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Bisbiphenylenes: New Cross-Linking Reagents for Thermally Stable Polymers

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ABSTRACT: Cross-linking agents containing two biphenylene units linked by thermally stable aromatic units were synthesized such that the aromatic units resembled certain thermally stable polymers the bisbiphenylenes were intended to cure. Thus, bisbiphenylenes linked by quinoline, isophthalamide, pyromellitimide, and diphenyl ether groups were used to cross-link polyquinoline, polyaramide, polypyromellitimide, poly(ether sulfone), and poly(phenylene ether) samples. Films from solutions containing polymer, cross-linking agent, and, in some examples, a transition-metal catalyst were plasticized, resulting in lower glass transition temperatures and dynamic storage moduli than film samples devoid of cross-linking agent and catalyst. The samples were cured by heating to the temperature at which the biphenylene ring underwent the ring-opening reaction, generally 300–400 °C. Samples could not be cured below their glass transition temperatures, and no ring-opening exotherm was observed below T_g regardless of the exotherm exhibited by pure bisbiphenylene. The addition of a transition-metal catalyst not only lowered T_g of the polymer samples further but effected the cure at lower temperatures and shorter times. Cross-linked polymer samples were insoluble and had higher T_g's as measured by dynamic storage and loss moduli.

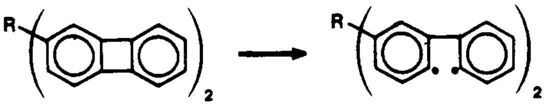
Introduction

Most thermally stable polymers, as a result of rigid aromatic units in the chain, either are partially crystalline, with the attending high crystalline transition temperatures, or are amorphous but have high glass transition temperatures. Both crystalline and, to some extent, amorphous materials tend to have poor solubility in common organic solvents. Those polyaromatics that are amorphous, and have relatively low T_g's, are processed readily, but their use temperature is limited to the glass transition temperature, a temperature far below the thermal decomposition temperature.

In an effort to produce thermally stable polymers that could be fabricated readily and then converted to a material with high use temperatures, we have explored cross-linking reactions of aromatic polymers. Unfortunately, there are few good cross-linking reactions of polyaromatics, in part because of their chemically inert structure and the reduced chain mobility. However, because biphenylene reacts with aromatic structures to form stable links, we have been able to effect the cross-linking reaction of polyaromatics by incorporating biphenylene into the polyaromatic main chain.[1-5] Thus, polyquinolines, polyamides, polyquinoxalines, and a polybenzimidazole, all containing biphenylene units, cross-link thermally or with the aid of transition-metal catalysts to give insoluble materials with higher and usually less intense (or absent) T_g's, as well as higher moduli above T_g. In every case, cross-linking took place only above T_g. The applicability of this reaction is demonstrated by the fact that a poly(ketone ether)[6] containing biphenylene in the chain underwent compression molding at temperatures near 350 °C, rapidly thermosetting to a molded resin.

Cross-linking through biphenylene units incorporated in the main chain requires, however, the synthesis of a difunctional biphenylene in monomer-grade purity followed than its inclusion in the polymerization reaction to give a polymer with a fixed (desired) amount of cross-linking agent. These disadvantages could be overcome by the addition of an external cross-linking agent to a previously synthesized polymer. The additive could be dispersed in the polymer at some stage before processing and then cured to cross-link the prefabricated polymer. Such a cross-linking agent should meet the following requirements: (1) It should generate a reactive intermediate that will react rapidly with aromatic nuclei. (2) The reaction should afford a thermally stable link, preferably an aryl–aryl bond. (3) The reaction should be initiated under convenient conditions; control of the reaction temperature is especially desirable. (4) No volatiles can be generated. (5) The additive should be of high enough molecular weight so that it, its fragments, or its byproducts will not evolve from the polymer during the curing process. (6) Compatibility of the additive with the polymer, such that it will be molecularly dispersed, is necessary. Formation of domains of additive will not lead to cross-linked polymer. (7) The additive should have solubility in common organic solvents that are good solvents for the polymer so that homogeneous films or fibers can be obtained from solution. (8) Long shelf life, including stability in common organic solvents, is desirable such that shipping and handling can be accomplished.

These requirements for a cross-linking additive presumably could be met with certain bisbiphenylenes, the synthesis of which should present fewer demands than the synthesis of pure difunctional biphenylene monomers and their corresponding polymers. This work describes such an approach to the cross-linking problem.



Results and Discussion

Bisbiphenylenes: Synthesis and Properties. The approach to the synthesis of various bisbiphenylenes was to obtain structures that would be the most compatible with the polymers that they were intended to cross-link. Thus, a series of cross-linking agents having quinoline, aromatic amide, aromatic ketone, aromatic amide acid, and aromatic imide were synthesized (Scheme I).

The reaction of 2-acetylbiphenylene with 4,4′-diamino-3,3′-dibenzoyldiphenyl ether gave 6,6′-oxybis[2-(2-biphenylenyl)-4-phenyl]quinoline (**1**), which was soluble in chloroform and *m*-cresol. This compound showed an exotherm at 415 °C (maximum) which could be attributed to the ring-opening reaction of biphenylene (Table I). The bisbiphenylene containing amide links, *N*,*N*′-bis(2-biphenylenyl)isophthalamide (**2**), shows two exotherms and solubility in dimethylformamide (DMF) and dimethylacetamide (DMAC). The amide–acid mixture (**3**) dehydrates before melting to give imide (**4**). Although the

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Chart I

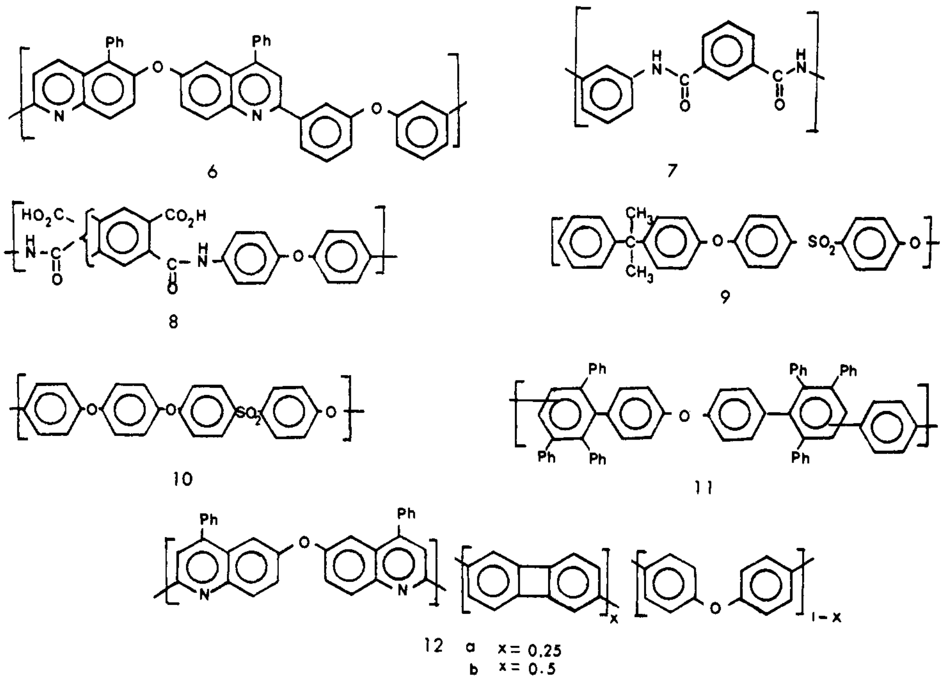


Table I
Properties of Bisbiphenylene Cross-Linking Agents[a]

compd	mp, °C	onset of exotherm,[b] °C	exotherm max, °C	solubility (solvent)
1	242	305	420	$CHCl_3$, *m*-cresol
2	341	345	350, 450–475[c]	DMF, DMAC
3	*d*	450	465	DMF, Me_2SO
4		440	450	insoluble
5	274	350	380, 405[c]	most organics

[a] Transition temperatures determined by DSC. [b] Temperature at which 5% of the exothermic maximum was reached. [c] Shows two exothermic maxima. [d] Endotherms at 150, 175, and 245 °C attributed to imide formation.

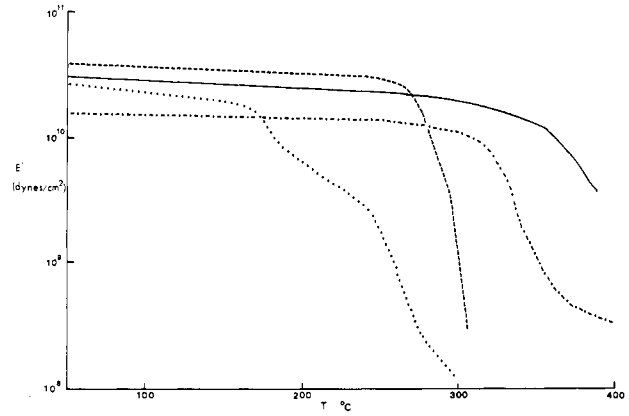


Figure 1. Dynamic storage moduli of polyquinoline **6** before and after cross-linking: (—) 15% **1** after curing 3 h, 405 °C; (···) 15% **1** before curing; (- - -) **6** without **1**; (-··) **6** without **1**, heated for 3 h, 405 °C.

Table II
Plasticizing Effect of Bisbiphenylenes 1 and 5 on Polyquinoline 6

bisbiphenylene			
no.	amt added, wt %	T_g,[a] °C	$E'_{25\,°C} \times 10^{-10}$,[b] dyn/cm²
1	10	170	4
1	15	160	2.7
5	6	170	3.3
5	13	125	2.5

[a] $T_g(6) = 260$ °C. [b] $E'(6) = 4 \times 10^{10}$ dyn/cm².

amide acid **3** is soluble in DMF and dimethyl sulfoxide (Me_2SO), dehydration to **4** produces an insoluble imide. The ether ketone (**5**) was obtained by the Friedel–Crafts reaction of biphenylene-2-carboxoyl chloride with diphenyl ether and is a mixture of di- and tribenzoylated material.

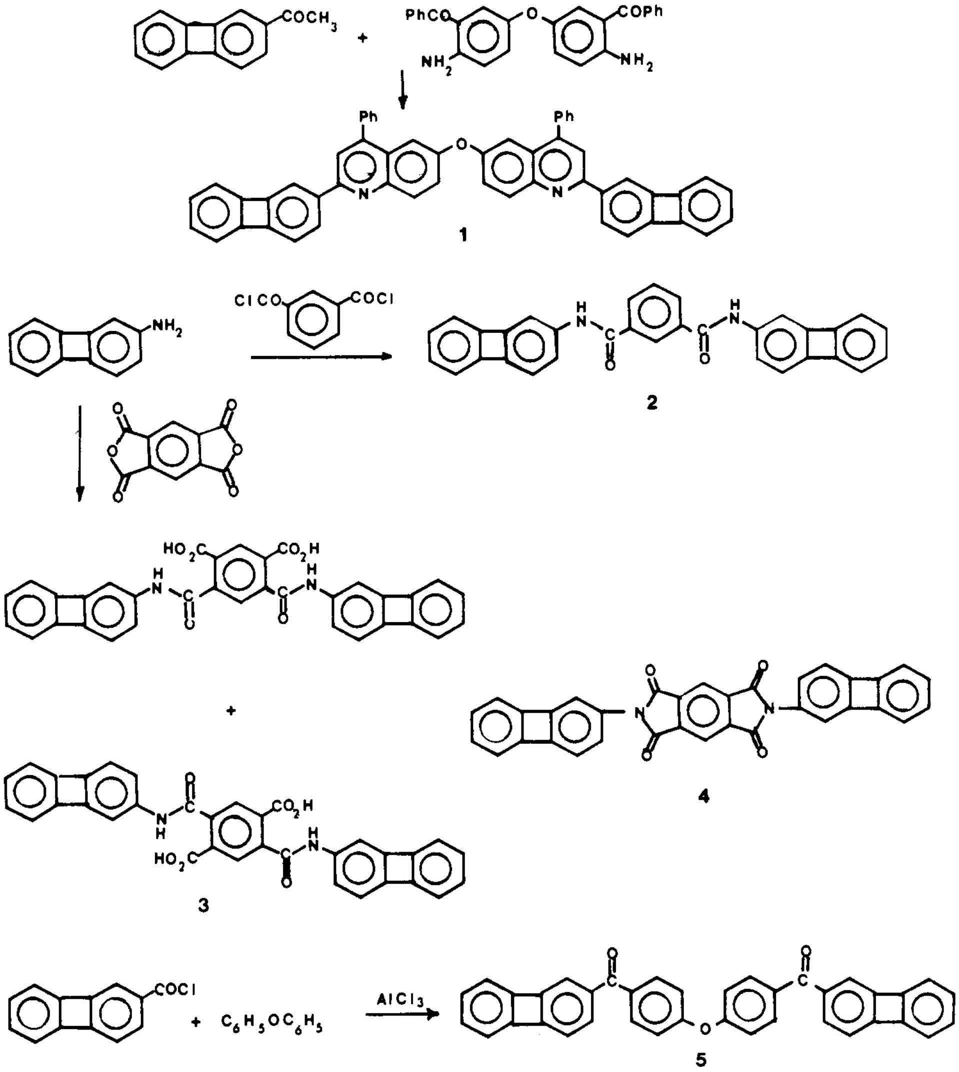
Cross-Linking Reactions. Cross-linking reactions were carried out with six different aromatic polymers: a polyquinoline (**6**), a commercial sample of poly(*m*-phenyleneisophthalamide) (**7**), a poly(amide acid) (**8**), two poly(ether sulfones) (**9** and **10**), and a phenylated polyphenylene (**11**). In cross-linking studies, films were cast from solutions containing polymer, cross-linking agent, and, in some cases, a catalyst. The cross-linking agent for each polymer was chosen to match, generally, the structural features of the polymer so that homogeneous films were produced.

1. Poly[2,2′-(*p*,*p*′-oxydiphenylene)-6,6′-oxybis(4-phenylquinoline)] (6). The temperature at which the uncatalyzed ring-opening reactions of any of the bisbiphenylenes take place is above the glass transition temperature, 250–260 °C, and below the thermal decomposition temperature, 525 °C, of polyquinoline **6**. Two bisbiphenylene cross-linking agents, **1** and **5**, both of which were compatible with the polymer, were used as curing agents. These cross-linking agents served as plasticizers for the polymer film, lowering the modulus and the glass transition temperature (Table II, Figure 1).

Films containing cross-linking agents **1** or **5** showed exotherms (DSC) at the same temperatures as the pure samples of **1** and **5**. Curing was carried out below 420 °C, since above this temperature cross-linking of **6** takes place in the absence of bisbiphenylene.

First, it should be noted (Table III, Figure 1) that heating a polyquinoline film that does not contain cross-linking agent to a temperature near 400 °C for 3 h increases the glass transition by 40–50 °C as measured by

Scheme I
Synthesis of Bisbiphenylene Cross-Linking Agents



the dynamic storage and loss moduli. In all cases except one, after thermal treatment the room-temperature storage modulus of the cross-linked polymers did not reach that value exhibited by the original, unadulterated polyquinoline. For comparison purposes, heating a film of this polyquinoline to 400 °C for 3 h resulted in a decrease of its room-temperature modulus to 1.6×10^{10} dyn/cm². However, the room-temperature storage modulus of cross-linked films was always greater than this value and, in one example in which a curing of **6** was carried out with **5** at a slightly lower temperature (300–400 °C) and a shorter period of time, a room-temperature modulus of over 5×10^{10} dyn/cm² was achieved, a value greater than that of virgin polyquinoline.

The glass transition temperatures of the cured polyquinolines were always greater than those of the parent untreated polyquinolines. Thus, by curing, the plasticizing effect of the biphenylenes, which could lower T_g by as much as 160 °C, was overcome to produce a T_g of cross-linked material that could be 70 °C higher than that of **6**.

Cross-linking compound **5** is more efficient than cross-linking **1**, probably because its average functionality is greater than 2. At a constant temperature (400–410 °C) the storage modulus (E') increases exponentially with time. The time necessary to reach a modulus of 10^{10} dyn/cm² was 1.3, 2.7, and 4.2 h, respectively, for 13% **5**, 6% **6**, and 15% **1** (Figure 2). Cross-linking bisbiphenylenes **1** and **5** is more effective than incorporating biphenylene into the polymer main chain (12), since higher T_g's were obtained with **1**, even with shorter curing times.

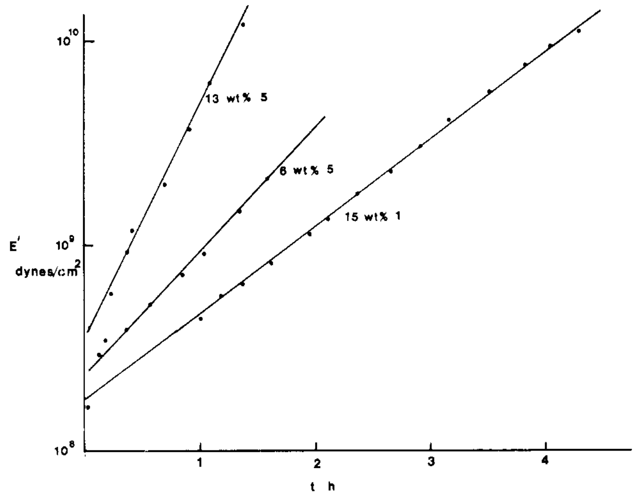


Figure 2. Rate of curing polyquinoline **6** with bisbiphenylenes **1** and **5** at 400–410 °C.

All samples of polyquinolines were insoluble in all organic solvents following cross-linking with **1** or **5**. Polyquinoline **6** that was heated to 405 °C for 3 h without cross-linking agent remained soluble. The thermal stability of cross-linked samples was not decreased but was essen-

Table III
Effect of Cross-Linking Polyquinoline 6

bisbiphenylene			curing conditions		T_g,[a] °C			
no.	amt added, wt %	catalyst (wt %)	T, °C	t, h	E''_{max}	$E'_{1/2}$	ΔT,[b] °C	$E'_{25 °C} \times 10^{-10}$, dyn/cm^2
					295	272		4
			405	3	336	320	+41/+48	1.6
1	10				245	180	−50/−92	4
	10		405	1	293	286	−2/+14	2.2
	10		405	3	347	328	+52/+56	2.2
	10	Ni[c] (1.7)			200	184	−95/−88	1.6
	10	Ni[c] (1.7)	275	0.67	258	254	−37/−18	1.8
	10	Ni[c] (3.5)			138	112	−157/−160	2.4
	10	Ni[c] (3.5)	320-380	2	309	292	+14/+20	1.8
	10	Rh[d] (0.6)			160	148	−135/−124	2.8
	10	Rh[d] (0.6)	300-400	2	333	320	+38/+48	2.1
	15				162	173	−133/−99	2.7
	15		405	3	>371	345	>+76/+73	2.5
12a			350-380	6	324	308	+29/+36	3.3
5	6				195	180	−100/−92	3.3
	6		25-440	1	375	338	+80/+66	2.1
	13				147	136	−148/−136	2.5
	13		405	3	e			0.8
	13		300-400	1.5	300	280	+5/+8	5
12b		Ni[c] (3.5)			185	176	−110/−96	3.2
			335-350	0.5	312	318	+17/+46	2.9

[a] T_g's were taken as the temperature at which the loss modulus (E''), as measured with the Rheovibron, was at the maximum and the temperature at which the storage modulus (E') was decreased by 50%. [b] The difference in the T_g's of the treated polymer and a pure sample of untreated polyquinoline (6) as determined by the loss (E'') and storage ($E'_{1/2}$) moduli, respectively: $\Delta T = T_g(E'') - 295$ °C/$\Delta T = T_g(E'_{1/2}) - 272$ °C. [c] Nickel catalyst, dicarbonylbis(triphenylphosphine)nickel(0), was added in an amount corresponding to 10 and 20 mol % of the biphenylene moiety present. [d] Rhodium catalyst, bis[(norbornadiene)chlororhodium]. [e] No T_g detected.

tially the same as that for the original material.

Although the ring opening of strained cyclic hydrocarbons is accomplished by rhodium(I) complexes[7,8] and has been successfully applied to the cross-linking of polyquinolines containing biphenylene in the main chain,[2] not only is rhodium an expensive catalyst but the cross-linking reaction is still too slow at moderate reaction temperatures. There are a number of other catalysts that are known to effect the rearrangement of strained-ring hydrocarbons.[9] Even though the mechanisms for most of these reactions are not known with certainty, they probably take place by oxidative addition of a carbon–carbon bond to the metal.

The conversion of biphenylene to tetrabenzocyclooctatetraene is catalyzed at 100 °C by dicarbonylbis(triphenylphosphine)nickel(0).[10] Nickel(0) complexes, such as bis(acrylonitrile)nickel(0), also catalyze the ring-opening of quadricyclone.[11] Although biphenylene will dimerize at 100 °C in the presence of a nickel catalyst, higher temperatures are required when a bisbiphenylene cross-linking agent is added to polyquinoline **6** or when biphenylene is incorporated in the polyquinoline chain (**12**), since cross-linking does not take place below T_g. An important feature of a catalyzed bisbiphenylene cure is that the polymer is plasticized not only by the biphenylene but also by the nickel complex, so that the resulting T_g of a polyquinoline containing 10 wt % bisbiphenylene **1** and 3.5 wt % nickel catalyst is 110–140 °C.

Polymer films could be cast from *m*-cresol or chloroform solutions containing catalyst and cross-linking agent. Although the nickel catalyst underwent a loss of carbonyl groups in the *m*-cresol solvent, nevertheless, the catalyst remained active. Alternatively, molecular dispersion of the catalyst could be achieved by dissolving the catalyst in a solvent that had swelled the polymer. The exothermic maximum for ring-opening occurred at a lower temperature (316 °C) for polymer **12b**, containing biphenylene in the main chain, and 3.5 wt % nickel catalyst than the same polymer without catalyst (470 °C). Even more dramatic, and of a decided advantage, is the lowering of the exothermic maximum for polyquinoline **6** containing 10 wt % bisbiphenylene **1** from 417 °C (without catalyst) to 267 °C with 10 wt % catalyst.

2. Poly(*m*-phenyleneisophthalamide) (7). Cross-linking polyamide **7** with bisbiphenylene **1** or bisbiphenylene **2**, which resembles the polymer structure, was not particularly effective (Table IV). This could be a result of the high degree of crystallinity in the polymer and a high crystalline transition temperature (428 °C, DSC). The bisbiphenylenes probably are concentrated in the amorphous regions, since there is little plasticizing effect either by cross-linking agent or by nickel catalyst.

Although bisbiphenylenes **1** and **2** show ring-opening exotherms at 418 and 350 °C, respectively, the exotherms for the cross-linking of polyamide **7**, containing **1** and **2**, occur at 477 and 420 °C, respectively. Cross-linking takes place rapidly only above T_m. Addition of dicarbonylbis(triphenylphosphine)nickel(0) lowers the cross-linking exotherm to 365 °C.

The largest increase in T_g as measured by $E'_{1/2}$, as a result of cross-linking with **1**, was 39 °C (1 h, 380 °C). With bisbiphenylene **2**, when the film sample was heated from ambient temperature to 426 °C and then cooled to room temperature, an increase in T_g of 87 °C was realized. The crystallinity decreased during this treatment such that the crystalline endotherm could no longer be detected by DSC and the storage modulus dropped to 6×10^9 dyn/cm^2 from an initial value of 3×10^{10} dyn/cm^2. Cross-linking can take place below T_m; but above T_g, at 380 °C, it occurs presumably in the amorphous phase. The storage modulus of this cross-linked polymer remains essentially the same after this treatment as before the treatment, but the T_g disappears as a result of cross-linking in the amorphous regions.

Table IV
Effect of Cross-Linking Polyamide 7

bisbiphenylene[a]	catalyst[b]	curing conditions		T_g,[c] °C				$E'_{25\,°C} \times 10^{-10}$, dyn/cm²
		T, °C	t, h	E''_{max}	$E'_{1/2}$	DSC	ΔT,[d] °C	
				260	263	272		2.8
		340	3	293	300		+33/+37	2.3
1				280	280	261	+20/+17	2.3
		280	1	290	288		+30/+25	3.4
		340	1	299	296		+39/+33	3.0
		380	1	316	302		+56/+39	2.0
		340	3	308	300		+48/+37	2.6
2				269	269	243	+9/+6	3.0
		25–426	1	>300	350		+40/+87	0.6
		380	1	none	e			2
	Ni			273	270	238	+13/+7	1.8
	Ni	315	0.75	270	277		+10/+14	2.6
	Ni	325–370	0.75	300	292		+40/+29	2.3

[a] 10 wt % bisbiphenylene was added. [b] Dicarbonylbis(triphenylphosphine)nickel(0), 1.8 wt %. [c] T_g's were taken as the temperature at which the loss modulus (E''), as measured by the Rheovibron, was at the maximum and the temperature at which the storage modulus (E') was decreased by 50%. [d] The difference in the T_g's of the treated polymer and a pure sample of untreated polyamide (7) as determined by the loss (E'') and storage ($E'_{1/2}$) moduli, respectively: $\Delta T = T_g(E'') - 260$ °C/$\Delta T = T_g(E'_{1/2}) - 263$ °C. [e] Storage modulus lost less than 25% of its initial value up to 435 °C.

Table V
Effect of Cross-Linking Polysulfone 10 with 1

added bisbiphenylene, wt %	catalyst	curing conditions		T_g,[b] °C				$E'_{25\,°C} \times 10^{-10}$, dyn/cm²
		T, °C	t, h	E''_{max}	$E'_{1/2}$	DSC	ΔT,[c] °C	
				195	194	221		2.4
10				126	132		−69/−62	2.2
10	Ni[a]	300	1	239	240		+44/+46	2.5

[a] Dicarbonylbis(triphenylphosphine)nickel(0), 3.4 wt %. [b] T_g's were taken as the temperature at which the loss modulus (E''), as measured by the Rheovibron, was at the maximum and the temperature at which the storage modulus (E') was decreased by 50%. [c] The difference in the T_g's of the treated polymer and a pure sample of untreated polysulfone 7 as determined by the loss (E'') and storage ($E'_{1/2}$) moduli, respectively: $\Delta T = T_g(E'') - 195$ °C/$\Delta T = T_g(E'_{1/2}) - 194$ °C.

Table VI
Effect of Cross-Linking Poly(phenylene oxide) 11 with 1

added bisbiphenylene, wt %	curing conditions		T_g,[a] °C				$E'_{25\,°C} \times 10^{-10}$, dyn/cm²
	T, °C	t, h	E''_{max}	$E'_{1/2}$	DSC	ΔT,[b] °C	
			345	318	322		2.1
	405	3		346		—/+28	2.0
10			294	280		−51/−38	2.2
10	405	1.33	349	325		+4/+7	1.4
10	405	3	368	354		+23/+36	1.9

[a] T_g's were taken as the temperature at which the loss modulus (E''), as measured by the Rheovibron, was at the maximum and the temperature at which the storage modulus ($E'_{1/2}$) was decreased by 50%. [b] The difference in the T_g's of the treated polymer and a pure sample of untreated poly(phenylene oxide) 11 as determined by the loss (E'') and storage ($E'_{1/2}$) moduli, respectively: $\Delta T = T_g(E'') - 345$ °C/$\Delta T = T_g(E'_{1/2}) - 318$ °C.

3. Poly[*N*,*N*′-bis(4,4′-oxydiphenylene)pyromellitic diamide diacid] (8). Two bisbiphenylenes, 1 and 3, were used in cross-linking reactions. Bisbiphenylene 1 plasticized the polyamic acid to some extent as shown by the decrease in storage modulus from 4.4×10^{10} to 10^9 dyn/cm² between 100 and 150 °C. Following imide formation, the modulus rose to 10^{10} dyn/cm² at 200 °C. When 8 containing bisbiphenylene 1 is cured for 3 h at 405 °C a major decrease in the storage modulus for the polyimide derived from 8 occurs at 370 °C. When bisbiphenylene 3 (5% by weight) is used to cure the polyamic acid, plasticization occurs, as evidenced by a drop in the storage modulus to less than 10^8 dyn/cm² at 360 °C. Curing for 1.25 h at 410–425 °C gives a polyimide that shows no mechanical loss up to 500 °C.

4. Polysulfones 9 and 10. Films of polysulfone 9 (T_g of 186 °C) are plasticized by bisbiphenylene 1, 10 wt % lowering the glass transition to 100–120 °C. At 140 °C, the storage modulus of the films was too low to maintain mechanical properties necessary for modulus measurements and curing. The polymer was cured in the melt, at 380 °C, a temperature at which a strong exotherm was observed. This material showed promise as an adhesive, since the cured material bonded the metal plates between which the resin was cured.

A commercial sample of polysulfone 10 (T_g of 221 °C) was cured with 10 wt % bisbiphenylene 1 and 3.5 wt % nickel catalyst. These additives lowered T_g of a film sample; curing at 300 °C for 1 h increased T_g to 240 °C (Table V).

5. Poly(phenylene oxide) 11. Bisbiphenylene 1 was used to cure samples of poly(phenylene oxide) 11 at 405 °C. Addition of 10 wt % of the cross-linking agent to 11 plasticized the film, lowering T_g from 318 ($E'_{1/2}$) to 280 °C (Table VI). Although 11 that contains no bisbiphenylene undergoes a cross-linking reaction under these conditions by the loss of pendent phenyl groups,[12] cross-linking in the presence of 1 produces a higher T_g under the same conditions.

Experimental Section

2-Acetylbiphenylene. To a solution of 3 g (0.02 mol) of biphenylene[13] in carbon disulfide (distilled from phosphorus pentoxide) were added 1.65 g (0.021 mol) of distilled acetyl chloride and 12 g of aluminum chloride in small portions to the stirred mixture at 25 °C under nitrogen. Stirring was continued for 3 h and the mixture was allowed to stand for 15 h. The mixture was then cooled to 0 °C, added to an ice–concentrated hydrochloric acid mixture, and filtered. The organic layer was separated, washed with water, and dried over sodium sulfate. Removal of the solvent under reduced pressure and sublimation of the residue yielded 2.3 g (60%) of 2-acetylbiphenylene, mp 133–135 °C (lit.[14] mp 134–135 °C).

Biphenylene-2-carboxylic Acid. To a solution of 2.3 g (0.012 mol) of 2-acetylbiphenylene in 138 mL of dioxane at 70 °C was added 100 mL of a sodium hypochlorite solution (freshly prepared from 23 g of sodium hydroxide and 16.8 g of chlorine in 230 mL of water), and the mixture was stirred at 95 °C for 30 min. An additional 50-mL portion of sodium hypochlorite solution was added, and the mixture became homogeneous. Stirring was continued for 45 min at 95 °C. The mixture was then concentrated until a slight cloudiness was noted. The mixture was then treated with sodium bisulfate and acidified to pH 2, to give a yellow precipitate that was removed by filtration, washed with water, and dried to yield 2.10 g (89%) of product, mp 216–218 °C (lit.[14] mp 223–224 °C).

2-Aminobiphenylene. This compound was obtained by the Schmidt reaction[15,16] on 2-acetylbiphenylene. To a solution of 1 g (5 mmol) of 2-acetylbiphenylene in 18 g of trichloroacetic acid at 60 °C was added 0.5 g (8 mmol) of powdered sodium azide in one portion. Nitrogen evolution from the red-orange solution started at once. After 1 h, the nitrogen evolution had ceased and another 0.5 g of sodium azide was added. After 6 h, the mixture was poured into 25 g of ice and extracted with benzene. The benzene layer was washed with 10% hydrochloric acid, 10% sodium hydroxide, and water and then dried over sodium sulfate. Filtration removal of the benzene and washing the residue with petroleum ether afforded 0.9 g (86%) of crude *N*-(2-biphenylene)acetamide. A solution of the crude amide in 50 mL of ethanol and 2 mL of concentrated hydrochloric acid was heated to reflux for 24 h. The ethanol was removed under reduced pressure, and the residue was taken up in 75 mL of hot water and filtered. The filtrate was made basic with ammonium hydroxide to afford a yellow precipitate which was dried to yield 0.5 g (54% overall) of 2-aminobiphenylene. Sublimation gave pure product, mp 128–129 °C (lit.[14] mp 123–124 °C).

Bis(2-biphenoyl)diphenyl Ether (5). A solution of 1.29 g (6.6 mmol) of dry biphenylene-2-carboxylic acid in 60 mL of freshly distilled thionyl chloride was heated to reflux for 17 h. The thionyl chloride was removed at aspirator pressure, 60 mL of dry benzene was added, and the benzene was distilled. This was repeated with benzene and again with carbon disulfide.

A solution of 0.5 g (3.3 mmol) of diphenyl ether in 60 mL of carbon disulfide (distilled from phoshorus pentoxide) was added to the acid chloride. The solution was cooled to 0 °C and 1.2 g (9 mmol) of aluminum chloride was added. The red solution was stirred for 22 h at 20 °C and then poured onto an ice–concentrated hydrochloric acid mixture. After removal of the carbon disulfide under reduced pressure, the mixture was filtered and the precipitate was washed with water and acetone. The precipitate was dried to yield 0.93 g (54%) of crude product which, after recrystallization from hot xylene, gave 0.2 g of a yellow powder. Recrystallization from chlorobenzene gave product, mp 275 °C (DSC). Anal. Calcd for $C_{38}H_{22}O_3 \cdot 2H_2O$: C, 81.12; H, 4.66. Found: C, 80.85; H, 4.06.

***N,N'*-Bis(2-biphenylenyl)terephthalamide (2).** To a solution of 0.9 g (5.4 mmol) of 2-aminobiphenylene in 20 mL of dry 1-methyl-2-pyrrolidinone under nitrogen at 0 °C was added 1.5 mL of propylene oxide. The mixture was then cooled to −25 to −30 °C and, with rapid stirring, 0.548 g (2.7 mmol) of isophthaloyl chloride was added. The solution was stirred for 1 h at −30 °C and then for 4 h at 25 °C. The mixture was poured into 300 mL of methanol and kept overnight. The precipitate was filtered, washed several times with methanol until the washings were colorless, and dried to yield 1.02 g (96%) of product, mp 332–334.5 °C. Anal. Calcd for $C_{32}H_{20}N_2O_2$: C, 82.76; H, 4.31; N, 6.03. Found: C, 82.94; H, 4.11; N, 6.06.

Table VII

polymer	solvent	ref or source
poly[2,2′-(*p*,*p*′-oxydiphenylene)-6,6′-oxybis(4-phenylquinoline)] (6)	*m*-cresol	17
poly(*m*-phenyleneisophthalamide) (7)	*N*,*N*-dimethylacetamide, 10% lithium chloride	T-450 Nomex Staple (Du Pont)
poly[*N*,*N*′-(4,4′-oxydiphenylene)pyromellitic diamide diacid] (8)	*N*,*N*-dimethylacetamide	18
poly[*p*,*p*′-(2,2-diphenylpropyl)-4′,4″-dioxydiphenyl sulfone] (9)	hexamethylphosphoric triamide	Aldrich
poly[4,4′-bis(*p*,*p*′-oxydiphenylene)diphenyl sulfone] (10)	*N*-methyl-2-pyrrolidinone	Victrex 300P (ICI)
poly[2,2‴,3,3‴,6,6‴-hexaphenyl-*p*-pentaphenylene-4′,1″-oxy-4,4⁗-ylene] (11)	toluene	19

6,6′-Oxybis(2-biphenylenyl-4-phenylquinoline) (1). To a homogeneous solution of the product of the reaction of 3.31 g of phosphorus pentoxide and 8 mL of *m*-cresol (obtained by heating the two reagents at 140 °C for 2 h under nitrogen) were added 0.186 g (2 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether[17] and 0.776 g (4 mmol) of 2-acetylbiphenylene. The solution was stirred for 6 h at 135 °C after which 4 mL of *m*-cresol was added and the solution was stirred for 11 h at 135 °C. The mixture was poured into 200 mL of methanol to give a dark orange, clear solution, to which 25 mL of triethylamine was added slowly until the solution turned yellow. On standing, the mixture yielded a yellow precipitate, and a dark orange viscous liquid appeared. The precipitates were treated with a solution of 10 mL of triethylamine in 50 mL of methanol to give 1.3 g (90%) of a yellow precipitate, mp 229–234 °C. Recrystallization from 14 mL of xylene gave 1.2 g of product, mp 238–240 °C. Anal. Calcd for $C_{54}H_{32}N_2O$: C, 89.50; H, 4.42; N, 3.88. Found: C, 89.29; H, 4.93; N, 3.50.

***N,N'*-Bis(2-biphenylenyl)-1,3-(and -1,4-)dicarboxylic Amide 4,6-(and 3,6-)Dicarboxylic Acid (3).** To a solution of 0.9 g (5.4 mmol) of 2-aminobiphenylene in 13 mL of pyridine (distilled from maleic anhydride) at 10–15 °C was added under nitrogen 0.589 g (2.7 mmol) of pyromellitic anhydride (recrystallized from acetic anhydride) in small portions over a period of 45 min. During the addition, the temperature rose to 25 °C and after half of the anhydride had been added, a precipitate formed. The mixture was stirred for 6 h, allowed to stand for 48 h, and then filtered. The precipitate was washed with absolute ethanol until the washings were colorless and free of pyridine. Two isomers, one soluble in pyridine and the other insoluble in pyridine, were isolated in equal amounts totaling 1.49 g (100%). No melting point was observed below 355 °C. IR 3276 (NH), 1695 (C═O, acid), 1645 (C═O, amide) cm^{-1}.

***N,N'*-Bis(2-biphenylenyl)pyromellitimide (4).** The imide was formed by heating 180 mg (0.33 mmol) of either the soluble or insoluble isomer 3 under reduced pressure at 200–205 °C for 3 h to produce the theoretical amount (168 mg, 0.33 mmol) of 4: mp >360 °C; IR 1720 (C═O, imide) cm^{-1}. Anal. Calcd for $C_{34}H_{16}N_2O_4$: C, 79.06; H, 3.12; N, 5.42. Found: C, 78.77; H, 3.26; N, 5.32.

Polymer Films. Polymer films were cast from different solvents, depending on their solubilities and the solubilities of the bisbiphenylenes. Solutions of the polymer alone, or polymer solutions containing the bisbiphenylene/catalyst additives were spread on a glass plate with a doctor's knife and allowed to evaporate at 25 °C. The air-dried films on the plate were then transferred to a vacuum oven, where the temperature was gradually raised to 80 °C at 20 mmHg. Complete drying took as long

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as 3–4 days. When the polyamide solution containing lithium chloride was cast, the film was washed with water for several hours and then dried.

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References and Notes

(1) Garapon, J.; Stille, J. K. *Macromolecules* **1977**, *10*, 627.
(2) Recca, A.; Garapon, J.; Stille, J. K. *Macromolecules* **1977**, *10*, 1344.
(3) Recca, A.; Stille, J. K. *Macromolecules* **1978**, *11*, 479.
(4) Stille, J. K. *Pure Appl. Chem.* **1978**, *50*, 273.
(5) Stille, J. K. *Vysokomol. Soedin.* **1979**, *11*, 2545.
(6) Swedo, R. J.; Marvel, C. S. *J. Polym. Sci., Polym. Lett. Ed.* **1977**, *15*, 683. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 2815.
(7) Cassar, L.; Eaton, P. E.; Halpern, J. *J. Am. Chem. Soc.* **1970**, *92*, 3515.
(8) Gassman, P. G.; Reitz, R. R. *J. Am. Chem. Soc.* **1973**, *95*, 3057.
(9) Bishop, K. C. *Chem. Rev.* **1976**, *76*, 461.
(10) Chatt, J.; Guy, R. G.; Watson, H. R. *J. Chem. Soc.* **1961**, 2332.
(11) Noyori, R.; Umeda, I.; Kawauchi, H.; Takaya, H. *J. Am. Chem. Soc.* **1975**, *97*, 812. Noyori, R.; Kawauchi, H.; Takaya, H. *Tetrahedron Lett.* **1974**, 1749.
(12) Noren, G. K.; Stille, J. K. *J. Polym. Sci., Part D* **1971**, *5*, 385.
(13) Logullo, F. M.; Seitz, A. H.; Friedman, L. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, p 54.
(14) Baker, W.; Barton, J. W.; McOmie, J. F. W. *J. Chem. Soc.* **1958**, 2666. Baker, W.; Boarland, M. P. V.; McOmie, J. F. W. *Ibid.* **1954**, 1476.
(15) Dice, J. R.; Smith, P. A. S. *J. Org. Chem.* **1949**, *14*, 179.
(16) Bachmann, W. E.; Boatner, C. H. *J. Am. Chem. Soc.* **1936**, *58*, 2097.
(17) Norris, S. O.; Stille, J. K. *Macromolecules* **1976**, *9*, 496.
(18) Sorenson, W. R.; Campbell, T. W. "Preparative Methods of Polymer Chemistry", 2nd ed.; Interscience: New York, 1968; p 170.
(19) Stille, J. K.; Mukamal, H. *Macromol. Synth.* **1977**, *6*, 45.

Acyclic Azoester Modification of 1,4- and 1,2-Polybutadienes. Structure and Properties

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ABSTRACT: This paper reveals salient structure–reactivity and structure–property relationships for the isopropyl azodicarboxylate (IAD) modification of high 1,4(*cis*)-, 1,4(*trans*)-, 1,4(mixed *cis,trans*)-, and 1,2-polybutadienes. It has been found that the 1,4 and 1,2 adducts differ in sequence distribution. The 1,2 product exhibits an essentially random distribution of functionality and single-phase morphology. In contrast, the modified 1,4 material evinces blocky character and multiphase morphology. It has been learned that both the forward ene reaction and the retroene process are more facile for the 1,4 backbone than for the 1,2 substrate. Consistent with an ene cycloaddition mechanism, the IAD modification of 1,4-polybutadiene involves no cis–trans isomerization of the unmodified olefin units; the IAD modification of 1,2-polybutadiene involves isomerization of vinyl units to internal double bonds. The IAD reactions are simple add-on processes. Yet, there is some evidence of free-radical leakage, especially in the case of the 1,2 substrate. The structures of the products of the IAD modification of 1,4- and 1,2-polybutadienes have been proven by ^{13}C NMR, IR, UV, GPC, membrane osmometry, and TGA measurements. Supermolecular structures have been determined by DTA and dynamic thermomechanical measurements.

Introduction

Substantial progress has been made toward an understanding of the ene reaction of acylic azoesters with monoolefins, e.g., isomeric butenes and pentenes. Yet most acylic, as well as cyclic, azo ene reactions on polymers have been performed on only 1,4 backbones, e.g., SBR and natural rubber.[3-12] Comparable modifications of 1,2 substrates have been virtually ignored. A notable exception is the recently reported reaction of 1,2-polybutadiene with one class of cyclic azoenophiles, the triazolinediones.[12] However, acyclic ene modifications of 1,2-polydienes have not been mentioned or studied. The relationship between cyclic and acyclic enophiles is also not well established. Moreover, salient questions of mechanism, structure, and sequence distribution for all such processes and products have remained unanswered.

Table I
Characterization of Backbone Types

polybutadiene type	microstructure % cis	% trans	% 1,2	$10^{-5}M_n$[a]	[η]
high 1,4 (mixed cis,trans)	34.7	54.0	11.2	1.07	2.06
high 1,4 (cis)	95.5	2.0	2.1	1.03	1.94
high 1,4 (trans)	11.5	84.2	3.3	0.82	1.32
high 1,2	1.4	0.2	98.0	1.38	1.39

[a] By osmometry.

This paper describes hitherto unrecognized structural and sequence information for the polymeric products of the reaction of an acyclic azoester, isopropyl azodicarboxylate (IAD), with high 1,4(*cis*)-, 1,4(*trans*)-, 1,4-(mixed *cis,trans*)-, and 1,2-polybutadienes. Also developed are backbone structure–reactivity and product structure–property relationships.

IAD was chosen for this work because of its commercial availability and easily managed liquid physical state. Also, unlike the triazolinedione modification of polydienes, the IAD process is homogeneous in hydrocarbons even up to high levels of modification. In the course of these studies,

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