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Biphenylene as a Cross-Linking Site. Curing Conditions, Glass Transition Temperatures, and Moduli of High Molecular Weight Polyquinolines Containing Biphenylene Units in the Chain

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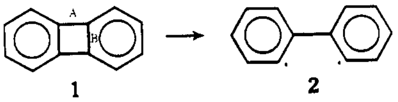
ABSTRACT: A series of polyquinolines containing biphenylene units in the main chain were prepared by substituting 2,6-diacetylbiphenylene for 4,4′-diacetyldiphenyl ether in polymerizations with 3,3′-dibenzoyl-4,4′-diaminodiphenyl ether. As the incorporation of biphenylene units increased, T_g and the temperature for the onset of cross-linking by opening of the biphenylene ring increased. Cross-linking takes place only above T_g and the onset of cross-linking parallels T_g of the polymer sample. Cross-linked polymers are characterized by higher T_g's, or disappearance of the T_g, and higher moduli both below and above T_g. The higher degree of cross-linking obtained from polymers containing higher incorporation of biphenylene resulted in higher moduli. Rhodium catalyzed the cross-linking reaction, allowing lower curing temperatures and shorter times.

The incorporation of biphenylene into thermally stable, totally aromatic polymers, such as polyquinolines, affords an attractive method of cross-linking these thermally stable materials that have proven to be difficult to cure.[1,2] The cross-linking reaction takes place at convenient temperatures, no volatiles are formed, and the structures produced are thermally stable.

Biphenylene (**1**) undergoes thermolysis at ~400 °C and, depending on the reaction conditions, yields tetrabenzocyclooctatraene, polymer, or biphenyl, resulting from radical abstraction of hydrogen from solvent.[3,4] Although the structure of the polymer was not determined, it likely contains poly(*o*-phenylene) segments. These reports suggest a diradical (**2**) as the reactive intermediate in pyrolysis. Thus, any structure formed as a result of the thermolysis of a biphenylene unit in a thermally stable polymer would be expected to maintain the high-temperature structural integrity of the polymer.



1 **2**

SCF–MO calculations suggest[5] that biphenylene is antiaromatic and should be somewhat chemically unstable, undergoing reactions which would disrupt the conjugative effects in the antiaromatic cyclobutadiene ring. Both calculations[6] and a structure determination[7] show longer bond lengths between the benzo units (A) than within the benzo units (B). Calculated heats of formation for biphenylene are higher by 27.5 kcal/mol than those observed from heats of combustion;[7] this difference has been attributed[5] to strain energy.

Results and Discussion

Polyquinolines containing biphenylene units could be cured thermally at temperatues (300–350 °C) somewhat lower than those known to effect thermolysis of biphenylene.[3,4] In an effort to lower the temperature and reduce the time necessary for curing, we had carried out the reaction in the presence of norbornadienechlororhodium dimer **3**. Although the rhodium catalyst decreased the curing time, it was necessary in all cases to heat the sample above the glass transition temperature of the polymer in order to effect cross-linking.

Although rhodium catalysts are known to open strained cyclic hydrocarbons by an oxidative addition mechanism,[8] the products of the rhodium catalyzed reaction of biphenylene were unknown. Pryolysis of biphenylene containing a catalytic amount of the rhodium catalyst at 200 °C produced dibenzocyclooctatetraene in a 44% yield (recrystallized) and polymer. Thus, the products of the catalyzed reaction are the same as those obtained from the uncatalyzed thermolysis. By analogy to the cubane reaction,[8] however, it might be expected that benzyne is the reactive intermediate. This reaction

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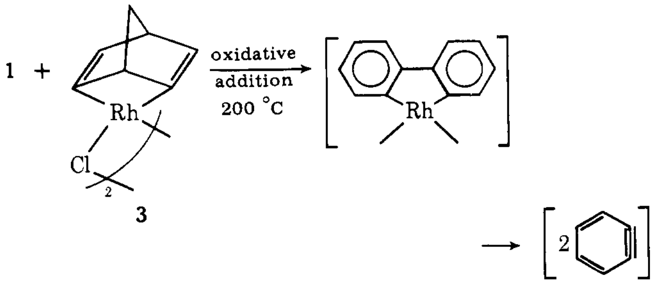
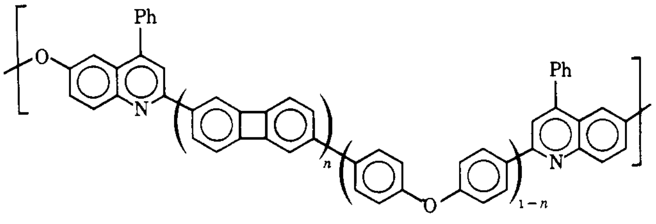
temperature is approximately 200 °C lower than that required for the uncatalyzed reaction.



In an effort to study the effect of curing temperature, curing time, added catalyst, and percentage of biphenylene units on the glass transition temperatures and thermomechanical properties of the cured polyquinoline, several polymer samples (**4–9**) were studied. The synthesis of the parent polyquinoline (**9**),[9] containing no biphenylene unit, as well as the syntheses of polyquinolines containing either a large percentage of biphenylene units (**5**, **6**) or a biphenylene group every repeat unit (**4**)[2] have been previously reported. The fraction of biphenylene units introduced can be conveniently adjusted by balancing the bismethylene ketone ratio, 2,6-diacetylbiphenylene to 4,4′-diacetyldiphenyl ether, in the polymerization reaction.



4, $n = 1$ **6**, $n = 0.25$ **8**, $n = 0.025$
5, $n = 0.5$ **7**, $n = 0.05$ **9**, $n = 0$

Glass-Transition Temperature. A summary of the glass-transition temperatures of cured and uncured polyquinolines **4–9** (Table I) shows (Figure 1) the dependence of the glass-transition temperature and the onset of curing as a function of biphenylene percentage. Biphenylene adds stiffness to the chain, and accordingly as the percentage of biphenylene decreases, T_g drops. Introduction of a few percent of biphenylene units (**7** and **8**) lowers the T_g (~30 °C) from that of the parent homopolymer (**9**), possibly due to a copolymer effect. The onset of the exotherm for cross-linking increases with an increasing biphenylene amount and parallels the increase in T_g. In order for cross-linking to take place, a temperature above T_g must be achieved. Apparently enough segmental mobility must be available either to allow collision of the two biphenylene units or the interaction of a biphenylene unit with another chain segment. As the dilution of biphenylene units in the chain increases, the formation of tetrabenzocyclooctatetraene links would be disfavored, and radical abstraction of aromatic hydrogen on adjacent chains would be expected to lead to the predominate mode of cross-linking.

Thermomechanical Properties. Curing of polymer **4** leads to the disappearance of its glass-transition temperature, at least as detected by DSC. Cured polymers having a higher percentage of biphenylene units exhibited higher glass-transition temperatures.

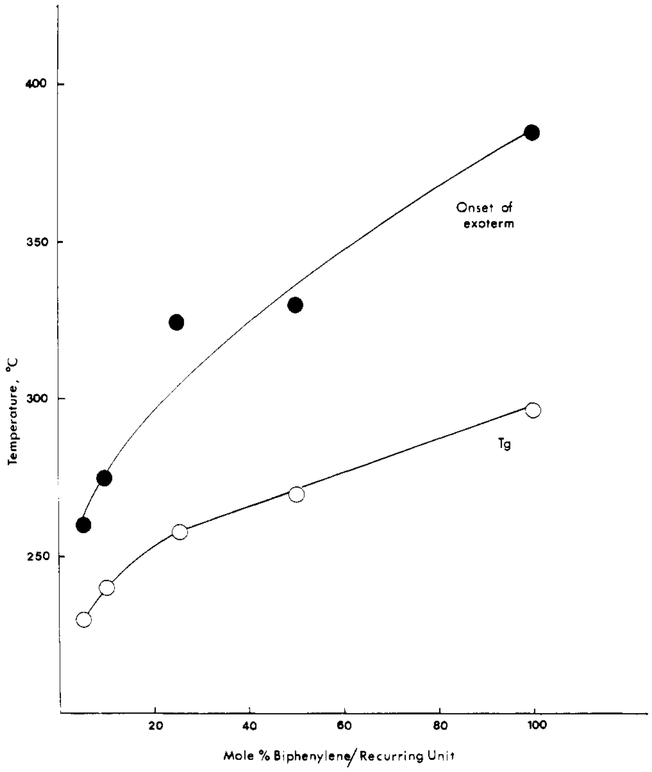


Figure 1. Dependence of the glass-transition temperature and the onset of the cross-linking exotherm as a function of biphenylene percentage.

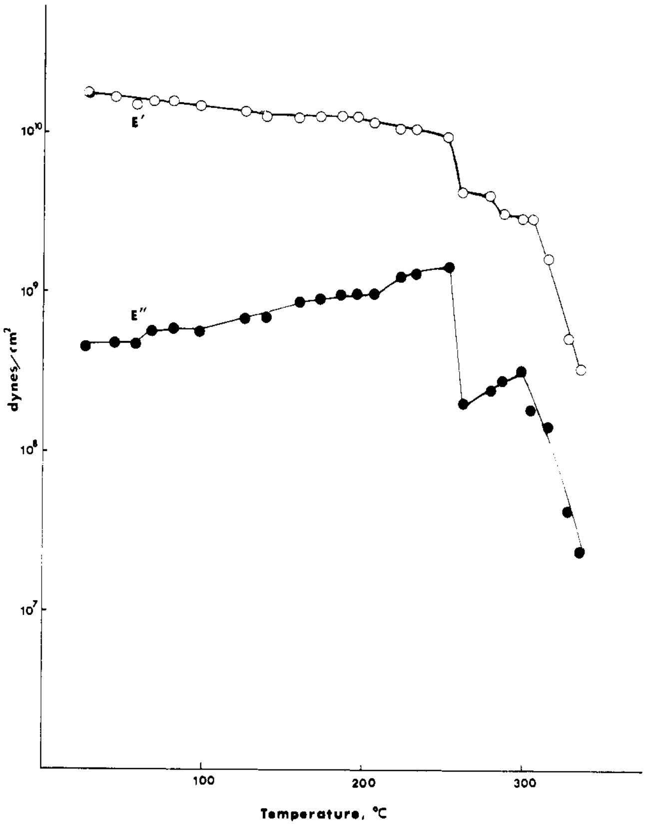


Figure 2. Dynamic storage and loss modulus vs. temperature for polymer **5**.

The dynamic mechanical properties of uncured and cured films of polyquinolines **4–9** (Table II) were obtained from room temperature up to 380 °C. Under the mild tensile stresses required, the mechanical performances of films are relatively constant up to the glass-transition temperature[10,11] (Figures 2–5). Youngs modulus increases from $\sim 1.8 \times 10^{10}$ dyn/cm^2 for polymers **5** and **6** containing a relatively larger amount of biphenylene to $\sim 3.3 \times 10^{10}$ dyn/cm^2 for polyquinolines **7** and **8**. Although higher moduli would be expected for polyquinolines **5** and **6** that contain larger amounts of bi-

Table I
Properties of Polyquinolines (T_g, Uncured and Cured Samples by DSC)

Polymer	[η]	T_g (uncured), °C	Exotherm onset, °C	Curing conditions T, °C	Curing conditions Time, min	T_g (cured), °C
4	4.4[b]	297	385	380	60	
				380	180	
5	2.3[c]	270	330	360	240	320
6	1.9[c]	258	325	360	240	295
				380	180	303
6[a]			300	280	30	280
7	0.93[d]	240	275	380	60	262
7[a]				380	60	265
				380	30	262
				280	60	262
8	2.1[d]	232	260	380	60	265
8[a]				380	60	265
				380	30	262
				280	60	242
9	1.8[d]	266	None			

[a] Films cast in the presence of $[(C_7H_8)ClRh]_2$. [b] Measured in formic acid. [c] Measured in *m*-cresol. [d] Measured in chloroform.

Table II
Thermomechanical Properties of Polyquinolines

Polymer[d]	T_g(DSC), °C	$T(E''_{max})$,[b] °C	E'(25 °C), dyn/cm²	E'(above T_g),[d] dyn/cm²	E_c[g]
5	270	251,[c] 298	1.8×10^{10}	*e*	1.7
		317,[c] 348	3.0×10^{10}	1.4×10^9	
6	258	225,[c] 292	1.9×10^{10}	*e*	1.8
		324	3.5×10^{10}	9.8×10^8	
7	240	284	3.5×10^{10}	*e*	1.4
		318	4.8×10^{10}	7.0×10^8	
8	232	242	3.3×10^{10}	*e*	1.4
		300	4.5×10^{10}	3.8×10^8 (6.8×10^8)[f]	

[a] Figures in the first row indicate thermomechanical properties of uncured sample; figures in the second row indicate thermomechanical properties of a sample cured for 6 h at 350–380 °C. [b] Applied frequency, 110 Hz. [c] Secondary absorption before T_g. [d] E' above T_g was measured on cured samples at a temperature above that on which the rapid decrease in E' had stopped. [e] Unable to obtain even at the highest instrument sensitivity. [f] Films cured for 6 h at 350–380 °C in the presence of $[(C_7H_8)RhCl]_2$. [g] Where E_c = [E'(25 °C, cured polymer)]/[E'(25 °C, uncured polymer)].

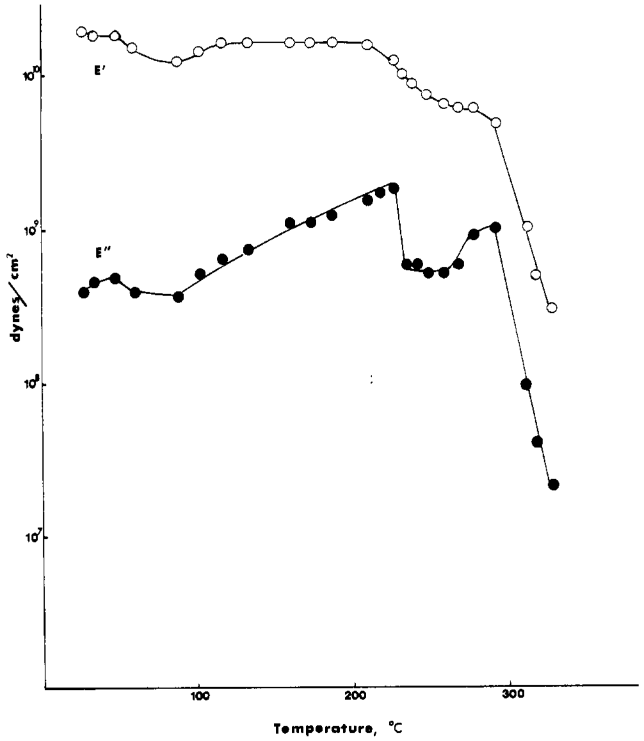


Figure 3. Dynamic storage and loss modulus vs. temperature for polymer **6**.

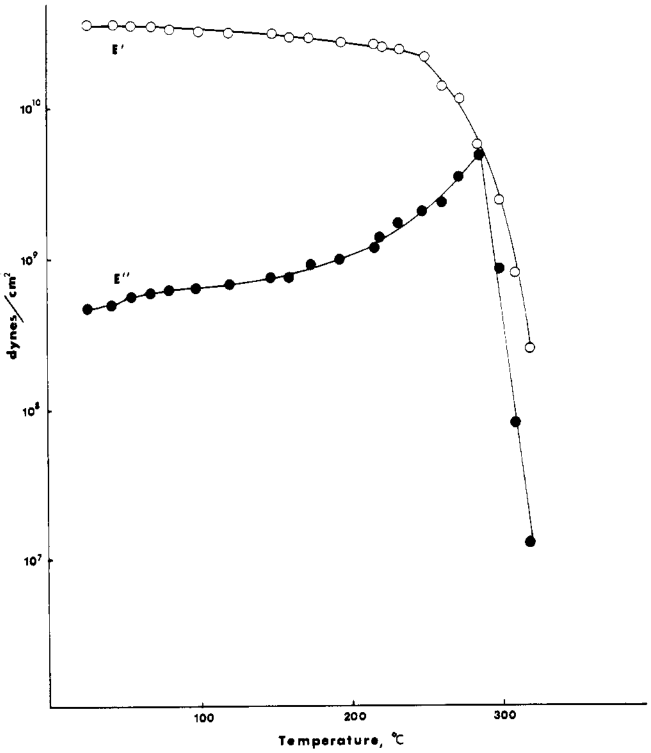


Figure 4. Dynamic storage and loss modulus vs. temperature for polymer **7**.

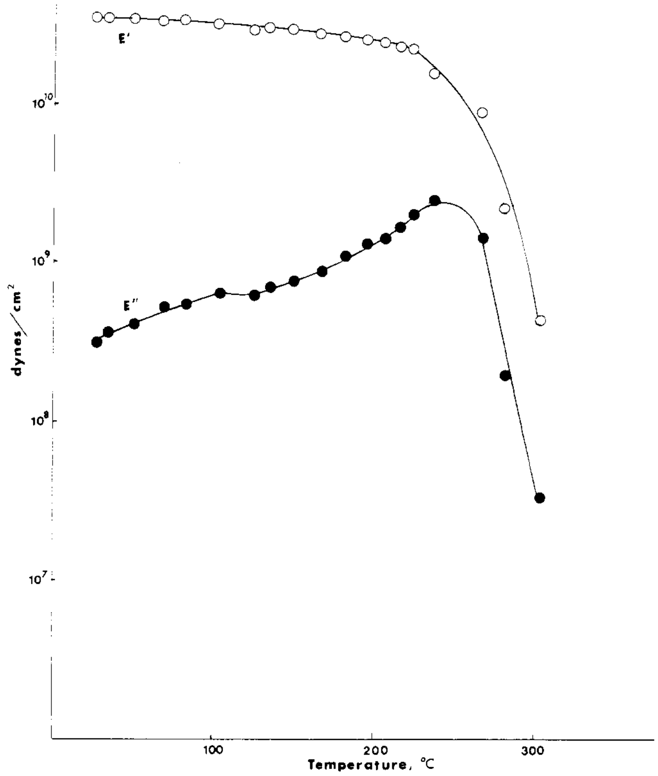


Figure 5. Dynamic storage and loss modulus vs. temperature for polymer **8**.

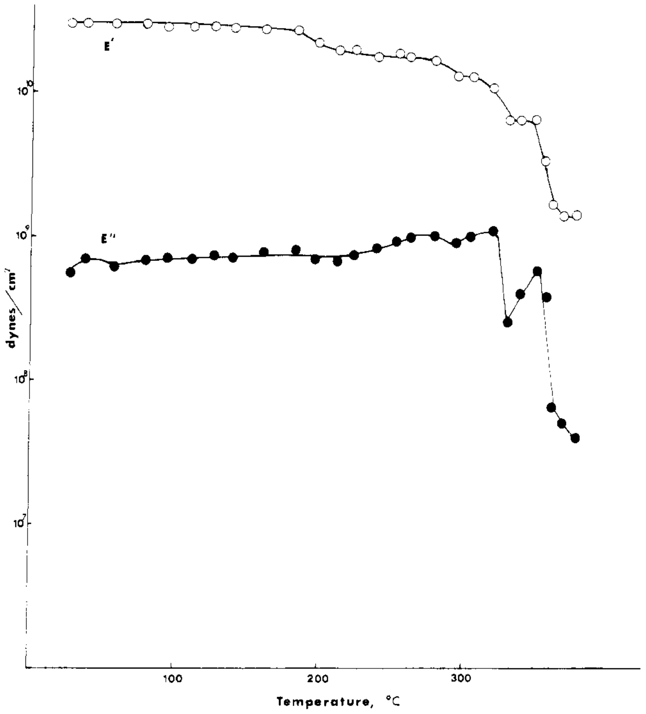


Figure 6. Dynamic storage and loss modulus vs. temperature for polymer **5**: 6 h cure at 350–380 °C.

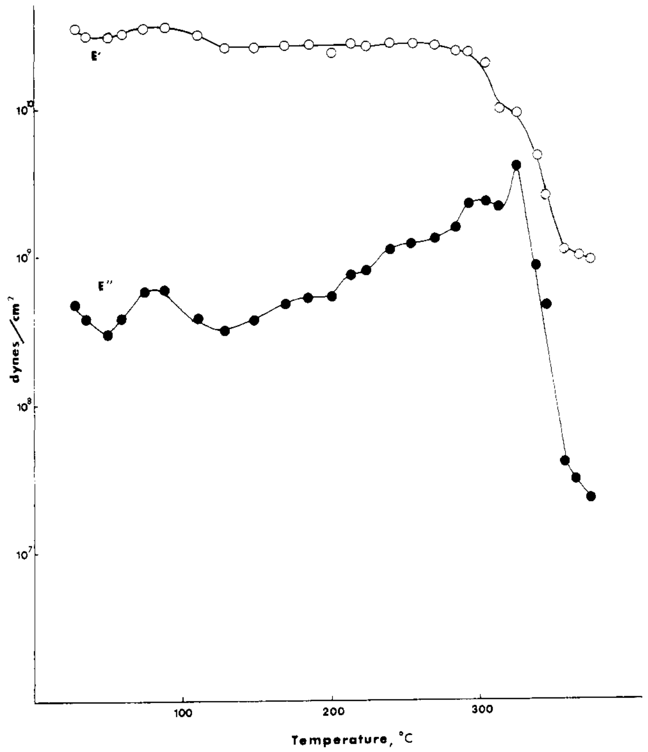


Figure 7. Dynamic storage and loss modulus vs. temperature for polymer **6**: 6 h cure at 350–380 °C.

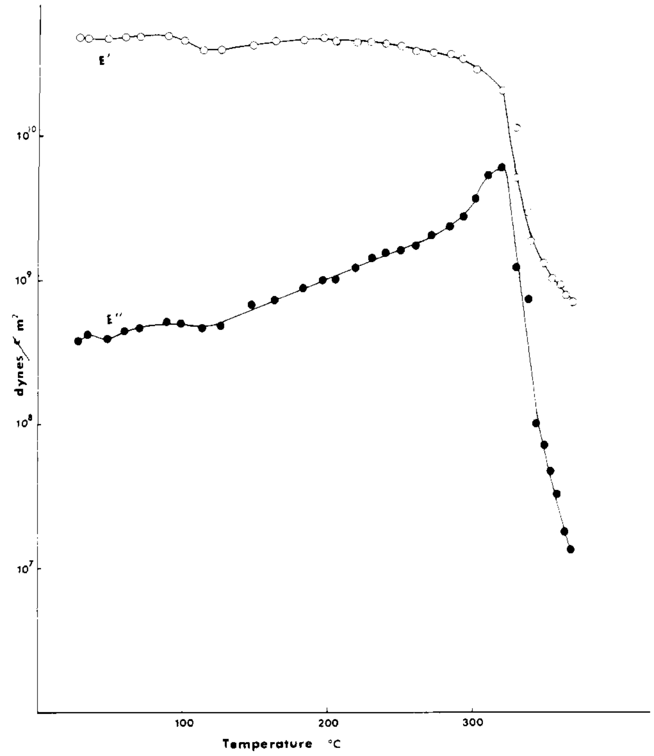


Figure 8. Dynamic storage and loss modulus vs. temperature for polymer **7**: 6 h cure at 350–380 °C.

phenylene, the modulus is dependent on the previous history, especially the thermal history.[11] Even under ambient conditions, several hundred degrees below the glass transition temperatures, polyquinolines are subject to continuous change or reorganization. Within the limits of the time these samples were prepared and their dynamic mechanical measurements were made, equilibrium was not achieved.

Uncured samples of copolymers **5** and **6**, containing larger percentages of biphenylene units (50 and 25%), showed a secondary dispersion in E' (and corresponding absorptions in E'') at 251 and 225 °C, respectively (Figures 2 and 3). These dispersions are followed by a loss of modulus at T_g. The origin of this secondary dispersion is unknown although it is possible that this is a result of relaxation originating from opening the biphenylene ring to a biphenyl diradical of the type **2**. This secondary dispersion is not visible in cured samples of **6**

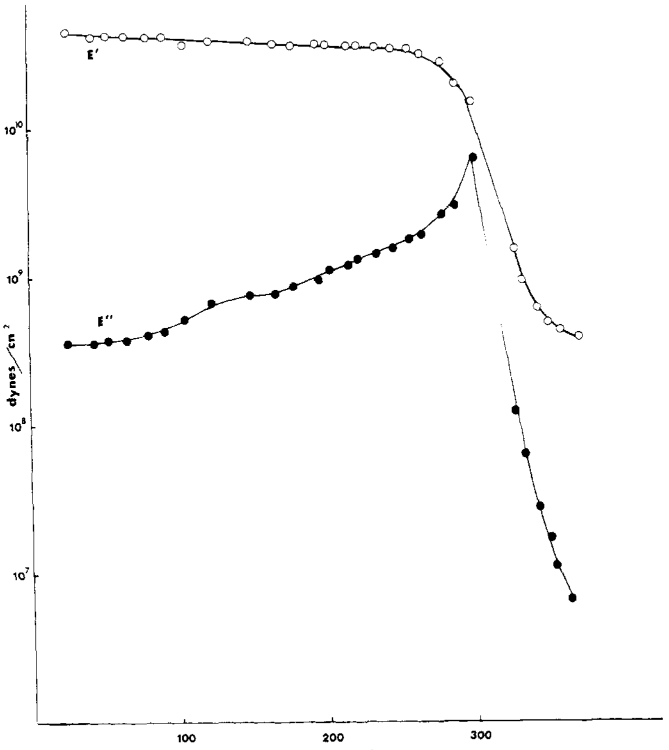


Figure 9. Dynamic storage and loss modulus vs. temperature for polymer 8: 6 h cure at 350–380 °C.

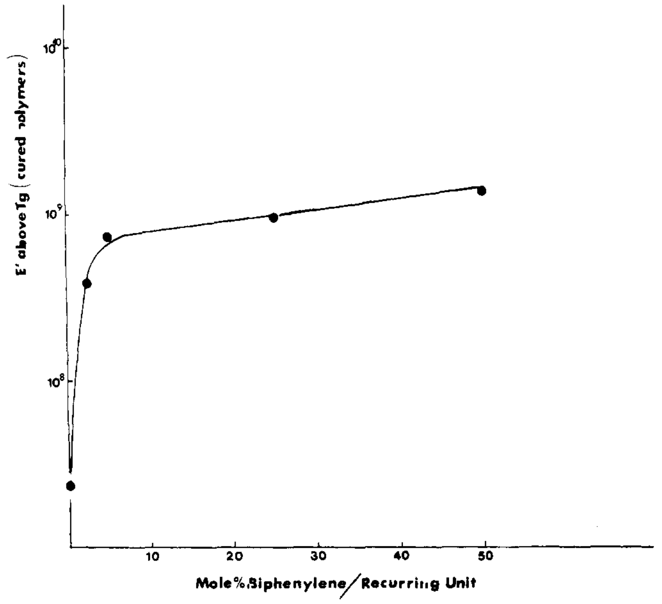


Figure 10. Dependence of the modulus of cured polymers above T_g as a function of percent biphenylene in the copolymer.

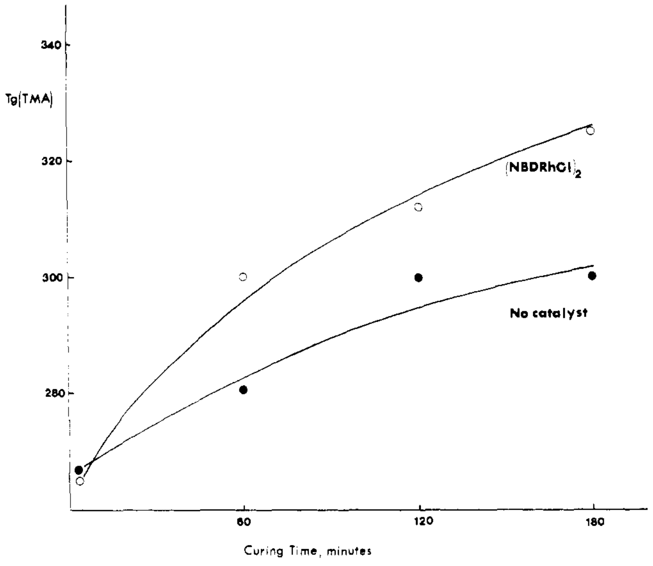


Figure 11. Dependence of glass transition (TMA) as a function of the curing time for polymer 8.

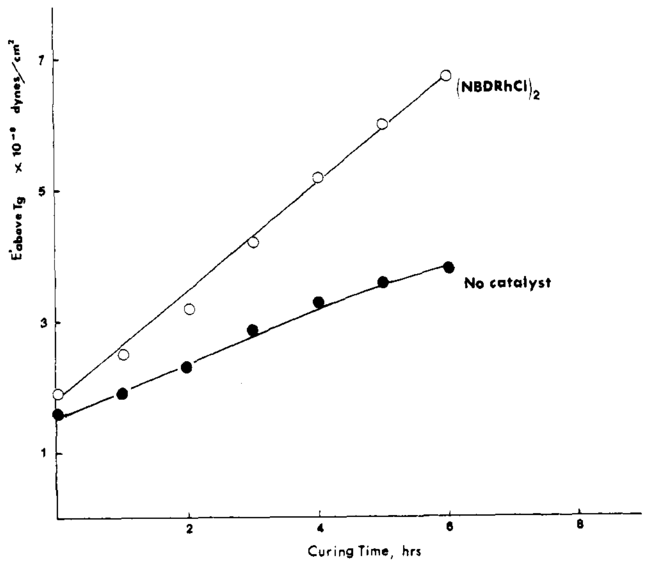


Figure 12. Dependence of dynamic storage Moduli (E') above T_g for polymer 8 as a function of curing time.

(Figure 7) and is only slightly visible in a cured sample of 5 (Figure 6).

The dynamic moduli of the cured polymers at low temperatures (25–250 °C) are, as expected, higher than those of the uncured polymers (Table II). The glass-transition temperatures after curing are 30–60 °C higher than the uncured samples, as measured by the moduli. More importantly, the moduli of the cured polymers above T_g (Table II) are much higher than that of the homopolymer, 9,[10] and are a function of the percent biphenylene in the copolymer (Figure 10). Even a low biphenylene incorporation (2.5%, 8) is sufficient to raise the value from 2.4×10^7 to 3.8×10^8 dyn/cm².

Rhodium(I)-Catalyzed Cross-linking. Since biphenylene (melt) undergoes a rhodium-catalyzed ring opening at much lower temperatures to afford the same products as obtained from the uncatalyzed reaction, curing was carried out on polymer samples containing catalytic amounts of norbornadienechlororhodium(I) dimer (Tables I–III). Generally, lower temperatures and shorter reaction times were used to effect the same cross-linking reaction. The thermal mechanical analysis of polymers 6 and 7 (Table III) showed that curing at 380 °C for 1 h was sufficient to erase the glass-transition temperature. In polymer 8, a very high glass-transition temperature is observed after curing at 380 °C for 1 h. At 380 °C, the effect of curing time on the glass-transition temperature of this polymer 8 containing only 2.5% biphenylene units is to increase T_g. Rhodium catalysis does this more effectively (Figure 11). At a curing time of 3 min, the difference in the rhodium cures and the catalyzed curing is most pronounced with polymer 6, containing 25% biphenylene (Figure 11).

Finally, it is instructive to compare the dynamic storage moduli (E') above T_g for polymer 8 cured with and without catalyst as a function of curing time (Figure 12, Table II). As

Table III
TMA of Polyquinolines in the Absence and in the Presence of $[(C_7H_8)RhCl]_2$

Polymer	T_g(TMA), °C	Cure temp, °C	Cure time, min	No catalyst	$[(C_7H_8)RhCl]_2$ (1%)
6	270	280	3	*a*	287
			60	*a*	300
			180	*a*	305
		380	3	287	315
			60	295	*b*
			180	*b*	*b*
			360	*b*	*b*
7	250	280	3	*a*	260
			60	*a*	260
			180	*a*	260
		380	3	267	275
			60	280	*b*
			180	305	*b*
			360	*b*	*b*
8	225	280	3	*a*	230
			60	*a*	257
			180	*a*	260
		380	3	267	265
			60	280	300
			180	300	325
			360	*b*	*b*

[a] No effect was generally observed curing the uncatalyzed sample at 280 °C. [b] No T_g was visible also at highest sensitivity of the instrument.

expected, the catalytic effect is reflected by the generation of higher moduli for the same curing time.

The thermal-gravimetric analysis of cured polymer samples and of the parent polymer **9** that does not contain the biphenylene units showed breaks at the same temperatures and under nitrogen suffered the same weight loss up to 800 °C.[9] This provides some evidence that in the curing reaction stable cross-links are indeed being formed.

Conclusion

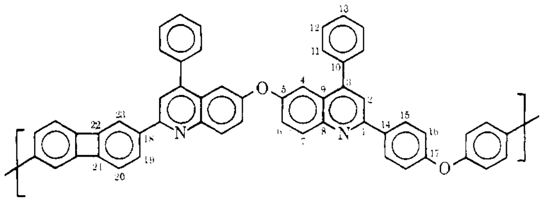
As anticipated, efficient thermally induced cross-linking occurs in polymers containing relatively low contents of biphenylene in the chain. The temperature of the uncatalyzed cross-linking reaction is dependent on the percentage of biphenylene units in the chain and generally parallels the glass-transition temperature of the copolymer, as a result of the necessity of having sufficient chain mobility (above T_g) for the cross-linking reaction to occur. The cross-linking reaction affords complete insolubility, a higher T_g or disappearance of the T_g, and a higher modulus both below and above T_g. Rhodium-catalyzed cross-linking reactions occur more rapidly and at lower temperatures.

Experimental Section

Thermolysis of Biphenylene in the Presence of Bis(norbornadienechlororhodium). To a solution of 1.52 g (10 mmol) of biphenylene in 20 mL of chloroform was added 0.046 g (0.1 mmol) of bis(norbornadienechlororhodium). The solvent was evaporated, and the mixture was dried under reduced pressure and was placed in an ampule. The system was alternately evacuated and filled with nitrogen and then sealed under nitrogen. After heating the ampule at 200 °C for 1 h, the crude product was extracted with benzene. The benzene was removed under reduced pressure and the residue was sublimated at 200 °C (0.05 Torr). Recrystallization from acetone, followed by drying under reduced pressure, gave 0.67 g (44%) of white tetraphenylene, mp 231–233 °C (lit. 232–233 °C),[4] mol wt 302 (calcd for $C_{24}H_{16}$, 305). The molecular weight was determined by vapor pressure osmometry in benzene. IR (KBr) 748 cm^{-1} (1,2-disubstituted aromatic).

Polymer Synthesis. The synthesis and characterization of polymers **4–6** and **9** have been described previously.[2,9] Polymers **7** and **8** were synthesized according to the same procedure described for polymers **4–6** and **9**.[2,9] The ^{13}C NMR spectra are shown in Table IV.

Table IV
^{13}C NMR of Copolymers 7 and 8



Carbon No.	Copolymer 7 and 8	Carbon No.	Copolymer 7 and 8
1	155.2	13[a]	128.7
2	122.8	14	134.9
3	148.4	15[a]	129.1
4	112.5	16	119.3
5	154.6	17	158.1
6	119.3	18–23	*b*
7	132.0		
8	145.9		
9	126.5		
10	138.0		
11[a]	128.7		
12	129.3		

[a] Assignments different from those reported[9] as a result of a better resolution. [b] Signal-to-noise ratio too low for clear assignment.

Glass Transitions and Thermomechanical Analysis. Thermal transitions were measured using a Differential Scanning Calorimetry Cell attachment for a Du Pont 990 Differential Thermal Analyzer, under 40 mL/min flow of nitrogen and at a heating rate of 20 °C/min, the reference being glass beads.

Thermomechanical analyses (TMA) were conducted on film samples of the polymers using a Du Pont 990 and 943 Thermomechanical Analyzer at a heating rate of 5 °C/min.

The 950 Thermogravimetric Analyzer attachment was used at a heating rate of 5 °C/min under circulating air or nitrogen atmospheres.

The dynamic mechanical properties of samples were determined as follows using the Rheovibron (Model DDV-II): Samples were cut into narrow strips approximately 3 cm in length, 0.3 cm in width, and 0.001 cm in thickness. Runs were made at a frequency of 110 Hz at a heating rate of 5 °C/min in an inert sample atmosphere. The dynamic moduli of films were calculated using the following equation:

$$|E^*| = \frac{2}{(A)(\mathrm{DF}-K)}\frac{L}{S} \times 10^9 \text{ dyn/cm}^2$$

where A is a constant given by the instrument manual,[12] DF is the value of the dynamic force dial when measuring tan δ, L is the length of sample, S is the cross-sectional area in cm^2, and K is an error constant due to the modulus of electricity and displacement of the stress gauge. Values of Young's modulus E' and the loss modulus E'' were obtained as follows:

$$E' = |E^*| \cos \delta$$

and

$$E'' = |E^*| \sin \delta$$

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Solid-State and Solution Conformation of *N-tert*-Butyloxycarbonyl-L-prolylglycine[1]

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ABSTRACT: The occurrence of the oxy analogue in the trans-II 4 → 1 intramolecularly hydrogen-bonded nonhelical peptide conformation, recently proposed for *t*-BOC-L-Pro-Gly-OH in the solid state on the basis of infrared absorption evidence, has been disproved by x-ray diffraction analysis. This type of folding is also absent in polar solvents. However, in solvents of low polarity the presence of this folded form cannot be excluded.

For a full picture of the spatial architecture of peptide molecules the combined application of x-ray diffraction and spectroscopic techniques[3,4] has proved to be highly fruitful. X-ray analysis, while yielding the most exact information on the three-dimensional structure in the crystal state, leaves unanswered questions concerning conformation and conformational equilibria in solution. Such problems may be attacked by a combined use of physicochemical methods so that many important factors influencing peptide conformation (e.g., solvent, temperature, concentration) can be investigated. Obviously, the most reliable and complete information is obtained when solution studies are coupled with x-ray analysis.

We have applied this approach in the present study that represents a part of our continuing investigation of the occurrence, both in the solid state and in solution, of the oxy analogues of the 4 → 1 intramolecularly hydrogen-bonded nonhelical peptide conformations (β turns, C_{10} ring structures).[5] The presence of these folded structures has been recently proposed in the solid state for *t*-BOC-Gly-L-Pro-OH (*t*-BOC, *tert*-butyloxycarbonyl), *t*-BOC-L-Pro-Gly-OH, *t*-BOC-L-Pro-D-Pro-OH, and *t*-BOC-L-Pro-L-Pro-D-Pro-OH on the basis of infrared (IR) absorption evidence.[6] In a previous study from our laboratories[5] we showed by x-ray diffraction that *t*-BOC-Gly-L-Pro-OH does not adopt in the solid state the structure oxy analogous to the β turn (trans-II′ type),[6] which however could account, at least in part, for the strong negative Cotton effect near 230 nm observed in the circular dichroism spectra in solvents of low polarity. In this paper we describe the IR absorption and x-ray diffraction results of the second of the *N*-protected peptides listed above, namely *t*-BOC-L-Pro-Gly-OH, in the solid state. Its circular dichroism (CD) and IR absorption properties in solvents of widely different polarity and at different concentrations are also discussed. The conclusions were supported by comparison with the data obtained for a number of derivatives and model compounds.

The structure proposed by Deber[6] for *t*-BOC-L-Pro-Gly-OH (oxy analogue to the *trans*-II β turn) is illustrated in Figure 1.

Experimental Section

Synthesis of Peptides. *t*-BOC-L-Pro-Gly-OMe[7] was synthesized from *t*-BOC-L-Pro-OH and HCl (HCl·H-Gly-OMe) via the dicyclohexylcarbodiimide coupling method:[8,9] mp 67–68 °C, after recrystallization from ethyl acetate–petroleum ether; $[\alpha]^{21}{}_{\mathrm{D}}$ −63.3° (*c* 0.85; methanol); R_f (TLC; SiO$_2$; Merck; chloroform–ethanol 9:1) 0.75. *t*-BOC-L-Pro-Gly-OH[10] was prepared by alkaline hydrolysis in an aqueous/dioxane mixture of *t*-BOC-L-Pro-Gly-OMe: mp 171–172 °C, after recrystallization from methanol–ethyl ether; $[\alpha]^{21}{}_{\mathrm{D}}$ −67.3° (*c* 0.86; methanol); R_f (TLC; SiO$_2$, Merck; chloroform–ethanol 9:1) 0.15. *t*-BOC-L-Pro-Sar-OMe[11] was synthesized from *t*-BOC-L-Pro-OH and HCl·H-Sar-OMe via the dicyclohexylcarbodiimide method:[8,9] oil, after precipitation with petroleum ether from an ethyl ether solution: $[\alpha]^{21}{}_{\mathrm{D}}$ −47.2° (*c* 0.94; methanol); R_f (TLC; SiO$_2$, Merck; chloroform–ethanol 9:1) 0.75. *t*-BOC-L-Pro-Sar-OH[6,12] was prepared by alkaline hydrolysis in an aqueous methanol solvent mixture of *t*-BOC-L-Pro-Sar-OMe: mp 145–146 °C, after recrystallization from ethyl acetate–petroleum ether; $[\alpha]^{21}{}_{\mathrm{D}}$ −26.5° (*c* 1; dimethylformamide); R_f (TLC; SiO$_2$, Merck; chlorofrom-ethanol 9:1) 0.10. *t*-BOC-L-Pro-OH and *t*-BOC-L-Pro-OMe were synthesized as described in our previous paper.[13] Ac-Gly-OH was a commercial product (Fluka).

Infrared Absorption. Infrared absorption spectra were recorded using a Beckman Model IR 9 spectrophotometer. For the solid state