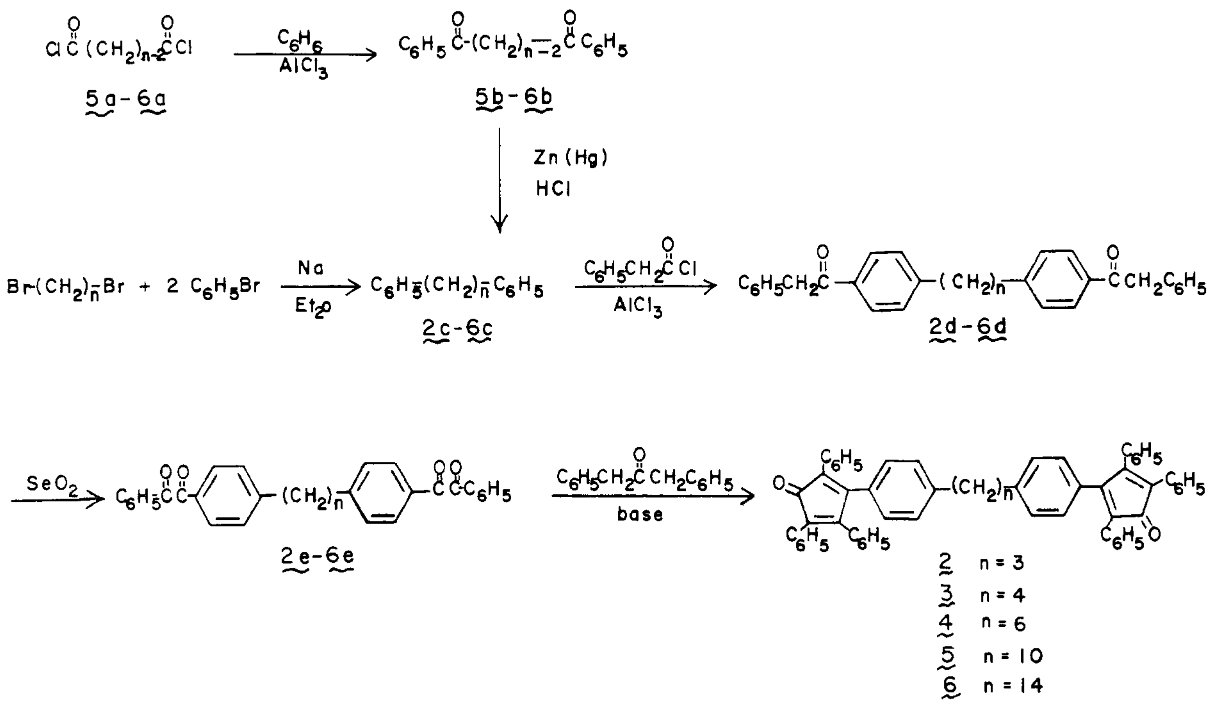

Figure 1. Monomer synthesis.

groups between the aromatic rings resulted in a decrease in the yields of products, especially in the Friedel–Crafts reaction of the diphenylalkanes with phenylacetyl chloride. Moreover, longer reaction times were required for the formation of products in the syntheses of the monomers with ten and fourteen methylene groups. The over-all yields for the syntheses of the alkylated bistetracyclones ranged from 2 to, at most, 10%. All the bistetracyclones were dark purple solids.

The purification of the bistetracyclones **2**–**6** was effected by column chromatography; a final check for the presence of only one compound was accomplished by thin layer chromatography in the synthesis of the bistetracyclones **5** and **6**.

B. Polymers. The utilization of the Diels–Alder reaction of the bistetracyclones **2**–**6** with the diethynylbenzenes **7** and **8** afforded polymers **9a**–**e** and **10a**–**e** containing phenylated phenylene units linked by methylene groups (Figure 2). Although the Diels–Alder reaction can take place to produce either *meta* or *para*

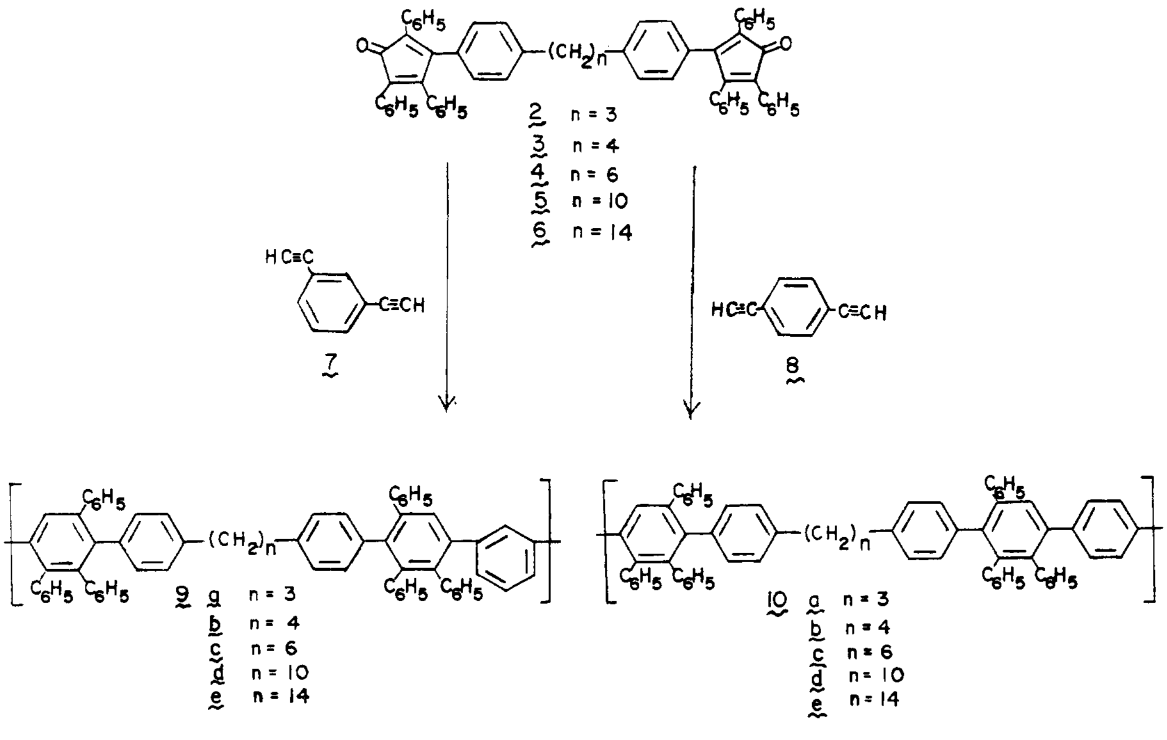

Figure 2. Polymer synthesis.

TABLE I
POLYMERIZATION RESULTS

Bistetracyclone, g (mmol)	Diacetylene, g (mmol)	Polymer	Yield, g (%)	Calcd, %		Found, %	
				C	H	C	H
2, 0.7118 (0.8797)	**7**, 0.1110 (0.8797)	**9a**	0.61 (79)	94.28	5.73	93.13	5.74
2, 0.5307 (0.6559)	**8**, 0.0826 (0.6559)	**10a**	0.4465 (77)	94.28	5.73	92.06	6.04
3, 1.000 (1.215)	**7**, 0.1533 (1.215)	**9b**	0.9790 (90)	94.12	5.88	93.98	5.75
3, 1.000 (1.215)	**8**, 0.1533 (1.215)	**10b**	0.9850 (91)	94.12	5.88	93.57	6.05
4, 1.001 (1.176)	**7**, 0.1483 (1.176)	**9c**	1.062 (98)	93.87	6.13	93.61	6.29
4, 1.005 (1.180)	**8**, 0.1488 (1.180)	**10c**	0.8152 (75)	93.87	6.13	91.79	6.32
5, 1.002 (1.104)	**7**, 0.1393 (1.104)	**9d**	0.9874 (91)	93.39	6.60	92.76	7.18
5, 1.001 (1.102)	**8**, 0.1390 (1.102)	**10d**	1.035 (96)	93.39	6.60	91.09	6.62
6, 1.006 (1.044)	**7**, 0.1318 (1.044)	**9e**	0.8960 (83)	92.97	7.02	93.16	7.26
6, 1.003 (1.042)	**8**, 0.1314 (1.042)	**10e**	0.9504 (88)	92.97	7.02	92.50	7.12

attachments on the phenylated phenylene ring, only *para* links are depicted.[16]

Severe polymerization conditions (350°, 48 hr), employed in the preliminary polymerization runs, gave lower molecular weight polymers ($[\eta] = 0.1$) and small amounts of a black, insoluble solid. In fact, when the bistetracyclone **2** was heated without the diacetylene as comonomer at 300° for 48 hr, complete decomposition of the bistetracyclone resulted, as evidenced by the formation of a yellow solid and a viscous oil. Tetraphenylcyclopentadienone is known to undergo decomposition at 410° to yield at least three different compounds.[13] Since such degradation reactions obviously interfered with monomer balance, the polymerization temperature was lowered to 225°.

A series of polymerizations in which the concentration of the monomers in solution was varied from 10 to 30 wt % was carried out. There was a noticeable trend of the viscosities to increase as the monomer concentration of the solution was increased. For the polymerization of bistetracyclone **3** with diethynylbenzene **8**, the best concentration appeared to be 21%, since concentrations of 25 and 30% resulted in gel formation. Monomer concentrations of 21% were used for all subsequent polymerizations. This unusual dependence of molecular weight on the monomer concentration has been reported in other cases. In the polymerization of bismaleimides with cyclopentadienones, the higher the monomer concentration, the higher is the reduced viscosity, and thus the molecular weight of the resulting polymer.[5]

The light colored polyphenylenes were obtained in high yields (Table I) and showed good solubility in common organic solvents. There was a slight increase in the solubility of the polymers as the length of the methylene segment of the polymer chain increased. Clear films of all the polymers could be cast from chloroform. The infrared spectra of these films were similar. The main difference occurred in the C–H stretching region[17] at 2920 and 2850 cm^{-1}; as the number of methylene groups increased, the intensity of this doublet also increased. The molecular weights of these polymers (Table II) ranged from 30,000 to 60,000 and the intrinsic viscosities from 0.36 to 1.5.

TABLE II
INTRINSIC VISCOSITIES AND MOLECULAR WEIGHTS

Polymer	Polymer: Methylene group	Polymer: Dienophile	$[\eta]^a$	M_n^b
9a	C_3	*meta*	0.36	46,500
10a	C_3	*para*	0.52	59,000
9b	C_4	*meta*	0.61	58,400
10b	C_4	*para*	0.59	42,600
9c	C_6	*meta*	0.71	45,100
10c	C_6	*para*	1.51	63,400
9d	C_{10}	*meta*	0.60	48,500
10d	C_{10}	*para*	1.30	50,500
9e	C_{14}	*meta*	0.48	31,300
10e	C_{14}	*para*	0.77	32,700

[a] Intrinsic viscosities in toluene at 25°. [b] Obtained with a Hewlett-Packard high-speed membrane osmometer using a superdense membrane at 30° in toluene.

The differential thermal analyses (DTA) of the polymers (Figures 3 and 4) gave poorly resolved curves showing several changes in the slope of ΔT *vs.* T lines. There was a slight trend for the temperature of this main second-order transition to decrease as the number of methylene groups increased in the polymer. The polyphenylenes which were connected by *meta* linkages (Figure 3) had lower transition temperatures than the

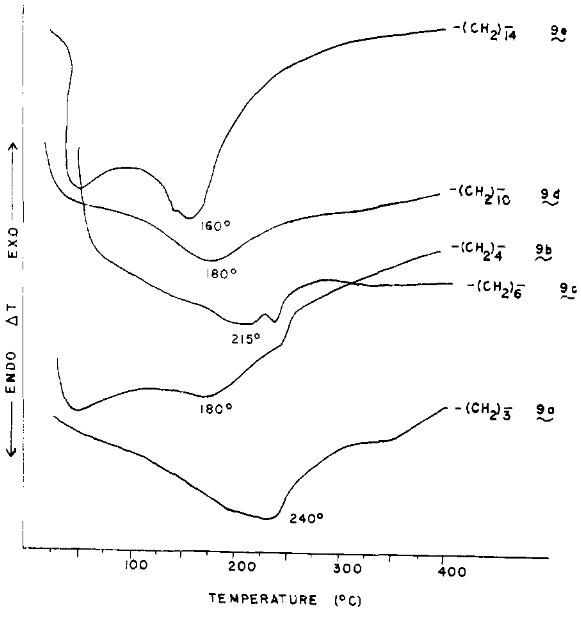

Figure 3. Differential thermal analysis of **9a–e**.

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(16) A study of the direction of addition taken during this polymerization is currently under investigation.

(17) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.

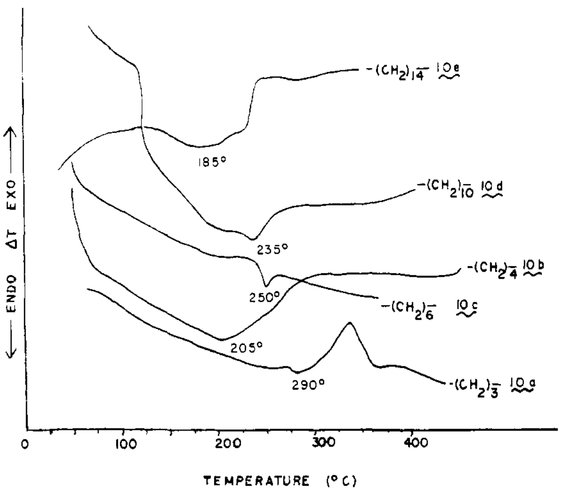

Figure 4. Differential thermal analysis of **10a–e**.

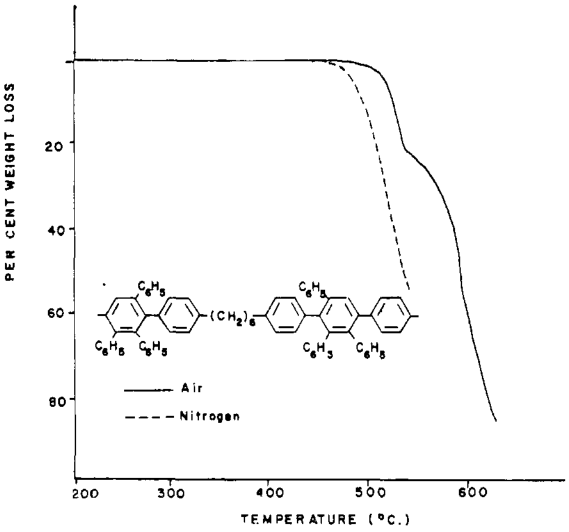

Figure 5. Thermal gravimetric analysis of **10c**.

corresponding polyphenylenes with *para* linkages (Figure 4). This phenomenon has been noted in other polymeric systems such as the polyimides.[18] Polymer **9a** showed no crystallinity as determined by an X-ray powder pattern.

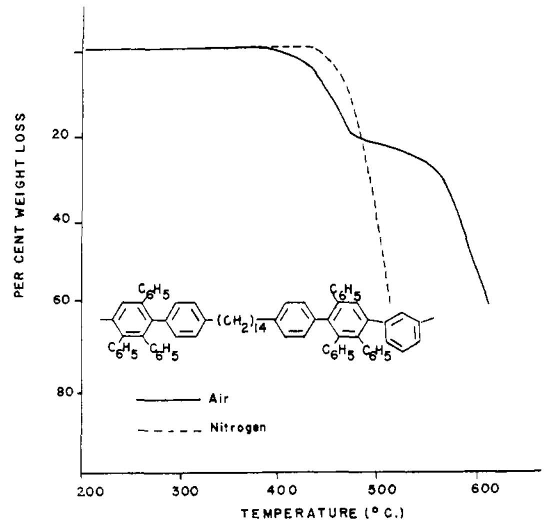

Figure 6. Thermal gravimetric analysis of **9e**.

Thermal gravimetric analyses (TGA) of the polymers (Table III) revealed that the loss of weight under nitrogen occurred in the range of 465–485°. A double break in the TGA curve was observed for all the polyphenylenes under an atmosphere of air (Figures 5 and 6). The polymers **9a**, **9b**, **10a**, **10b**, and **10c** surprisingly showed greater thermal stability in air than in nitrogen, undergoing a weight loss at 500–520°. The second break in air occurred at 550–560° for all the polyphenylenes. This high thermal stability of polyphenylenes which contain aliphatic linkages in the backbone of the polymer chain is quite unusual. An insight as to the mode of decomposition of the polymers in nitrogen was given by a comparison of the infrared spectra of the polymer before and after heating to a temperature just above the decomposition temperature (500°). After this treatment, the brown, completely insoluble polymer showed a decrease in the intensity of the C–H stretching peaks at 2920 and 2850 cm^{-1} and also a decrease in the maxima at 755 and 695 cm^{-1}, attributable to C–H bending of five adjacent hydrogens on the pendant phenyl groups.[17] These results substantiate at least a partial loss of the methylene linkage and some of the pendant phenyl groups.

The decomposition of the polyphenylenes in air was more extensive than in nitrogen, as evidenced by the infrared spectra taken at the start of the decomposition in air at 520°. A considerable broadening of the peaks had occurred and the C–H stretching doublet was barely visible in the spectrum. An infrared spectrum taken after the second break in the TGA curve at 560° showed the complete disappearance of the doublet at 2920 and 2860 cm^{-1} and only very broad peaks in the 900–700-cm^{-1} region. The black polymer residue probably consisted of a cross-linked, polynuclear structure. The weight loss between the first and second breaks in the thermal gravimetric analysis curves (Figures 5 and 6) ranged from 15 to 30%. This weight loss is equivalent to the loss of all of the

Table III
Thermal Gravimetric Analyses of Polymers
9a–e and **10a–e**

Polymer	TGA dec pt,[a] °C (nitrogen)	Temp, °C (air)
9a	470	520, 560
10a	470	500, 540
9b	485	520, 560
10b	485	515, 570
9c	485	470, 560
10c	485	520, 560
9d	480	460, 560
10d	480	475, 550
9e	465	430, 560
10e	465	440, 550

[a] The temperatures of decomposition reported are those corresponding to the intersection of the slopes of the two lines.

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[18] S. Nishizaki and A. Fukami, *Kogyo Kagaku Zasshi*, **66**, 382 (1966); *Chem. Abstr.*, **64**, 17, 729c (1966).

methylene groups and at least one benzene ring per recurring unit of the polymer.

Experimental Section

Monomers. 3,3′-Propylenedi-*p*-phenylenebis(2,4,5-triphenylcyclopentadienone) (2) was prepared as previously described.[15] From the reaction of 11.3 g (0.054 mol) of benzyl ketone and 8.2 g of **2e**[15] and 1.0 g (0.018 mol) of potassium hydroxide was obtained 10.0 g (68%) of purple crystals, mp 248–251° (lit.[15] mp 248–255°). Approximately 1.0 g of this product was dissolved in 10 ml of chloroform and chromatographed on Woelm neutral alumina with toluene as eluent. Evaporation of the toluene and recrystallization of the resulting solid from benzene–ethanol gave 0.8 g of purple crystals, mp 259–262° (lit.[15] mp 255–256°).

Anal. Calcd for $C_{61}H_{44}O_2$: C, 90.54; H, 5.48. Found: C, 90.46; H, 5.88.

***p,p*′-Diphenylglyoxalyl-1,4-diphenylbutane (3e).** Preparation of this compound as described[15] was abandoned because starting material was recovered at the end of the reaction. A mixture of 44.1 g (0.098 mol) of **3d**[15] and 23.3 g (0.21 mol) of selenium dioxide in 250 ml of dioxane was allowed to reflux for 12 hr. The mixture was filtered and the solvent was removed at reduced pressure to afford a yellow solid. The impure product was redissolved in glacial acetic acid and the red solution, after evaporation of the acetic acid to one-half the starting volume, was filtered by gravity to remove any remaining selenium. The filtrate was cooled in ice and the precipitated product was filtered, taken up in acetone and chromatographed on Woelm acid alumina with acetone as eluent. Evaporation of the acetone and recrystallization of the resulting solid from ethanol–acetone gave 22.1 g (45%) of yellow powder, mp 148–151° (lit.[15] mp 149.5–151°).

3,3′-Butylenedi-*p*-phenylenebis(2,4,5-triphenylcyclopentadienone) (3). Since benzyltrimethylammonium hydroxide (Triton B) in triethylene glycol afforded higher melting products in this condensation than potassium hydroxide in ethanol, the rest of the tetracyclones were synthesized by the following method. To a solution of 15.8 g (0.033 mol) of **3e** and 14.02 g (0.067 mol) of benzyl ketone in 100 ml of triethylene glycol heated to 100° was added 2 ml of 40% solution of Triton B in methanol. After the temperature of the solution dropped to 80°, 15 ml of methanol was added and the solution was allowed to cool to room temperature. After filtration of the mixture, the black solid was washed with cold absolute alcohol, redissolved in hot benzene and added dropwise to absolute alcohol. The dark purple crystals, which were obtained after cooling and filtering the solution, were dissolved in chloroform and chromatographed on Woelm neutral alumina with toluene as eluent. Evaporating the toluene to dryness on a roto evaporator, dissolving the resulting solid in benzene and adding the purple benzene solution dropwise to absolute alcohol afforded 5.3 g (18%) of dark purple crystals, mp 252–253° (lit.[15] mp 234–235°).

Anal. Calcd for $C_{62}H_{46}O_2$: C, 90.47; H, 5.63. Found: C, 90.33; H, 5.64.

***p,p*′-Diphenylglyoxalyl-1,6-diphenylhexane (4e)** was prepared by a method analogous to that described for **3e**. From the reaction of 9.86 g (0.021 mol) of **4d**[15] and 4.8 g (0.044 mol) of selenium dioxide in 250 ml of dioxane was obtained 6.1 g (58%) of yellow solid, mp 117–120° (lit.[15] mp 109–111°).

3,3′-Hexylenedi-*p*-phenylenebis(2,4,5-triphenylcyclopentadienone) (4) was synthesized under the same reaction conditions described for **3**. The reaction of 6.1 g (0.012 mol) of **4e**, 5.17 g (0.024 mol) of benzyl ketone and 1.5 ml of 40% solution of Triton B in 20 ml of triethylene glycol yielded 3.08 g (28%) of red-purple crystals, mp 215–217° (lit.[15] mp 109–110°).

Anal. Calcd for $C_{64}H_{50}O_2$: C, 90.32; H, 5.92. Found: C, 90.09; H, 5.69.

1,10-Diphenyldecane (5c). A mixture of 360 g of mossy zinc, 36 g of mercuric chloride, 36 ml of concentrated hydrochloric acid, and 500 ml of water was stirred for 5 min. The aqueous solution was decanted and to the zinc amalgam was added sufficient concentrated hydrochloric acid to cover about one-half of it, followed by 40 g (0.12 mol) of 1,10-diphenyl-1,10-decadione (**5b**)[19] in 650 ml of xylene. The mixture was heated under reflux for 7 hr, during which time gaseous hydrogen chloride (generated by dropping concentrated sulfuric acid into a mixture of sodium chloride and hydrochloric acid) was passed into the bottom of the flask to replace losses. At the end of the reflux time, a fresh sample of zinc–mercury amalgam was prepared (using one-half the starting amounts of zinc and mercury) and was added to the reaction mixture. After 24 hr of reflux, the mixture was cooled and the two layers were separated. The xylene layer was dried over anhydrous sodium sulfate and concentrated on a roto evaporator to give a yellow oil. The infrared spectrum of the oil showed only a trace of a carbonyl peak. Distillation of the product under reduced pressure afforded a colorless viscous oil, bp 180–190° (0.05 mm) (lit.[20] bp 240° (14 mm)), in a yield of 20.3 g (58%). The infrared spectrum showed no carbonyl absorption at 1700 cm^{-1}.

***p,p*′-Diphenacetyl-1,10-diphenyldecane (5d)** was prepared by a method analogous to that described for **3d**.[15] From the reaction of 26.1 g (0.088 mol) of **5c**, 27.2 g (0.176 mol) of phenylacetyl chloride and 35.2 g (0.26 mol) of aluminum chloride was obtained 20.5 g (45%) of white product, mp 95°. The nuclear magnetic resonance spectrum showed four main peaks: $\tau_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 8.7 ($-(CH_2)_8-$ multiplet), 7.4 ($-CH_2-C_6H_5$ triplet), 5.8 ($-CH_2C(=O)-$ singlet), 2.8, 2.1 (C_6H_6 split multiplet). Integration of the areas of the peaks of the nmr spectrum agreed with the theoretical values of the types and numbers of protons present in this compound.

Anal. Calcd for $C_{38}H_{42}O_2$: C, 85.99; H, 7.97. Found: C, 85.92; H, 7.71.

***p,p*′-Diphenylglyoxalyl-1,10-diphenyldecane (5e)** was synthesized under the same reaction conditions described for the preparation of **3e**. When the reaction of 20.5 g (0.038 mol) of **5d** and 17.2 g (0.155 mol) of selenium dioxide was allowed to reflux for 3 days, a yellow product, mp 85–86°, was obtained in a yield of 6.8 g (32%): nmr, $\tau_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 8.7 ($-(CH_2)_8-$ multiplet), 7.4 ($-CH_2C_6H_5$ triplet), 2.5, 2.0 (C_6H_6 split multiplet). Integration of the nmr spectrum confirmed the structure.

Anal. Calcd for $C_{38}H_{38}O_4$: C, 81.69; H, 6.85. Found: C, 81.18; H, 6.79.

3,3′-Decylenedi-*p*-phenylenebis(2,4,5-triphenylcyclopentadienone) (5) was synthesized under the same reaction conditions described for **3**. The reaction of 3.16 g (0.0056 mol) of **5e**, 2.37 g (0.011 mol) of benzyl ketone, and 1.0 ml of 40% solution of Triton B in 20 ml of triethylene glycol yielded a black-purple solid which was dissolved in chloroform and chromatographed on Woelm neutral alumina with benzene as eluent. Evaporation of the benzene to dryness on a roto evaporator yielded a dark purple oil which could not be induced to crystallize from benzene–ethanol. The oil was then dissolved in acetone and added dropwise to 95% alcohol to yield 2.1 g (41%) of light purple solid: mp 158–160°; nmr spectrum, $\tau_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 8.7 ($-CH_2)_{10}-$ multiplet), 3.1, 2.8 (C_6H_6 split multiplet). Integration of the nmr spectrum confirmed the structure. The presence of only one com-

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(19) C. G. Overberger and M. Lapkin, *J. Amer. Chem. Soc.*, 77, 4651 (1955).

(20) W. Borsche and J. Wollemann, *Ber.*, **44**, 3185 (1911).

pound was shown by thin layer chromatography on silica gel with benzene as eluent.

Anal. Calcd for $C_{68}H_{58}O_2$: C, 90.03; H, 6.44. Found: C, 89.86; H, 6.35.

1,14-Diphenyl-1,14-tetradecadione (6b). The procedure for the preparation of this compound is the same as that described for **5b.**[19] Tetradecanedioyl chloride (**6a**) was prepared from the reaction of tetradecanedioic acid (Aldrich Chemical Co.) with thionyl chloride. The excess thionyl chloride was removed under reduced pressure and the acid chloride residue was used without purification. From the reaction of 92 g (0.69 mol) of aluminum chloride and 68 g (0.19 mol) of tetradecanedioyl chloride in 600 ml of dry benzene was obtained 61 g (85%) of product, mp 95–96°. Three recrystallizations from absolute alcohol and a final recrystallization from methanol afforded white crystals: mp 102–103°; nmr spectrum, $\tau_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 8.7 (–$(CH_2)_{10}$– multiplet), 7.1 (–$CH_2C(=O)$– triplet), 2.5, 2.0 (C_6H_6 split multiplet).

Anal. Calcd for $C_{26}H_{34}O_2$: C, 82.49; H, 9.05. Found: C, 82.45; H, 9.05.

1,14-Diphenyltetradecane (6c) was synthesized under the same reaction conditions described for the preparation of **5c**. From the reduction of 61 g (0.17 mol) of **6b** with zinc–mercury amalgam in xylene was obtained 22.2 g (37%) of colorless oil: bp 220° (0.3 mm) (lit.[21] bp 262–265° (8 mm)) which solidified on standing; mp 36–37; nmr spectrum, $\tau_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 8.7 (–$(CH_2)_{12}$– multiplet), 7.4 (–$CH_2C_6H_5$ triplet), 2.8 (C_6H_6). The infrared spectrum showed no carbonyl absorption at 1700 cm^{-1}.

***p,p*′-Diphenacetyl-1,14-diphenyltetradecane (6d).** The procedure for the preparation of this compound is the same as that described for the preparation of **3d.**[15] From the reaction of 22.2 g (0.063 mol) of **6c**, 19.5 g (0.13 mol) of phenylacetyl chloride and 25.2 g (0.19 mol) of aluminum chloride was obtained 15.1 g (41%) of white solid: mp 98–100°; nmr spectrum, $\tau_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 8.7 (–$(CH_2)_{12}$– multiplet), 7.4 (–$CH_2C_6H_5$ triplet), 5.8 (–$CH_2C(=O)$– singlet), 2.8, 2.1 (C_6H_6 split multiplet).

Anal. Calcd for $C_{42}H_{50}O_2$: C, 86.87; H, 8.59. Found: C, 86.91; H, 8.27.

***p,p*′-Diphenylglyoxalyl-1,14-diphenyltetradecane (6e)** was synthesized under the same reaction conditions described for the preparation of **3e**. The reaction of 15.0 g (0.025 mol) of **6d** and 9.0 g (0.08 mol) of selenium dioxide in 300 ml of dioxane yielded 10.9 g (71%) of yellow product: mp 75–76°; nmr spectrum, $\tau_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 8.7 (–$(CH_2)_{12}$– multiplet), 7.4 (–$CH_2C_6H_5$ triplet), 2.5, 2.0 (C_6H_6 split multiplet).

Anal. Calcd for $C_{42}H_{46}O_4$: C, 82.05; H, 7.54. Found: C, 81.94; H, 7.73.

3,3′-Tetradecylenedi-*p*-phenylenebis(2,4,5-triphenylcyclopentadienone) (6) was synthesized under the same reaction conditions described for **3**. The reaction of 6.0 g (0.0097 mol) of **6e**, 8.2 g (0.039 mol) of benzyl ketone and 1 ml of 40% solution of Triton B in 20 ml of triethylene glycol yielded 11.0 g of black solid which was purified by "dry column" chromatography with silica gel as packing and benzene as solvent. The first fraction was collected by cutting the packed nylon tubing at the point where the first purple band ended. The product was then removed from the silica gel by washing the silica gel with anhydrous ether in a sintered glass funnel. Evaporation of the ether yielded a purple oil which was dissolved in acetone and added dropwise to 95% alcohol. Filtration of the precipitated product afforded 3.1 g (33%) of dark purple solid: mp 115–117°; nmr spectrum, $\tau_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 8.7 (–$(CH_2)_{14}$– multiplet), 3.1, 2.8 (C_6H_6 split multiplet). Integration of the nmr spectrum confirmed the structure. Thin layer chromatography on silica gel with benzene as eluent showed the presence of only one compound.

Anal. Calcd for $C_{72}H_{66}O_2$: C, 89.77; H, 6.90. Found: C, 89.87; H, 6.90.

***m*-Diethynylbenzene (7)** was prepared as previously described.[22] Distillation of the product under reduced pressure yielded a clear liquid: bp 30° (0.25 mm) (lit.[22] bp 78° (14 mm)).

***p*-Diethynylbenzene (8)** was obtained by the dehydrobromination of *p*-diethyldibromobenzene.[22] Before each polymerization, *p*-diethynylbenzene was resublimed to yield colorless plates, mp 92–95° (lit.[22] mp 95°).

Solvent. The solvent used throughout for polymerization, membrane osmometry, and viscosity measurements was reagent-grade toluene. No attempt to purify it further was undertaken.

Polymers. All polymerizations were carried out by the same method (Table I); a typical polymerization to yield the poly(hexaphenylpentaphenylene butane) (**10b**) was run as follows. A mixture of 0.1533 g (1.215 mmol) of *p*-diethynylbenzene (**8**) and 1.000 g (1.215 mmol) of 3,3′-butylenedi-*p*-phenylenebis(2,4,5-triphenylcyclopentadienone) (**3**) was placed in a 20-ml polymerization tube with 5.0 ml of toluene. The contents of the tube were degassed by several freeze–thaw cycles at liquid nitrogen temperatures and then sealed *in vacuo*. Toluene (300 ml) was added to a 1 l Parr pressure reactor, the tube was placed inside, and the reactor was closed and heated to 225° for 24 hr and 250° for 12 hr. After the reactor had cooled to room temperature, the contents of the tube were poured into 250 ml of acetone. The precipitated polymer was filtered and dried *in vacuo* at room temperature for 24 hr. The white polymer, $[\eta]$ = 0.59 (25° in toluene), was obtained in a yield of 0.9850 g (91%). An analytical sample was prepared by dissolving the polymer in benzene, freezing the solution in a Dry Ice–acetone bath, and removing the solvent at reduced pressure for 24 hr.

Physical Determinations. A. Viscosities. All viscosities (intrinsic) were taken on toluene solutions of 0.25 g of polymer/100 ml of solvent at 25° with a Cannon–Ubbeholde microdilution viscometer, No. 75. The intrinsic viscosities for the polymers are listed in Table II.

B. Film Formation. The most suitable method for producing films of the polymers was to cast them from concentrated solutions of chloroform onto glass plates. The glass plates were placed in a hood to dry and the film was stripped from the plate. The film was then dried *in vacuo* at 110° for 24 hr. The polyphenylene films were yellow, translucent, very soft and flexible.

C. Thermal Gravimetric Analysis and Differential Thermal Analysis. The thermal stabilities of the polymers (Figures 5 and 6) were measured both in air and nitrogen atmosphere on a Du Pont 950 thermogravimetric analyzer by heating a continuously weighed polymer sample (20 mg) from 25 to 800° at a rate of 5°/min.

The differential thermal analyses of the polymers (Figures 3 and 4) were carried out on a Du Pont 900 differential thermal analyzer. The samples were heated under an atmosphere of nitrogen at a rate of 20°/min.

D. Molecular Weights. The molecular weights (Table II) were obtained with a Hewlett-Packard high-speed membrane osmometer using a superdense membrane at 29.5° in toluene. The concentrations of the solutions ranged from 10 to 0.5 g/l.

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