The cluster function given by eq 12 is shown in Figure 6f for an athermal solution and in Figure 6g for a system with $\chi = 0.45$. The cluster function determined from eq 6 is given by

$$G_{11}/\bar{v}_1 = -[(v_2/v_1)(C - D)/(C - D - v_2/v_1)] - 1 \quad (15)$$

where

$$C = mcv_2\left[1 + \frac{(y - 1)}{xmc} + 2\chi v_2\right]\Big/(1 + mc) \quad (16)$$

and

$$D = [2x(1 + mc) - y^2v_2]/ \left[1 + \frac{y^2}{2(x - y)} - \frac{(1 + mc)x}{(x - y)v_2}\right](1 + mc)2x \quad (17)$$

The cluster function derived from eq 7 differs from eq 16 only in the additional term of eq 16, $mv_2/(1 + mc)$. Calculated curves based on these equations are shown in Figure 6i.

The Flory-Leonard equation with $\chi = 0.45$ gives computer curves in good agreement with the experimental data, whereas $\chi = 0.6$ gave a better fit to the $a_1 - v_1$ data (Figure 5). The Wee equations, derived to determine the effect of flexible side chains on phase equilibria, do not fit as well. This is not surprising, as the rodlike character of the main chain still plays a significant role in the activity expression at low concentration, in contrast to the Flory-Leonard expression.

It is clear from the comparison of the experimental data with various theories that the free energy associated with the initial solution process is controlled by polymer side chain–solvent mixing. This is in marked contrast to more dilute polymer solutions, where the rodlike behavior of the molecules is of major importance to the thermodynamics of this system.[3,12]

Catenation and Kinetics of the Diels–Alder Step-Growth Reaction in the Synthesis of Phenylated Polyphenylenes[1]

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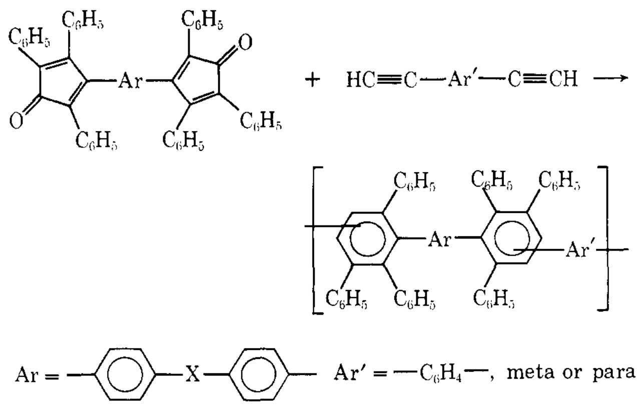
ABSTRACT: The Diels–Alder step-growth polymerization of biscyclopentadienones with bisacetylenes, which can produce either para or meta catenation in the benzene ring formed from the reaction, was shown by a model reaction to yield both types of catenation. The model reaction of 3-(4-biphenylyl)-2,4,5-triphenylcyclopentadienone with 4-ethynylbiphenyl gave products in which the ratios (para to meta) varied with the reaction temperature from 0.55 at 100° to 1.0 at 255°. The application of the Arrhenius law to the data yields a difference in the enthalpy of activation of ($\Delta H_m^{\ddagger} - \Delta H_p^{\ddagger}$) of -1.6 kcal/mol and a difference in the entropy of activation ($\Delta S_m^{\ddagger} - \Delta S_p^{\ddagger}$) of 3.0 eu. The polymerization reaction of 3,3′-(oxydi-*p*-phenylene)bis(2,4,5-triphenylcyclopentadienone) followed a second-order rate law, and the rate constants at the temperatures of 225, 200, and 175° were found to be 1.14×10^{-3}, 4.6×10^{-4}, and 2.6×10^{-4} l./(mol sec), respectively. The Arrhenius activation parameters as calculated from the rate constants were $\Delta H^{\ddagger} = 12.4$ kcal/mol and $\Delta S^{\ddagger} = -48$ eu, consistent with a Diels–Alder reaction which requires a low ΔH and a large negative ΔS.

The Diels–Alder reaction, or diene synthesis, has long been utilized in synthetic organic chemistry, and in many instances high yields of the adduct are obtained. The Diels–Alder reaction has been employed as a step-growth reaction in the formation of linear, ladder, and stepladder polymers.[2,3] Polymer formation is particularly effective when a small molecule such as carbon monoxide, carbon dioxide, or sulfur dioxide is lost during the reaction, and thus high yields of polymer can be obtained.

High molecular weight polymers containing the polyphenylene units have been successfully synthesized by the utilization of the Diels–Alder reaction of bistetracyclones and bisethynylbenzenes.[4–10] During the step-growth reaction of this poly-



X = nil, O, S, $(CH_2)_n$
$n = 3, 4, 5, 10, 14$

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(1) Taken in part from the Ph.D. thesis of G. K. Noren, University of Iowa, June 1971.

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

(3) W. J. Bailey in "Step Growth Polymerization," D. H. Solomon, Ed., Marcel Dekker, New York, N. Y., in press.

(4) H. Mukamal, F. W. Harris, R. O. Rakutis, and J. K. Stille, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **8**, 496 (1967).

(5) J. K. Stille, F. W. Harris, R. O. Rakutis, and H. Mukamal, *J. Polym. Sci., Part B*, **4**, 791 (1966).

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

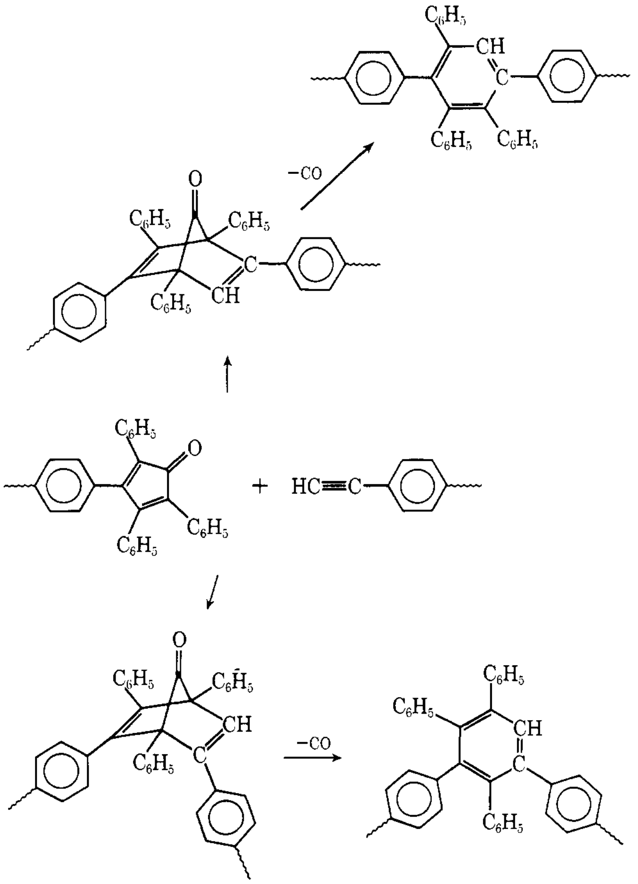
(7) J. K. Stille and G. K. Noren, *ibid., Part B*, **7**, 525 (1969).

(8) W. Wrasidlo and J. M. Augl, *ibid., Part B*, **7**, 519 (1969).

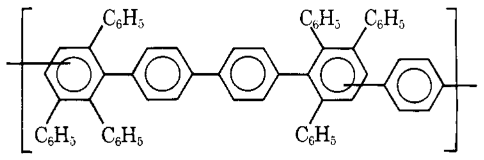
(9) W. Ried and D. Freitag, *Naturwissenschaften*, **53**, 306 (1966).

(10) J. K. Stille, R. O. Rakutis, H. Mukamal, and F. W. Harris, *Macromolecules*, **1**, 431 (1968).

merization, a new benzene ring containing pendent phenyl groups is formed. Depending on the direction of the cycloaddition, it is possible to obtain both meta and para catenation through the newly formed benzene ring.



One of the special properties of these polymers is their unusual solubility in common organic solvents such as benzene, toluene, and chloroform. This high degree of solubility, which is of particular interest in polyphenylene **1**, can be attributed to the presence of the pendent phenyl groups. However, a high degree of meta catenation in the polymer chain would also produce increased solubility, as has been observed with meta oligophenyls.[11]



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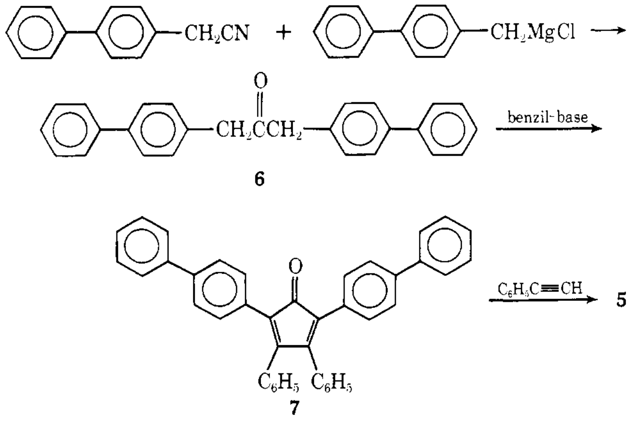
Discussion

(A) Model Reaction Study (See Scheme I). In order to determine the relative amount of each type of catenation, a study of the model reaction of 3-(4-biphenylyl)-2,4,5-triphenylcyclopentadienone[12] (**2**) with 4-ethynylbiphenyl[13] (**3**) to produce the meta- and para-linked isomers **4** and **5** was undertaken. The biphenyl moiety was chosen as a substituent for both functional types in order to obtain a stereochemical environment in the transition state of the model intermediate which would closely approximate that of the growing polymer.

Initially, the reaction was carried out at 200° in order to obtain a sufficient quantity of pure isomer for characterization. The pure isomers were separated from the crude reaction mixture by fractional crystallization to give a high melting isomer, 278° (after 15 crystallizations). A second isomer, mp 200°, was isolated by further fractional crystallizations. Following the separation of the isomers and a study of their physical properties, it was apparent that an unequivocal assignment of structure could not be made. Therefore, one of the isomers was independently synthesized.

The independent synthesis of 2'',4'',5''-triphenyl-*p*-quinquephenyl (**5**) was accomplished according to the following sequence. The Grignard reaction of 4-biphenylylmethylmagnesium chloride with 4-biphenylylacetonitrile produced 1,3-(4-biphenylyl)-2-propanone (**6**) in 40% yield. The tetracyclone **7** was obtained in 62% yield by standard conditions involving the base-catalyzed condensation of **6** with benzil. The Diels–Alder reaction of **6** with phenylacetylene at 200° gave an almost quantitative yield of the para isomer **5**, which had mp 275–277°.

Some of the properties of these phenyl-substituted oligophenyls are compared in Table I with those of known phenyl-substituted oligomers.[14,15] The melting points of unsubstituted polyphenyls in the para series containing from two to six phenylene units increase rapidly to greater than 450°, while the melting points of unsubstituted polyphenyls in the meta series increase only very slowly.[11] This can be attributed to a disturbance of the symmetry of the molecule caused by meta links and can be quantitatively expressed by the relationship



$$T_f = \Delta H_f/\Delta S_f$$

A reduction in symmetry would result in an increase in the entropy term and a corresponding lowering of the melting point. It should be noted that due to the reduction in symmetry caused by the presence of the phenyl substituents, all of the substituted polyphenyls in Table I are lower melting than unsubstituted *p*-sexiphenyl, which melts at 475°.[16] Thus the assignment of the meta structure **4** to the lower melting isomer obtained in the model reaction corresponds to those observations and indicates a lack of symmetry.

In the uv spectra of poly(*p*-phenyls), the first intense band increases in both wavelength and intensity from biphenyl

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[11] W. Ried and D. Freitag, *Angew. Chem., Int. Ed. Engl.*, **7**, 835 (1968).

[12] W. Dilthey, O. Trösken, K. Plum, and W. Schommer, *J. Prackt. Chem.*, **141**, 331 (1934).

[13] H. Tani, F. Toda, and K. Matsumiya, *Bull. Chem. Soc. Jap.*, **36**, 391 (1963).

[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).

[16] R. Pummer and K. Bittner, *Chem. Ber.*, **57**, 87 (1924).

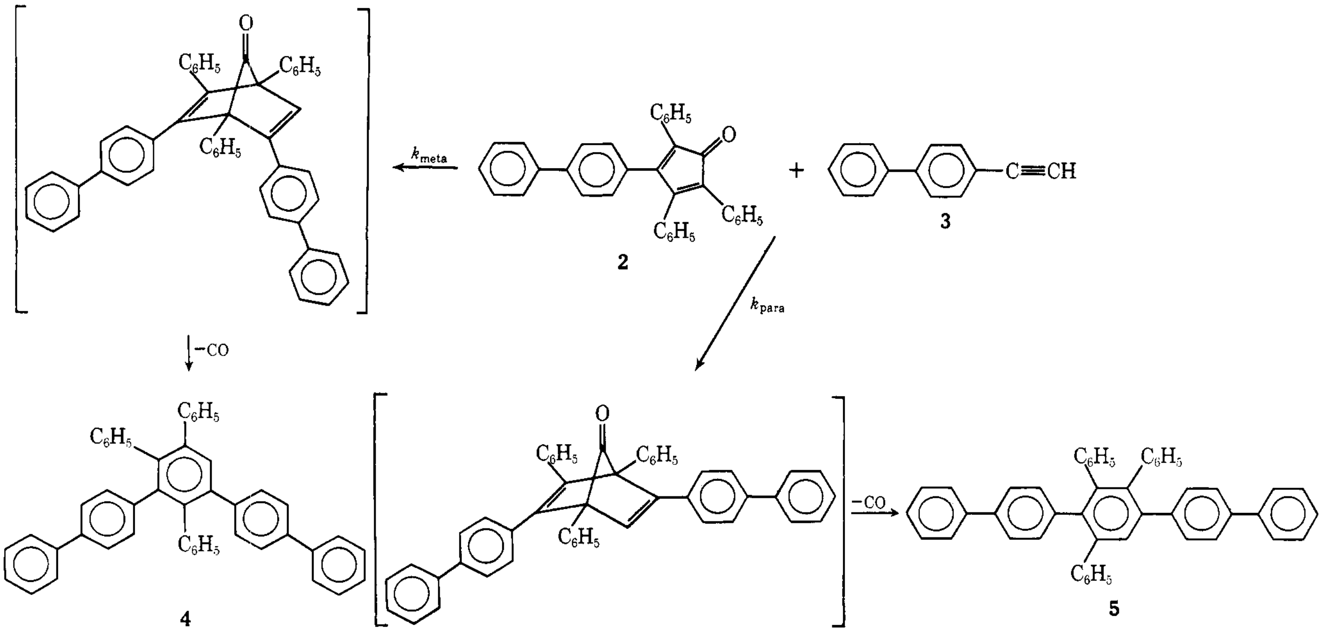
TABLE I

A COMPARISON OF THE PROPERTIES OF PHENYLATED POLYPHENYLS

Polyphenyl	Mp, °C	λ_1, nm	$\epsilon_1 \times 10^{-3}$, l./(mol cm)	λ_2, nm	$\epsilon_2 \times 10^{-3}$, l./(mol cm)	X-Ray,[a] Å	Ref
4	200	265.0	65.1	274	59.3	5.3, 4.1, 4.7, 4.4	This work
5	278 275–277	262.5	51.2	278	46.2	5.3, 5.8, 4.2, 9.3	This work
Hexaphenylbenzene (**8**)	464.5	247	56.8	266	34.7		14
2′,3′,5,′6′,3′′,5′′,6′′-Octaphenyl-*p*-quaterphenyl (**9**)	322–324	254	63.5	272	49.0		15
2′,3′,5′,6′,2′′′,3′′′,5′′′,6′′′-Octaphenyl-*p*-quinquephenyl (**10**)	468–470	252	77.7	278	53.0		15
2′,3′,5′,6′,2′′′′,3′′′′,5′′′′,6′′′′-*m*-Octaphenyl-*p*-sexiphenyl (**11**)	440–442	247	78.5	279	54.2		14

[a] Kα 1.9373 Å.

Scheme I



to *p*-sexiphenyl, while in the meta series the wavelength remains essentially the same and the intensity increases with increased chain length up to sedeciphenyl.[11] This band has been shown to be due to pure electronic interactions or π-electron repulsions between adjacent aromatic rings through a comparison of experimentally determined energy values[17] with theoretical values. In the calculations, both conjugation and the angle of twist between phenyl rings were neglected. In the phenylated polyphenyl series, this effect has been interpreted in terms of the increased steric crowding in the sequence **11–8,** causing increased restrictions on the oscillation of the benzene rings such that they become more nearly orthogonal to the central ring.[15] Although the wavelength (λ_1) remains constant, the corresponding absorptivity decreases as the steric crowding increases. A comparison of the ϵ_1 values of **4** and **5** (6.5 × 10⁴ and 5.12 × 10⁴ l./(mol cm), respectively) shows that there is more steric crowding in the para isomer.

The determination of the isomer ratios of the crude reaction mixtures was carried out by the application of Beer's law to the uv spectra. The complete uv spectra of the para and meta quinquephenyls are shown in Figure 1. The simi-

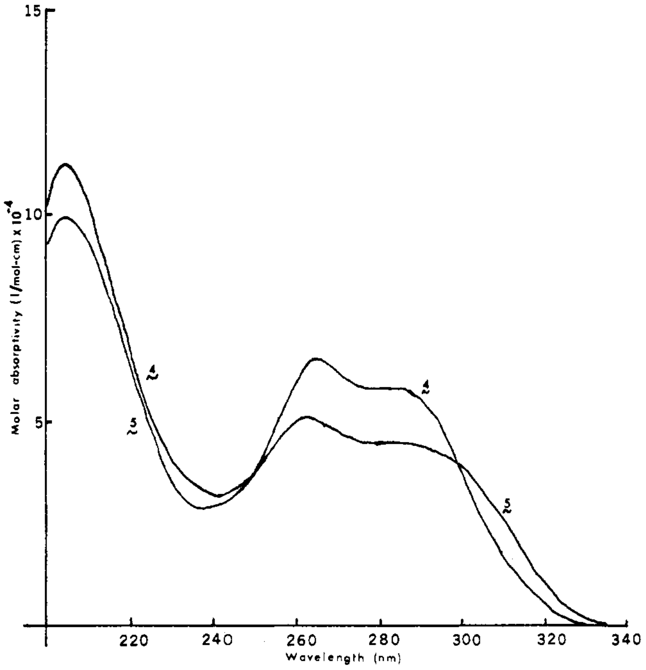


Figure 1. Uv spectra of the pentaphenyl isomers.

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[17] J. N. Murrell and H. C. Lonquet-Higgins, *J. Chem. Soc.*, 2532 (1955).

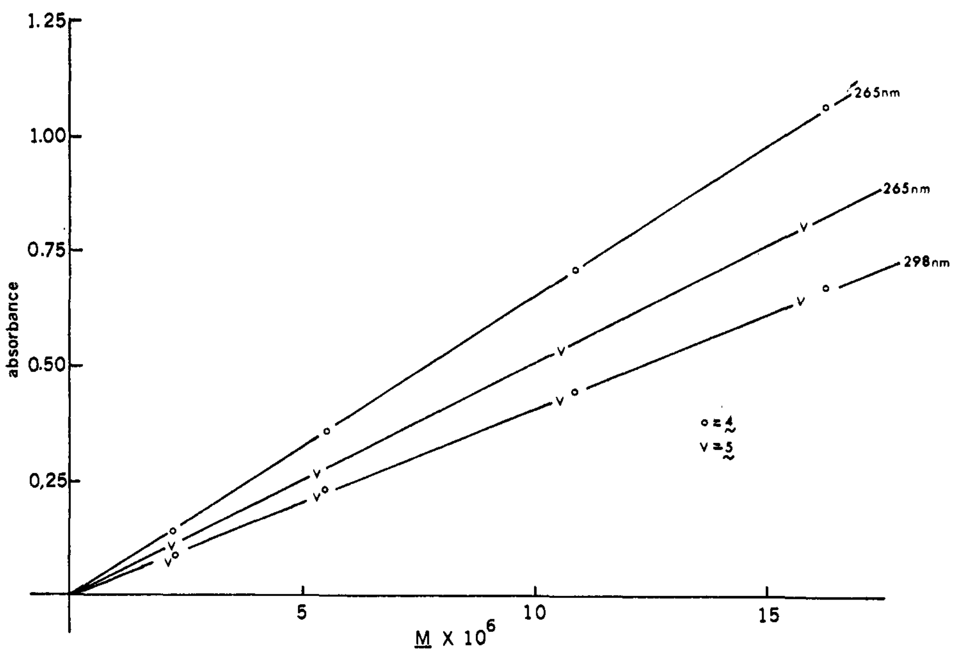

Figure 2. Beer's law plot of **4** and **5** at the points of analysis.

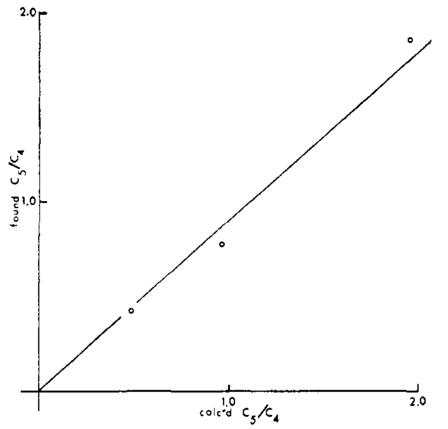

Figure 3. Correlation of the calculated c_5/c_4 ratio with the found c_5/c_4 ratio.

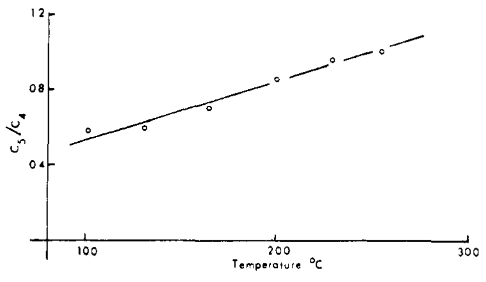

Figure 4. Temperature dependence of the isomer ratio.

larity of the two curves as well as the isosbestic point at 298 nm are very important features, since the application of Beer's law is often hampered by similar absorption spectra of the two compounds.

In the application of Beer's law to binary mixtures, two wavelengths (λ_1 and λ_2) are chosen and a series of two equations (1) in two unknowns is solved.

$$\begin{aligned} A_1 &= a_{x1}c_x + a_{y1}c_y \\ A_2 &= a_{x1}c_x + a_{y2}c_y \end{aligned} \qquad (1)$$

where A = absorbance, a = absorptivities, and c = concentration. The choice of wavelengths is important in determining the precision of the measurement. Ideally, the absorptivity ratios a_{y1}/a_{y2} and a_{x1}/a_{x2} should be less than one.[18] Since these conditions could not be met with the phenylated polyphenyl isomers studied, the wavelengths chosen were the λ_{max}'s for the meta isomer at 265 nm and the isosbestic point at 298 nm. This choice made one of the absorptivity ratios less than one, and at the same time simplified many of the calculations because eq 1 reduced to

$$\begin{aligned} A_i &= a_i c_{total} \\ A_2 &= a_{x2}c_x + a_{y2}c_y \end{aligned} \qquad (2)$$

Beer's law was shown to be obeyed by both **4** and **5** at 265 and 298 nm (Figure 2).

The absorptivity at the isosbestic point (a_i) was determined as 66.7 l./(g cm), while at 265 nm the absorptivity of **4** (a_4) was 106.9 l/(g cm) and the absorptivity of **5** (a_5) was 83.4 l./(g cm). The ratio of **5** to **4** was calculated using eq 3, which can be derived from eq 2. The absorbances A_i and A_2 were determined for the crude mixtures at 298 and 265 nm, respectively.

$$c_5/c_4 = (a_4A_i - a_iA_2)/c_4(a_iA_2 - a_5A_i) \qquad (3)$$

A check of the use of eq 3 and the validity of the Beer's law determination was carried out on a set of three mixtures of the pure isomers having known para to meta ratios. The results are plotted in Figure 3 and give a good linear correlation. The slope of 0.91 was so close to unity that no corrections were made on the actual determinations.

The model reaction was carried out over the temperature range 100–255° and the isomer ratios of the crude reaction mixtures were determined by uv analysis. The data are shown in graphical form in Figure 4. The straight line determined by least-squares analysis had a slope of 0.003 per degree. In the temperature range studied, para isomer comprises only

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(18) E. J. Meehan in "Treatise in Analytical Chemistry," I. M. Kolthoff and P. J. Elving, Ed., Wiley, New York, N. Y., 1964, p 2793.

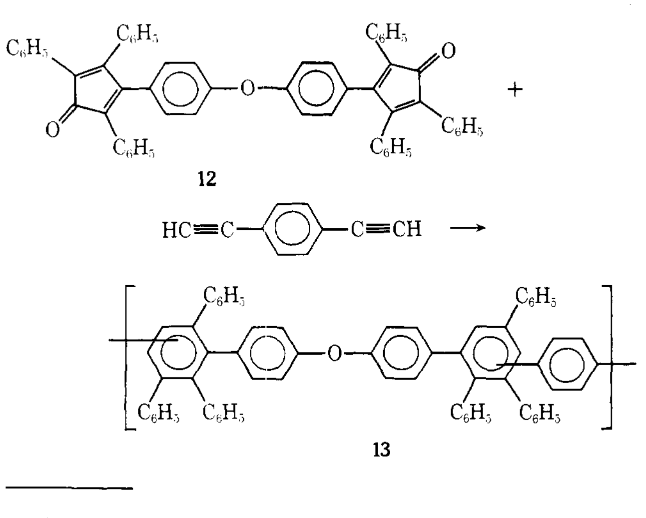
about 30–50% of the product. Similar ratios of meta and para linkages are expected to appear along the polymer chain backbone and add to the overall disorder of these polyphenylenes. This increased disorder can account for the unusual solubility properties of polyphenylenes produced from the Diels–Alder reaction.

Since the ratio of meta to para quinquephenyl varies with temperature, the data may be treated kinetically by application of the Arrhenius equation. The mechanism of the Diels–Alder reaction of tetracyclones consists of two steps.[19] The first step, which is the formation of a bridged carbonyl intermediate, has been shown to be rate determining, and the second step is the rapid loss of carbon monoxide.[20–22] Thus the ratio of products 5:4 is also the ratio of the rate constants $k_{para}:k_{meta} = k_{rel}$ and a plot of ln k_{rel} *vs.* the reciprocal of absolute temperature (Figure 5) yields a straight line with a slope of -0.797×10^3 and an intercept of 1.50. From these values, the difference in the enthalpy of activation ($\Delta H_m^{\ddagger} - \Delta H_p^{\ddagger}$) was found to be -1.6 kcal/mol and the difference in the entropy of activation ($\Delta S_m^{\ddagger} - \Delta S_p^{\ddagger}$) was found to be 3.0 eu. Thus, the meta isomer is favored by a lower enthalpy of activation and has a more positive entropy of activation, since the entropy of Diels–Alder reaction is usually large and negative. This entropy difference is reflected in the difference in melting points of the products. One reason for the preference of meta over para catenation could be the increased steric crowding in the transition state leading to the norbornadienone. Greater crowding in the para isomer of the final product is indicated by the lower molar absorptivity (ϵ_1) in Table I.

(B) Kinetics of the Diels–Alder Polymerization. The polymerization reaction of **12** with *p*-diethynylbenzene to give the oxygen-containing polyphenylene **13** was employed in the kinetic studies. This step-growth or condensation polymerization should follow second-order kinetics and obey the expression

$$C_0K't = 1/(1 - p) - \text{constant}$$

where C_0 is the initial concentration of reactive ends (both tetracyclone and acetylene) in moles per liter, t is time, p is the extent of reaction, and K' is the rate constant. The rate constant K' is the total rate constant for the polymerization and equal to the sum of the rate of meta catenation, K'_m, and the rate of para catenation, K'_p. The constant of integration contained in the equation should be equal to one. A modification of the kinetic expression was effected using the relationship $1/(1 - p)$ equal to the degree of polymerization (DP), with the following result.


12

13

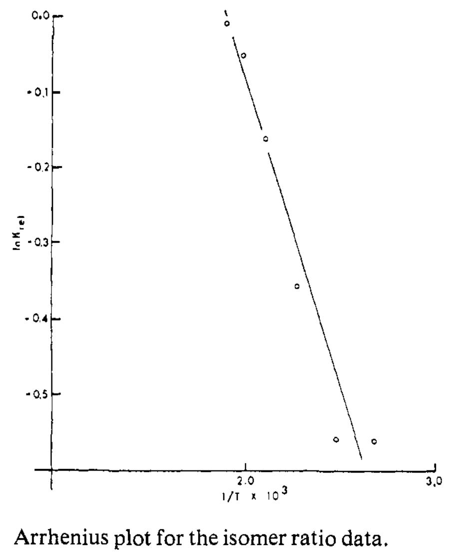


Figure 5. Arrhenius plot for the isomer ratio data.

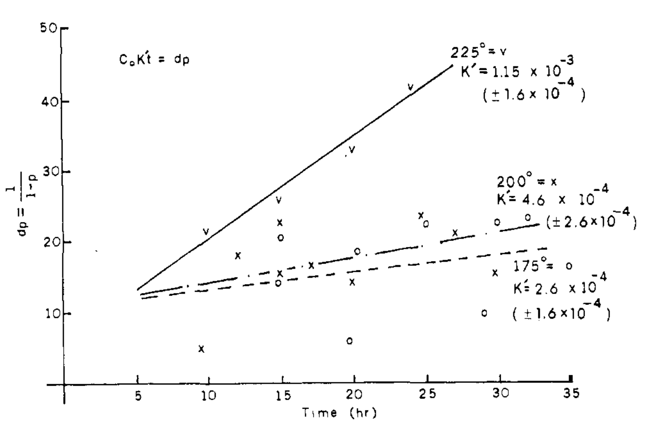


Figure 6. *Rates of polymerization at various temperatures.*

$$\text{DP} = C_0K't + 1$$

Thus a plot of degree of polymerization *vs.* time should yield a straight line with a slope of C_0K' and an intercept of one.

For the kinetic determinations, the degree of polymerization was obtained by utilizing the Mark–Houwink equation

$$[\eta] = K(\bar{M}_n)^a$$

and

$$\text{DP} = \bar{M}_n/M_0$$

where M_0 = the molecular weight of a structural unit. The constants $K = 2.48 \times 10^{-4}$ and $a = 0.742$ for the Mark–Houwink equation were determined from number-average molecular weight ($\bar{M}_n$) (osmotic pressure) and intrinsic viscosity ([η]) data on the polymer.[6] This allows the kinetic curves to be determined from an intrinsic viscosity measurement.

Polymerizations were carried out in sealed tubes at a concentration of 0.33 mol of reactive ends (both tetracyclone and acetylene) per liter of toluene for various times at temperatures of 175, 200, and 225°. The intrinsic viscosities were

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[19] A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, **65**, 261 (1965).

[20] I. Benghiat and E. I. Becker, *J. Org. Chem.*, **23**, 885 (1957).

[21] D. N. Mathews, Ph.D. Thesis, Polytechnic Institute of Brooklyn, June 1961.

[22] D. N. Mathews and E. I. Becker, *J. Org. Chem.*, **31**, 1135 (1966).

TABLE II
REACTION CONDITIONS AND PROPERTIES OF POLY(2,3,6,2''',3''',6'''-HEXAPHENYL-*p*-PENTAPHENYLENE-4',1''-OXIDE-4,4''''-YLENE) (**13**)

Reactive ends,[a] mmol	Toluene, ml	Reaction temp, °C	Reaction time, hr	$[\eta]$, dl/g[b]	$\overline{M}_n \times 10^{-4}$[c]	DP[d]
0.7444	2.26	175	15	0.283	1.35	15
0.8784	2.66	175	15	0.356	1.80	20
1.0492	3.18	175	20	0.138	0.50	5.7
0.9096	2.76	175	20.5	0.335	1.66	19
0.7900	2.39	175	25	0.385	2.00	23
0.9764	2.96	175	29	0.210	0.89	10
0.6104	1.85	175	30	0.383	1.99	23
0.5180	1.60	175	33	0.403	2.13	24
0.5768	1.75	200	9	0.127	0.45	5.1
1.7460	5.29	200	12	0.337	1.67	19
0.6192	1.87	200	15	0.294	1.39	16
1.0780	3.27	200	15	0.400	2.10	24
1.9308	5.85	200	17	0.304	1.46	17
0.6416	1.94	200	20	0.281	1.30	15
1.6496	5.00	200	21.5	0.301	1.44	16
0.6828	2.06	200	25	0.397	2.08	24
1.8616	5.63	200	27	0.362	1.84	21
4.1736	12.65	225	10	0.35	1.8	22
3.5452	10.74	225	15	0.41	2.2	26
3.5608	10.79	225	20	0.48	2.8	33
2.8532	8.65	225	24	0.61	3.6	41

[a] Total amount of tetracyclone and acetylene reactive ends. [b] Determined at 30° in reagent grade toluene with a No. 75 Cannon-Ubbelohde microdilution viscometer using the equation $a_0 = [\eta] = [-2n \pm 4n^2 + 2(\Sigma X)(\Sigma Y + \Sigma Z)]/\Sigma X$, where ΣX = the sum of the concentrations in grams per deciliter, ΣY = the sum of the inherent viscosities, ΣZ = the sum of the reduced viscosities, and n = the number of determinations. [c] Determined from the Mark–Houwink equation, $[\eta] = (2.48 \times 10^{-4})(\overline{M}_n)^{0.742}$. The constants K and a were calculated by solving the two simultaneous equations, $\ln 0.61 = \ln K + a \ln 36{,}000$, $\ln 0.38 = \ln K + a \ln 19{,}000$. The intrinsic viscosities and the number-average molecular weights (osmotic pressure) were obtained from the data of Mukamal.[6] [d] The weight of a repeating unit is 887.089.

TABLE III
ARRHENIUS PARAMETERS FROM RATES OF POLYMERIZATION

Reaction Temp,[a] °C		Activation parameters $\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
200	225	25.21	−22.41
175	225	12.62	−47.68

[a] The activation parameters from pairwise analysis of 175–200° are very far from reality and have not been included.

converted to degree of polymerization numbers (Table II) and subsequently plotted aginst time (Figure 6). Considerable scatter was noted in the data points for the lower temperature, and it is important to point out several peculiarities of the polymerization system. Each data point represents an individual experiment, since the polymerization must be carried out in sealed tubes so that the acetylene will not sublime out of the reaction mixture; therefore, aliquots of the reaction mixture could not be taken at various times. The tetracyclone monomer was not soluble at the concentration necessary to obtain high molecular weight polymers; therefore, a stock solution of the monomers could not be made. Also, the points for the 225° line were obtained with a much larger batch size than those for 200 and 175°. The slopes of the lines were obtained by a linear least-squares analysis, and the rate constants determined are of the same order of magnitude as those determined for the reaction of tetracyclone with methyl arylpropiolates.[22] From this it may be concluded that the polymerization does indeed obey second-order kinetics.

TABLE IV
MODEL REACTION CONDITIONS

Run no.	**2**, g	**3**, g	Toluene, ml	Temp, °C	Time, hr
1	0.1777	0.0703	2.8	100	48
2	0.2086	0.0825	3.8	130	24
3	0.0334	0.0132	0.6	165	24
4	0.1891	0.0748	2.8	200	24
5	0.5951	0.1349	9	230	24
6	0.1612	0.0638	2.4	255	24
7	0.0262	0.0104	0.5	295	24

A test of the Arrhenius law showed no linearity to the points of ln K' *vs.* the reciprocal of the absolute reaction temperature. This could be because of data scatter, as shown in Figure 6, or possibly because the rate constant K' is actually a complex rate constant; K' is the sum of the rate constant of para catenation (K_p') and that of meta catenation (K_m'). Recall that the ratio of the rate for the model reaction proved to vary with temperature. A forced linear relationship for all three temperatures gives the $\Delta H^{\ddagger}$ of polymerization of 12.4 kcal/mol and the $\Delta S^{\ddagger}$ of polymerization of −48 eu. In spite of the apparent lack of consistency in the data, these numbers are acceptable values for the Diels–Alder reaction, *i.e.*, a low $\Delta H^{\ddagger}$ and a large negative $\Delta S^{\ddagger}$. A pairwise analysis of the Arrhenius data is shown in Table III.

Experimental Section

The melting points were determined in a capillary tube on a Mel-Temp melting point apparatus and are uncorrected. The nmr spectra were measured with a Varian A-60 instrument; the samples were dissolved in deuteriochloroform. The ultraviolet and visible spectra were obtained with Cary 14 and Beckman DK-2A spectrophotometers. The infrared spectra were obtained in Nujol or neat, in the case of liquids, on a Perkin-Elmer Infracord spectrophotometer.

Spectroquality cyclohexane from Matheson Coleman and Bell was used for the ultraviolet spectra and reagent grade benzene was used for all the visible spectra.

2'',3'',5''-Triphenyl-*p*-quinquephenyl (5) and 2'',4'',5''-Triphenyl-1,1':4'',1'':3'',1''':4''',4''''-quinquephenyl (4). A mixture of 0.3683 g (0.82 mmol) of 3-(4-biphenylyl)-2,4,5-triphenylcyclopentadienone (**2**),[12] 0.1457 g (0.82 mmol) of 4-ethynylbiphenyl,[13] (**3**) and 5.5 ml of reagent grade toluene was placed in a drying ampoule. The mixture was submitted to three freeze–thaw degassing cycles that consisted of cooling to liquid nitrogen temperature, reducing the pressure to 0.5 mm, and allowing the mixture to warm to room temperature. The tube was sealed *in vacuo*, placed in a 600-ml Paar pressure reactor containing about 100 ml of toluene, and heated at 230° for 24 hr. The reaction was cooled, the solvent was removed at reduced pressure, and the crude material was dried *in vacuo* for 4 hr. A portion of the crude product (0.3110 g, mp 204–256°) was fractionally crystallized using cyclohexane. Compound **5**, mp 278°, was obtained after 15 crystallizations. The uv spectra of **5** showed λ_{max} 262.5 (5.12×10^4) and 278 nm (ϵ 4.62×10^4). Compound **4**, mp 200°, was isolated after 10 crystallizations from absolute ethanol. The uv spectra of **4** showed λ_{max} 265 (6.51×10^4) and 274 nm (ϵ 5.93×10^9).

Anal. Calcd for $C_{48}H_{34}$: C, 94.39; H, 5.61. Found: (**5**) C, 94.89; H, 5.84; (**4**) C, 94.48; H, 5.82.

Further model reactions were carried out for the study of the isomer ratio (Table IV).

1,3-(4-Biphenylyl)-2-propanone (6). To a solution of 4-phenylbenzylmagnesium chloride obtained from 6.2 g (0.0306 mol) of 4-phenylbenzyl chloride (Aldrich Chemical Co.) and 0.75 g (0.0306 g-atom) of magnesium in 100 ml of dry ether was added a solution of 2.96 g (0.015 mol) of 4-phenylphenylacetonitrile (Aldrich Chemical Co.) in 100 ml of dry ether. The mixture was heated at the reflux temperature for 3 hr, 100 ml of benzene was then added, the ether was removed, and the mixture was hydrolyzed with 30% hydrochloric acid by heating at the reflux temperature for 18 hr. The mixture was cooled and the benzene layer was separated and dried over magnesium sulfate. The benzene was removed at reduced pressure and the residue was recrystallized from 95% ethanol to give 2.3 g (41.6%), mp 146–148°. The ir spectrum showed a carbonyl peak at 1720 cm^{-1} and the nmr contained one nonaromatic peak at δ 3.77 (singlet).

Anal. Calcd for $C_{27}H_{22}O$: C, 89.47; H, 6.12. Found: C, 89.55; H, 6.59.

2,5-(4-Biphenylyl)-3,4-diphenylcyclopentadienone (7). A mixture of 1.0 g (2.8 mmol) of 1,3-(4-biphenylyl)-2-propanone (9) and 0.6 g (2.8 mmol) of benzil in 10 ml of triethylene glycol was heated to 100° and held there until solution was complete. Benzyltrimethylammonium hydroxide, 40% in methanol (1 ml), was added and the solution was heated at 100° for 10 min. The mixture was cooled, 60 ml of methanol was added, and the product was filtered to give 0.93 g (61.9%), mp 264–266°. The carbonyl absorption in the ir region appeared at 1710 cm^{-1}. The uv-vis spectrum showed λ_{max} at 350 (6.65×10^3) and 533 nm (ϵ 2.4×10^3).

Anal. Calcd for $C_{41}H_{28}O$: C, 91.76; H, 5.26. Found: C, 92.32; H, 5.29.

2'',3'',5''-Triphenyl-*p*-quinquephenyl (5). A mixture of 0.1160 g (0.114 mmol) of phenylacetylene and 0.6000 g (0.114 mmol) of 2,5-(4-biphenylyl)-3,4-diphenylcyclopentadienone (7) in 8 ml of reagent grade toluene was placed in a polymerization tube. After three freeze–thaw cycles at liquid nitrogen temperatures, the tube was sealed *in vacuo* and placed in a 500-ml Paar pressure reactor containing 50 ml of toluene. The reaction was carried out at 200° for 18 hr. The mixture was cooled, the toluene was removed at reduced pressure, and the white solid was recrystallized from cyclohexane to give 0.5921 g (85%) of product, mp 275–277°.

Anal. Calcd for $C_{48}H_{34}$: C, 94.39; H, 5.61. Found: C, 94.00; H, 5.85.

Poly(2,3,6,2''',3''',6'''-hexaphenyl-*p*-pentaphenylene-4',1''-oxide-4,4''''-ylene) (1). Polymerizations for the determination of the rate constants were carried out by the same method; a typical polymerization to yield poly(2,3,6,2',3''',6'''-hexaphenyl-*p*-pentaphenylene-4',1''-oxide-4,4''''-ylene) follows. A mixture of 0.2153 g (0.171 mmol) of freshly sublimed *p*-diethynylbenzene[23] (mp 94.5°) and 0.13362 g (0.171 mmol) of 3,3'-(oxydi-*p*-phenylene)bis-(2,4,5-triphenylcyclopentadienone)[14] (12), which had been purified by column chromatography on Woelm neutral alumina with benzene (mp 270°), was placed in a 20-ml polymerization tube with 2.06 ml of toluene. The contents of the tube were degassed by three freeze–thaw cycles at liquid nitrogen temperatures and then sealed *in vacuo*. Toluene (50 ml) was added to a 500-ml pressure bomb, the tube was placed inside, and the reactor was closed and heated to the desired temperature for the desired time. Then the pressure bomb was immediately cooled to room temperature by means of a cold water bath, the solution in the tube was filtered to removed solid impurities, and the toluene was removed at reduced pressure. The resultant polymers were freeze-dried from reagent grade benzene and the viscosities were taken. The results are summarized in Table II.

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Conformational Statistics of 1,3- and 1,4-Linked Homopolysaccharides

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ABSTRACT: Unperturbed dimensions have been calculated for several 1,3- and 1,4-linked homopolysaccharides. The characteristic ratio depends strongly on the bonding geometry and on the degree of rotational freedom about the glycosidic bonds. It appears that unperturbed dimensions can be predicted qualitatively from a knowledge of the regular conformations of the polysaccharide.

A number of authors have attempted to calculate the unperturbed dimensions of polysaccharides such as amylose,[1,2] cellulose,[3] and alginic acid,[4] from an assumed skeletal geometry and an assumed potential function which allows hindered rotation about the glycosidic bonds. Most of this work has been directed toward obtaining detailed information on particular homopolysaccharides, though a preliminary study has been made of the effects of bonding geometry and substituent position on the unperturbed dimensions of a range of 1,4-linked homopolysaccharides.[5]

Rees and Scott[6] have recently published an extensive surve of the regular conformations of a variety of 1,2-, 1,3-, 1,4-, and 1,6-linked pyranoglycans using a computer model-building approach based on a hard-sphere potential function. They find that polysaccharides can be categorized as (A) extended chains, (B) wide helices, (C) crumpled and contorted, and (D) flexible, but, on average, extended. It has been suggested[2] that the solution properties of polysaccharides can be predicted, at least qualitatively, from their regular conformations, and detailed calculations for 1,4-linked systems[5] indicate that this is generally true, with some reservations.

The primary aim of this work is to calculate characteristic ratios of a range of 1,3- and 1,4-linked homopolysaccharides

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