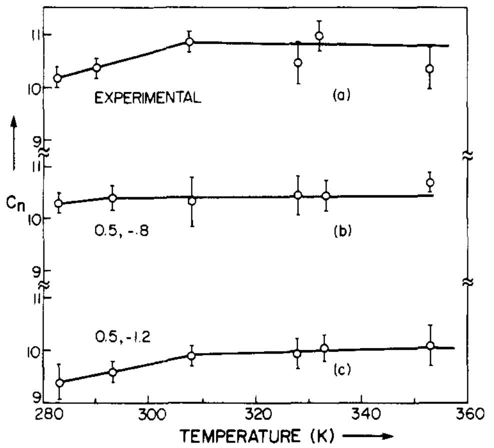

Figure 7. Experimental[14] (a) and calculated (b and c) values of C_n, as a function of temperature. The values of E_α and E_β, in that order, in kcal mol^{-1}, are given in (b) and (c).

E_α and E_β. The value of $f_i = 1$ corresponds to a purely isotactic chain and $f_i = 0$ refers to the syndiotactic chain.

Variations in C_n due to changes in the parameters are more pronounced in the regions of $f_i \approx 0$. This effect decreases as f_i approaches a value of about 0.5 and thereafter, as the chain assumes predominently isotactic character, the variations are small. This is in keeping with the results shown in Figure 5. The experimental data[12–14] on the characteristic ratios are also marked in Figure 6. The value of f_i in each case was taken as quoted by the authors of the experimental work. It is seen that values of $E_\alpha \approx 0.5$ and $E_\beta \approx -1.0$ kcal mol^{-1} reproduce the experimental results satisfactorily. These energy parameters are close to those deduced from the present calculations.

The effect of temperature on $\langle r^2 \rangle_0$ of PMS was investigated by Noda et al.,[14] using theta and apparent theta solvents. They found that the value of K_Θ increases in the range of 10 to 35 °C, and thereafter the effect is insignificant. The values of C_n, calculated for different temperatures, for an atactic chain with $f_i = 0.5$, are given in Figure 7. Two sets of values of E_α and E_β were used. The values of C_n, calculated from the experimental K_Θ values of Noda et al., are also given in this figure. It is seen that the calculated temperature dependence parallels that of the experimental results. Slight differences in the experimental and theoretical values of C_n may be due to the lack of precise information on the value of f_i for the polymer employed in the experimental work. This fact has been discussed by Noda et al.[14]

Acknowledgments. The author thanks Dr. M. L. Hair of this center for his interest in this work and the encouragement he provided.

References and Notes

(1) P. J. Flory, P. R. Sundararajan, and L. C. De Bolt, *J. Am. Chem. Soc.*, **96**, 5015 (1974).
(2) P. R. Sundararajan, L. C. De Bolt, and P. J. Flory, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **14**, 131 (1973).
(3) Since the distance between the interacting groups depends on rotations around two skeletal bonds, e.g., i and $i + 1$, these are called second-order interactions.[4]
(4) P. J. Flory, "Statistical Mechanics of Chain Molecules", Interscience, New York, N.Y., 1969.
(5) P. R. Sundararajan and P. J. Flory, *J. Am. Chem. Soc.*, **96**, 5025 (1974).
(6) U. W. Suter and P. J. Flory, *Macromolecules*, **8**, 765 (1975).
(7) D. Y. Yoon, P. R. Sundararajan, and P. J. Flory, *Macromolecules*, **8**, 776 (1975).
(8) D. Y. Yoon, U. W. Suter, P. R. Sundararajan, and P. J. Flory, *Macromolecules*, **8**, 784 (1975).
(9) E. Benedetti, C. Pedone, and G. Allegra, *Macromolecules*, **3**, 16, 727 (1970).
(10) A. I. Kitaigorodskii, "Organic Chemical Crystallography", Consultants Bureau, New York, N.Y., 1961.
(11) The effect of this truncation is pronounced, so as to alter the calculated relative energies significantly, in cases where the side group is bulky as in PMS or polystyrene.[7] Yoon et al.[8] found the changes to be small for poly(methyl acrylate). Unpublished results of this author, on PMMA, showed that the truncation procedure has very little effect on the results published earlier.[5]
(12) J. M. G. Cowie and S. Bywater, *J. Polym. Sci., Part A-2*, **6**, 499 (1968).
(13) J. M. G. Cowie, S. Bywater, and D. J. Worsfold, *Polymer*, **8**, 105 (1967).
(14) I. Noda, K. Mizutani, T. Kato, T. Fujimoto, and M. Nagasawa, *Macromolecules*, **3**, 787 (1970).

Biphenylene as Cross-Linking Sites for Polyquinolines

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ABSTRACT: Biphenylene units were incorporated into polyquinolines in order to provide a site which could enter into a thermal cross-linking reaction above 300 °C. The cross-linking reaction takes place thermally via a radical ring opened intermediate without the evolution of volatiles to afford thermally stable cross-links. The incorporation was accomplished by balancing the appropriate amounts of 2,6-diacetylbiphenylene in place of 4,4′-diacetyldiphenyl ether with 3,3′-dibenzoyl-4,4′-diaminodiphenyl ether in the synthesis of the polyquinoline. Lower curing temperatures and shorter curing times were possible in the presence of rhodium catalysts.

Since the strained biphenylene ring is known to open thermally at 375–400 °C giving dimeric or polymeric products, probably via a diradical intermediate,[1,2] biphenylene units incorporated into a macromolecular backbone could serve as cross-linking sites for high-temperature polymers. Such a cross-linking mode would be especially attractive because no volatile material is produced and the resulting cross-link would be thermally stable.

Recent work in this laboratory has shown that the Friedlander condensation of suitable bisaminoketones with ketomethylene monomers affords high molecular weight polyquinolines.[3,4] Thus, the introduction of biphenylene (**1**) into a polyquinoline backbone by polycondensation of an aminoketone monomer with the readily available 2,6-diacetylbiphenylene[5,6] (**2**) appeared to be feasible. In the present study, the thermal behavior and the cross-linking reaction of a homopolymer of **2** with 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**5**) and two copolymers containing **2** with variable amounts of 4,4′-diacetyldiphenyl ether (**6**) have been explored.

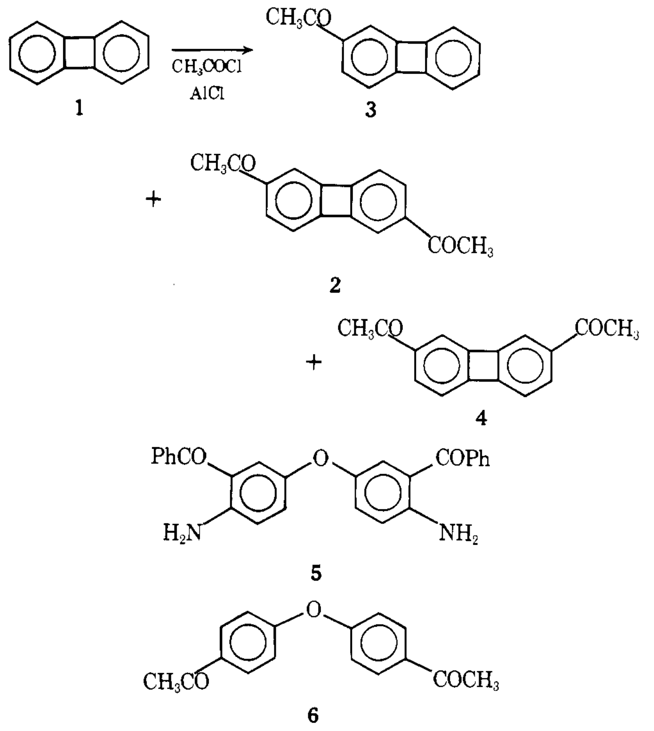
Results and Discussion

Monomers. Biphenylene was prepared in a 20% yield by aprotic diazotization of anthranilic acid followed by the liquid phase thermolysis of the orthodiazo carbonylate salt.[7] Friedel–Crafts acylation in chloroform or carbon disulfide gave 2,6-diacetylbiphenylene along with the 2-acetyl derivative **3** and small amounts of the 2,7-diacetyl isomer.[6] A higher yield of crude 2,6-diacetyl derivative was observed in carbon disulfide (quantitative) as compared to chloroform (49%) but in the former case the product was more difficult to purify by recrystallization. The preparation of bisaminoketone **5** via the benzisoxazole route has been described previously.[9] Polymerization of this monomer with oxyketone **6** has been shown to give a semirigid polymer of high molecular weight. The characteristics of this polymer ($\overline{M}_n$ = 97 000, T_g = 266 °C) make monomer **5** a suitable bisaminoketone candidate for our purpose.

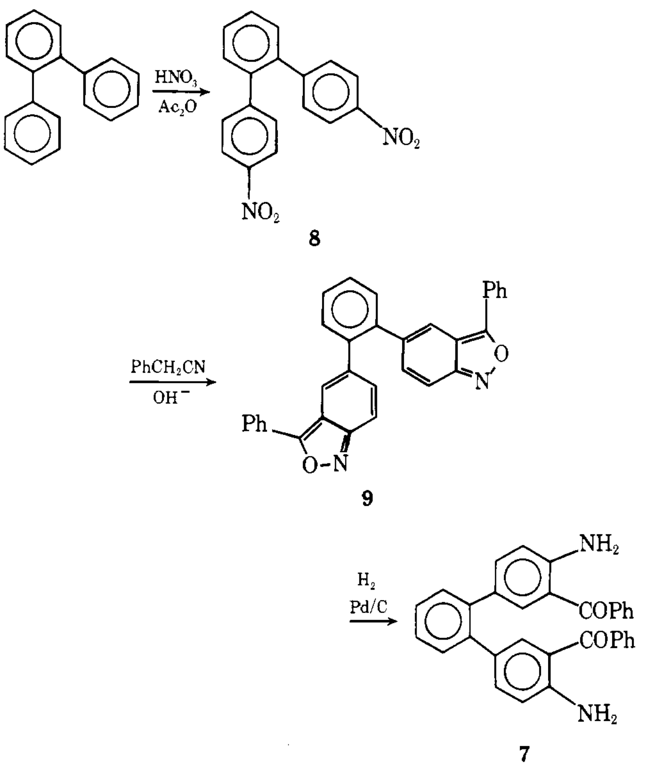
The same benzisoxazole condensation[8] used for the synthesis of **5** allowed the synthesis of **7** a nonoxygenated analogue. Thus, nitration of orthoterphenyl gave the 4,4″-dinitroisomer[9] **8** in 43% yield, which upon treatment with phenylacetonitrile in basic medium afforded bisbenzisoxazole **9** in 39% yield. Hydrogenation of **9** using palladium on charcoal gave bisaminoketone **7** in 71% yield.

Model Reactions. The best reaction medium for the Friedlander condensation has been shown to be a mixture of cresyl phosphates, obtained by heating phosphorous pentoxide in excess *m*-cresol.[4] Using this solvent, the bisquinolines **10–12** were prepared in quantitative yields by the reaction of diacetylbiphenylene (**2**) with *o*-aminobenzophenone and 2-acetylbiphenylene (**3**) with the two bisaminoketones **5** and **7**. The poor solubility of model **11** precluded a study of its ^{13}C NMR spectrum, at least in chloroform; bisquinoline **11** was soluble in trifluoracetic acid *d*-1 and its ^{13}C NMR spectrum was recorded. However, the assignment of the different carbons was prevented by the lack of information concerning the effect of solvent and protonation on the chemical shifts.

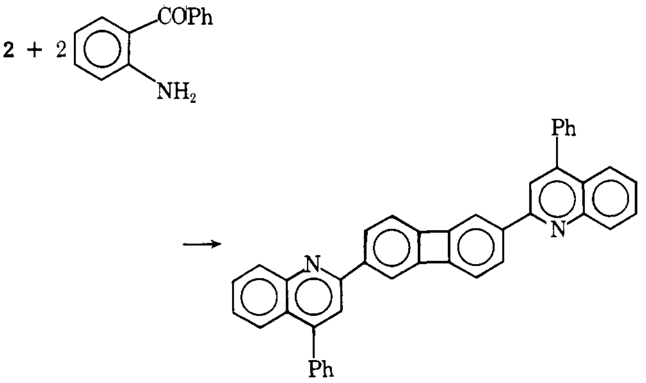
Polymers and Copolymers. The high yields obtained in the synthesis of model bisquinolines demonstrated that 2,6-diacetylbiphenylene was a suitable condensation monomer. Two series of polymers were prepared: homopolymer **13** of oxydiketone **2** and the oxybisaminoketone **5** as well as two copolymers **14** and **15** with added diacetyl diphenylether **6**, the molar ratio of **2**:**6** being 1:1 and 1:3, respectively. A second series of polymers included a homopolymer **16** of oxydiketone **2** and *o*-phenylenebisaminoketone **7** as well as a homopolymer **17** of oxydiketone **6** with **7**.



1 **3** **2** **4** **5** **6**



8 **9** **7**



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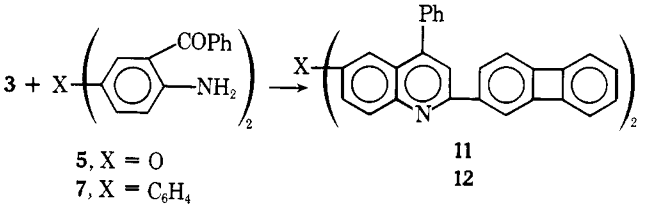


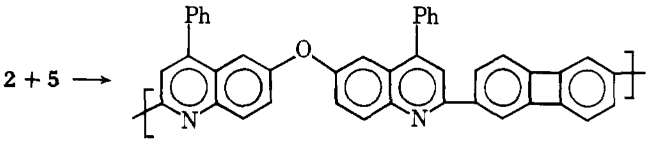
5, X = O
7, X = C$_6$H$_4$

11
12

Some characteristics of the polymers are summarized in Table I.

Although a highly purified sample of **7** was obtained, this monomer did not give high molecular weight polymers, even with the flexible oxydiketone **6**. There is no clear explanation for this behavior since the same batches of oxydiketone monomers gave reasonably high molecular weights in polycondensation with the oxybisaminoketone **5**.

Thermal Behavior of the Model Compounds. The differential scanning colorimetry (DSC) of the model bisquinolines (**10–12**) showed an exothermic reaction in the range 300–500 °C. The data demonstrate that the introduction of



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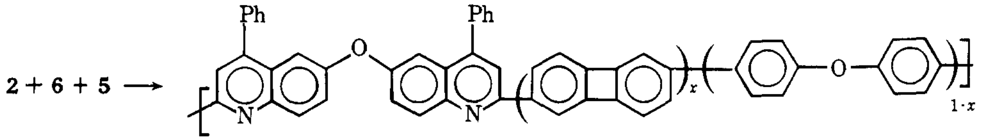
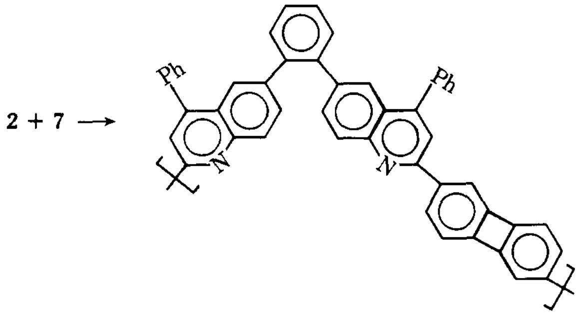


14, $x = 0.5$
15, $x = 0.25$



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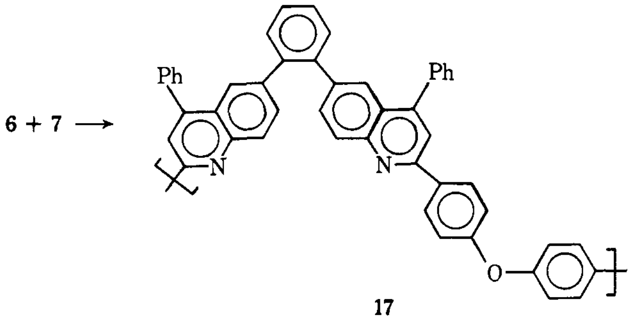


17

an ether linkage lowers the decomposition temperature by about 100 °C.

Cross-Linking Study. The DSC cell was used to cure 10–20-mg samples of polymer; both packed film disks and pressed polymer pellets were used. After curing, the T_g of the samples were recorded as well as their thermal behavior up to 500 °C. The data, including solubility of the cured samples in trifluoracetic acid, are shown in Table III. In all cases the magnitude of the deflection at T_g in the cured samples was sharply reduced compared to those recorded during the heating period up to the curing temperature. The DSC trace for all polymers containing the biphenylene units still exhibited an intense exothermic peak in the range 350–440 °C after curing.

The thermal behavior of low molecular weight polymers **16** and **17** was examined briefly. In the case of **17** the glass transition temperature at 305 °C was followed by an ill-defined exothermic process. The DSC run was stopped at 500 °C and after a rapid cooling the DSC was rerun on the sample; the same T_g was observed. However, the sample exhibited extensive swelling with little solubility in trifluoracetic acid although the starting polymer was initially totally soluble in this solvent. A Friedel–Crafts type polycondensation of the *o*-terphenyl unit,[9,10] catalyzed by traces of residual acid, may account for this unexpected cross-linking reaction. In the case of oligomer **15**, a broad endothermic discontinuity in the curve occurred at 340 °C followed by an exotherm at 410 °C. The value of 410 °C for the exothermic onset agrees with those observed for the model bisquinolines without an oxygen link.

An attempt to lower the curing temperature of copolymer **15** (25% biphenylene) was made by adding a soluble rhodium(I) catalyst (1 mol % catalyst per mol of biphenylene unit). Two different catalysts, tristriphenylphosphinerhodium

Table I
Properties of Polyquinolines 13–17

Polymer	13[a]	14[b]	15[b,c]	16	17
[η] (solvent)	4.4 (HCO_2H)	2.3 (*m*-cresol)	1.9 (*m*-cresol)	0.04 (H_2SO_4)	0.43 ($CHCl_3$)
T_g, deg	297	270	258	Absent	305
Onset of exothermic[d] peak above T_g, °C	385	330	325	415	340

[a] Insoluble in $CHCl_3$, H_2SO_4; soluble in HCO_2H, CF_3CO_2H. [b] Soluble in $CHCl_3$, *m*-cresol, HCO_2H, CF_3CO_2H, H_2SO_4; insoluble in CH_3CO_2H. [c] Insoluble in THF, HMPA, DMSO. [d] Defined at the intercept of an extrapolated baseline after T_g with tangent of the slope.

Table II
Exothermic Decomposition and Melting Points of Model Compounds (10–12)

Bisquinoline	Onset of exotherm, °C	DSC mp, °C	Capillary mp, °C
10	425	330	333–335
11	321	245	245–247
12	425	293	294–297

chloride (18) and norbornadiene chlororhodium dimer (19), were added to a chloroform solution of the copolymer from which films were cast. Strained ring hydrocarbons undergo oxidative addition to rhodium(I) complexes by carbon–carbon σ-bond scission.[11] Using the same technique as for the uncatalyzed curing, the following results were observed on the films (Table IV).

Upon heating to the curing temperature, the sample containing the norbornadiene complex (19) exhibited a sharp and well-resolved exotherm at 170 °C. Wilkinson's catalyst (18) did not induce such a clear-cut behavior. As in the noncatalyzed cross-linking, the cured materials showed an intense exothermic peak in the 300–350 °C range.

Conclusion

Biphenylene-containing polymers undergo cross-linking by heating at 340 °C for 2–3 h and these conditions ensure an almost complete insolubility. In addition, increased cross-link density can be obtained by curing at a higher temperature for a longer time. Since a copolymer containing an average 25% of biphenylene unit within the chain still exhibits a residual exothermic reaction after a rather drastic curing (380 °C, 4 h), it seems likely that efficient cross-linking also would occur with a lower content of biphenylene in the chain.

The temperature of this uncatalyzed cross-linking reaction seems rather low compared to the literature value for the pyrolytic dimerization of biphenylene in glass apparatus (400 °C) but is close to the reported value (350–375 °C) when the pyrolysis is effected in a stainless steel apparatus.[1] This low cross-linking temperature seems to be correlated with the presence of diphenyl ether linkages in the polymer and in the low molecular weight model compound. Rhodium complexes, especially the norbornadiene chlororhodium dimer **19**, catalyze cross-linking at a lower temperature which is below the glass transition of the material.

The conversion of biphenylene into tetraketone, diacid, and diamine monomers, among others, would also allow the incorporation of the biphenylene unit into polyquinoxalines, polybenzimidazoles, polyamides, etc., and thereby establish cross-linking systems for these polymers. Studies of such systems are in progress.

Experimental Section

Biphenylene (1). Biphenylene was prepared by the decomposition of *o*-diazocarboxylate;[7] butyl nitrite was used for the diazotization step. The yield of biphenylene did not depend significantly on the rate of addition of the diazocarboxylate salt to the 1,2-dichloroethane solution. The following yields were obtained: 15 min of addition, 18%, over five batches; 5 min of addition, 21%, over three batches.

Acetylation of Biphenylene (In Carbon Disulfide). To an ice-cooled solution of 1.52 g (10 mmol) of biphenylene and 5 mL (70 mmol) of acetyl chloride in 150 mL of carbon disulfide was added by portions 5.32 g (40 mmol) of powdered aluminum chloride. The suspension was stirred at 25–28 °C for 3 h and then allowed to stand at room temperature for 8 h. The reaction mixture was decomposed over hydrochloric acid and ice. The insoluble solid was collected by filtration and was washed with benzene, giving 2.2 g (92%) of crude 2,6-diacetylbiphenylene (2), mp 255–260 °C (lit.[5,6] mp 253–254.5 °C). The product can be sublimed under high vacuum (0.005 Torr) at 200 °C. The sublimate has a melting point of 258–260 °C.

Table III
Curing of Polymers 13–15

Curing conditions		T_g after curing (°C), T exotherm (°C),[a] and Solubility[b]		
T, deg	Time, h	**13**	**14**	**15**
340	1	302 (398) ss	285 (370) i	280 (350) ss
	3	307		*c*
	4	311 (390)		
	6	*315 (395) i*	*302 (380) i*	*288 (325) i*
360	3	Absent (420)		
	4		320 (400)	295 (393)
380	3	Absent (435)		303 (398)
	4			303 (390)

[a] Approximate values. [b] ss slightly soluble; i insoluble. [c] Very slightly soluble after 2 h.

Table IV
Rh(I) Catalyzed Cross-Linking of Copolymer 15

Catalyst	Curing conditions Temp, °C	Curing conditions Time, min	T_g after curing (°C), solubility
$(Ph_3P)_3RhCl$ (18)	280	30	265, i
	380	3	268
$(C_7H_8RhCl)_2$ (19)	280	30	280, i
	380	3	280

The soluble products from the carbon disulfide and benzene solutions were dissolved in benzene and separated by chromatography on a dry silica gel column. 2-Acetylbiphenylene (3) (0.35 g) was eluted first with benzene; mp, 138–140 °C (lit.[5] mp 132–134 °C). The column was eluted with methylene chloride until a second yellow band was well separated from a polar ring on the top of the column. After removal of the polar material, elution with ether gave 0.22 g of a material with mp 164–166 °C consisting mainly of 2,7-diacetylbiphenylene (4) contaminated with some 2,6-diacetyl isomer (2). Enough 2,7-diacetyl derivative, mp 173–175 °C (lit.[6] mp 174 °C), could be obtained by combining several batches. IR and ^{13}C NMR spectra are recorded in Table V.

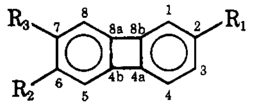
Acetylation of Biphenylene (In Chloroform). A solution of 10 mL (140 mmol) of acetyl chloride in 200 mL of chloroform was added to 10 g (75 mmol) of aluminum chloride. The homogeneous solution was cooled to 10 °C and 3.04 g (20.0 mmol) of biphenylene dissolved in 50 mL of chloroform was added over a period of 50 min. The solution was stirred at 27–28 °C for 6 h. The mixture was decomposed over hydrochloric acid (100 mL) and ice and a small amount of insoluble 2,6-diacetylbiphenylene was filtered. The organic phase was washed with acetone giving more insoluble 2,6-diacetyl derivative; the combined weight was 2.35 g (49%). Recrystallization from xylene (120 mL) gave 1.81 g of crystals, mp 257–260 °C (38%).

Several batches of **2** were obtained under different conditions and combined. Monomer grade purity was achieved by recrystallization in acetic acid and 1,2-dichloroethane, mp 256.5–259.5 °C. Chlorobenzene is the best recrystallization solvent for the crude products.

The acetone soluble fraction (2.02 g) contained mainly the 2-acetylbiphenylene (3), which was purified by chromatography and sublimation (110–120 °C, 0.25 Torr). The ^{13}C NMR of 2,6-diacetylbiphenylene (2) is recorded in Table V.

2,6-Bis(2-phenyl-4-quinolyl)biphenylene (10). To a solution of cresyl phosphates, obtained by heating 3.4 g of phosphoric anhydride in 8 mL of *m*-cresol at 140 °C for 2 h,[4] were added 0.472 g (2 mmol) of 2,6-diacetylbiphenylene (2) and 0.788 g (4 mmol) of *o*-aminobenzophenone. The solution was diluted with 4 mL of *m*-cresol and stirred at 130 °C for 5 h. The cooled solution was then diluted with 50 mL of methanol and enough triethylamine was added to precipitate the crude quinoline which was filtered, washed with methanol, and dried at 100 °C under reduced pressure to afford 1.07 g (95%) of product, mp 328–332 °C. Recrystallization from 45 mL of pyridine gave 0.908 g of yellow crystals, mp 333–335 °C. Anal. Calcd for $C_{42}H_{26}N_2$: C, 90.29; H, 4.69; N, 5.01. Found: C, 90.20; H, 4.85; N, 5.21.

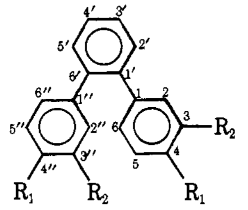
Table V
^{13}C NMR of Biphenylene Derivatives

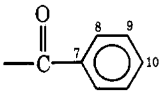


Carbon No.	R_1, R_2, R_3 = H $CDCl_3$[a]	R_1, R_2 = $COCH_3$, R_3 = H $CDCl_3$	R_1, R_2 = $COCH_3$, R_3 = H CF_3CO_2H	R_1, R_3 = $COCH_3$, R_2 = H $CDCl_3$	Calcd[c]
1	117.8	117.6[b]	119.8[b]	118.0	117.9
2	128.4	137.9	138.9	138.5	137.5
3	128.4	132.5	137.0	131.6	128.5
4	117.8	117.0	119.1	116.6	117.8
4a	151.7	155.3	159.5	154.6	155.9
8b	151.7	150.0	152.3	150.5	151.7
C=O		196.7	206.8	196.7	
CH_3		26.4	26.4	26.4	

[a] Taken from ref 12. [b] Tentative assignment obtained by calculation of the increments of the acetyl group, which is positive in ortho and negative in meta positions. The solvent effect induces a larger positive shift in ortho than in meta position. [c] Approximation using the increments of the acetyl group in benzene[13] and applying them to the parent biphenylene.

Table VI
^{13}C NMR of *o*-Terphenyl Derivatives





Carbon No.	R_1 = NO_2, R_2 = H	Calcd	R_1 = NH_2, R_2 = COPh	Calcd
1	146.8	147.4	128.8	131.6
2	129.1	128.3	130.4	130.0
3	123.5	124.1	117.8	125.0
4	147.5	147.3	149.8	147.0
5			117.1	115.4
6			135.7	131.9
1'	138.4	140.5	139.8	140.5
3'	130.7[a]	127.8	128.1[a]	127.8
5'	130.7[a]	127.7	127.2	127.7
C=O			199.0	
7			139.2	137.9
8			130.8	130.2
9			128.1[a]	128.3
10			135.9	132.1

[a] Overlapping resonances.

6,6′-Oxybis[2-(2-biphenylyl)-4-phenyl]quinoline (11). To a solution of cresyl phosphates obtained by heating 3.31 g of phosphoric anhydride in 8 mL of *m*-cresol at 140 °C for 2 h were added 0.816 g (2 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (5) and 0.776 g (4 mmoles) of 2-acetylbiphenylene (3) followed by 4 mL of *m*-cresol. The mixture was stirred at 130 °C for 6 h. The cooled solution was then diluted with 50 mL of methanol and the quinoline was precipitated with triethylamine to give 1.42 g (98%) of product, mp 243–245 °C. Recrystallization from 30 mL of xylene gave yellow crystals, mp 245–247 °C. Anal. Calcd for $C_{54}H_{32}N_2O$: C, 87.54; H, 4.35; N, 3.78. Found: C, 86.95; H, 4.87; N, 3.45.

4,4″-Dinitro-*o*-terphenyl (8). To a cooled solution of 125 g (0.5 mol) of *o*-terphenyl in 900 mL of acetic anhydride was added over a period of 130 min 150 mL of 90% nitric acid (ACS reagent) keeping the temperature at 10–15 °C. Precipitation of the product occurred at the end of addition. The slurry was stirred at 15 °C for 2 additional h and decomposed by pouring it onto crushed ice. Enough sodium hydroxide solution was added to yield a slightly acidic medium. The sticky mass was removed from water and washed with ether until a white insoluble material was obtained. Washing the solid with methanol followed by drying gave 88.7 g of crude material. Purification was realized by stirring the product in 500 mL of acetic acid at the reflux temperature, allowing the solution to cool, and then filtering the mixture to yield 70 g (43%) of material pure enough for the following step. An analytical sample, mp 221–225 °C (lit.[9] mp 218 °C), was obtained after two recrystallizations from acetic acid. The ^{13}C NMR spectrum of 8 in deuteriochloroform is shown in Table VI.

5,5′-*o*-Phenylenebis(3-phenyl-2,1-benzisoxazole) (9). To a solution of 70 g (1.750 mol) of sodium hydroxide in 500 mL of commercial 2-methoxyethanol was added at 60 °C a solution of 70 g (0.218 mol) of 4,4″-dinitroorthoterphenyl (8) in 500 mL of commercial tetrahydrofuran. To the stirred solution, 80 mL (0.669 mol) of phenylacetonitrile was added dropwise and the dark mixture was stirred at 60 °C for 15 h. The solvent was removed in vacuo and water was added to the residue. A brown insoluble precipitate was obtained after chopping with an electric blender and washing with water. The insoluble product was washed alternately with methanol and ether. When the washings became clear, 40 g (39%) of crude 9 remained. The product was stirred in 400 mL of acetic acid and enough toluene was added to get a complete dissolution at the reflux temperature. The solution was concentrated to ca. 150 mL under reduced pressure to afford 33 g of yellow crystals, mp 225–230 °C. Two recrystallizations gave an analytical sample: mp 234–235 °C dec; IR (KBr) 1625 (C=N). Anal. Calcd for $C_{32}H_{20}N_2O_2$: C, 82.74; H, 4.34; N, 6.03. Found: C, 82.89; H, 4.37; N, 6.03.

4,4″-Diamino-3,3″-dibenzoyl-*o*-terphenyl (7). A solution of 33 g (71.1 mmol) of bisbenzisoxazole (9) in 500 mL of tetrahydrofuran containing 10 mL of triethylamine was hydrogenated at atmospheric pressure over 3 g of palladium on charcoal until the uptake of hydrogen ceased. After filtration of the catalyst and removal of solvent the crude oil was dissolved in methanol to give yellow crystals. The solid was washed with methanol to afford 23.8 g (71%) of bisaminoketone. Monomer grade purity was achieved by two recrystallizations from acetic acid (250 and 180 mL) followed by a recrystallization from toluene (150 ml): mp 215–216 °C; IR (KBr) 3480 and 3350 (NH), 1620 (C=O), 1570 (NH), 1230 (C–N). Anal. Calcd for $C_{32}H_{29}N_2O_2$: C, 82.03; H, 5.15; N, 5.98. Found: C, 82.13; H, 5.28; N, 5.94. The ^{13}C NMR spectrum of 7 in deuteriochloroform is recorded in Table VI.

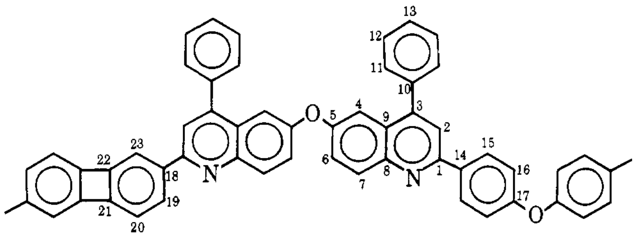
6,6′-*o*-Phenylenebis[2-(2-biphenylyl)-4-phenyl]quinoline (12). To a solution of cresyl phosphates prepared by heating 3.64 g of phosphoric anhydride in 8 mL of *m*-cresol at 140 °C for 2 h were added 0.935 g (2 mmol) of bisaminoketone (7) and 0.776 g (4 mmol) of 2-acetylbiphenylene (3) followed by 4 mL of *m*-cresol. The mixture was stirred at 130 °C for 11 h. Dilution of the cold solution with 50 mL of methanol followed by precipitation of the bisquinoline with triethylamine afforded 1.57 g (100%) of product, mp 286–289 °C. Recrys-

Table VII
Reaction Conditions for Polymerization of 13–17

Polymer	Monomers	Reaction conditions: *T*, °C	Reaction conditions: Time, h	Yield		Elemental Anal. C, H, N, Calcd	Elemental Anal. C, H, N, Found
13	**2** + **5**	135–140	20	2.73 g (95%)	$(C_{42}H_{24}N_2O)_n$	88.09; 4.22; 4.89	87.48; 4.20; 4.08[a]
16	**2** + **7**	135–140	44	2.99 g (94%)	$(C_{48}H_{28}N_2)_n$	91.09; 4.46; 4.43	89.26; 4.52; 3.92
17	**6** + **7**	135–140	20	2.83 g (89%)	$(C_{48}H_{30}N_2O)_n$	88.59; 4.65; 4.30	88.60; 4.77; 4.35
		180	6				
14	(0.5)**2** + (0.5)**6** + **5**	135–140	30	2.88 g (99%)	$(C_{42}H_{25}N_2O_{1.5})_n$	87.02; 4.35; 4.49	85.96; 4.35; 3.98
15	(0.25)**2** + (0.75)**6** + **5**	135–140	30	2.85 g (97%)	$(C_{42}H_{25.5}N_2O_{1.75})_n$	86.35; 4.40; 4.45	85.60; 4.43; 3.95

[a] Residue 1.07.

Table VIII
^{13}C NMR of Copolymers 14 and 15



Carbon No.	Copolymer 14	Copolymer 15	Carbon No.	Copolymer 14	Copolymer 15[c]
1	155.1	155.1	11[a]	128.6	128.6
2	122.8	122.8	12	129.2	129.2
3	148.3	148.3	13[a]	128.6	128.6
4	112.4	112.4	14	134.8	134.8
5	154.6	154.5	15[a]	129.0	129.0
6	119.2	119.2	16	119.2	119.2
7	132.0	132.0	17	158.1	158.1
8	145.9	145.9	18	*b*	140.0
9	126.4	126.4	19	*b*	*d*
10	138.0	138.0	20	*b*	116.8
			21	*b*	151.2 and 151.8[e]
			22	*b*	155.4
			23	*b*	117.7

[a] Assignments different from those reported[4] as a result of a better resolution.[14] [b] Signal-to-noise ratio too low for clear assignment. [c] Chemical shift assignment tentatively made by using the values of 2,6-diacetylbiphenylene. [d] Not detected. [e] Two different peaks suggesting two kinds of biphenylene units in the copolymer.

tallization from xylene (80 mL) gave 1.25 g (79%) of crystals, mp 294–297 °C dec. Anal. Calcd for $C_{60}H_{36}N_2$: C, 91.81; H, 4.62; N, 3.57. Found: C, 91.79; H, 4.80; N, 3.55.

Polymerizations. The polymerization solvent was prepared by quickly adding 8.5 g (29.9 mmol) of phosphorus pentoxide to 20 mL (191.5 mmol) of *m*-cresol and stirring the mixture under nitrogen at 140 °C for 2 h. The homogeneous solution was cooled to room temperature and 5 mmol of each monomer was added along with 10 mL of *m*-cresol. The resulting mixture was stirred at 135–140 °C for 20–44 h. The viscous solution was diluted with 50 mL of *m*-cresol at 100 °C and the polymer was precipitated in 500–700 mL of ethanol containing 50 mL of triethylamine. After filtration and air drying, the polymer was dissolved in *m*-cresol or formic acid and reprecipitated into an ethanol–triethylamine mixture. The fibrous material was then extracted in a Soxhlet with an ethanol–triethylamine mixture for at least 48 h, air dried, and finally dried under reduced pressure at 130 °C for several hours.

Experimental conditions as well as analytical data are summarized in Table VII. The ^{13}C NMR spectra of copolymers 14 and 15 are shown in Table VIII.

Thermal Analysis. The DSC were performed on a du Pont 990 thermal analyzer using a heating rate of 20 °C/min, under a 40 mL/min flow of nitrogen, the reference being glass beads. Each entry in Table III refers to a different sample.

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References and Notes

(1) L. Friedman and D. F. Lindow, *J. Am. Chem. Soc.*, **80**, 2324 (1968).
(2) L. Friedman and R. W. Rabideau, *J. Org. Chem.*, **33**, 451 (1968).
(3) J. F. Wolfe and J. K. Stille, *Macromolecules*, **9**, 489 (1976).
(4) S. O. Norris and J. K. Stille, *Macromolecules*, **9**, 496 (1976).
(5) W. Baker, J. W. Barton, and J. F. W. McOmie, *J. Chem. Soc.*, 2666 (1958).
(6) J. M. Blatchly, A. J. Boulton, and J. F. W. McOmie, *J. Chem. Soc.*, 4930 (1965).
(7) F. M. Logullo, A. H. Seitz, and L. Friedman, *Org. Synth.*, **48**, 12 (1968).
(8) R. B. Davis and L. C. Pizzini, *J. Org. Chem.*, **25**, 1884 (1960).
(9) C. F. H. Allen and F. R. Pinget, *J. Am. Chem. Soc.*, **64**, 2639 (1942).
(10) G. A. Olah and M. W. Meyer, *J. Org. Chem.*, **27**, 3682 (1962).
(11) L. Casser, P. E. Eaton, and J. Halpern, *J. Am. Chem. Soc.*, **92**, 3515 (1970). Biphenylene is converted to tetrabenzocyclooctatetraene at 200 °C in the presence of catalytic amounts of norbornadiene chlororhodium dimer; this study will be reported elsewhere.
(12) A. J. Jones, L. J. Garrat, and K. P. C. Vollhardt, *Angew. Chem., Int. Ed. Engl.*, **12**, 241 (1973).
(13) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972.
(14) W. Beever and J. K. Stille, to be published.