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(66) Grafting of the castor double bonds is lower than that of polybutadiene for two reasons: (1) lower concentration of double bonds in terms of moles per liter and (2) the OH group α to the double bonds provides a degree of hindrance (58). Also, the molecular weight of the castor oil prepolymer is lower than the polybutadiene.

Hexaarylbenzene Units as Cross-Linking Sites for Polyquinolines

G. L. Baker and J. K. Stille*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523.
Received December 13, 1978

ABSTRACT: Hexaarylbenzene units were incorporated into a polyquinoline backbone in order to provide a site which could enter into a thermal cross-linking reaction well above the T_g of the parent polyquinoline. The incorporation was accomplished by balancing the appropriate amounts of 1,2-bis(4′-acetyl-4-phenoxyphenyl)-3,4,5,6-tetraphenylbenzene in the place of 4,4′-diacetyldiphenyl ether with 3,3′-dibenzoyl-4,4′-diaminodiphenyl ether in the synthesis of the polyquinoline. The cross-linking reaction occurred rapidly at 400 °C to give insoluble polymers with enhanced mechanical properties.

The high values of T_g often limit the processability of thermally stable polymers.[1] One approach to the solution of this problem is to lower the T_g of the polymer by adding flexible groups such as ethers to allow processing and to convert the polymer to a network structure allowing the polymer to be used well above T_g. A suitable cross-linking agent for this transformation is one that forms thermally stable linkages between the polymer chains.

Recent work in our laboratories has shown that the incorporation of biphenylene into thermally stable polymers[2-5] allows the cross-linking of polymers at 340–380 °C. These cross-linked polymers exhibit higher T_g's and enhanced mechanical properties above T_g. One disadvantage to this curing reaction of biphenylene units is that the temperature range for processing, above the T_g but below the onset of the opening of biphenylene, is narrow. In an attempt to introduce cross-linking groups in a polymer chain that undergo reaction at higher temperatures, the hexaphenylbenzene nucleus was investigated as a reactive group. It had been shown that polyphenylated polyphenylenes cross-linked at elevated temperatures and that radicals were generated at 350 °C.[6]

Because the evolved products from this reaction were benzene and biphenyl, the cross-linking was attributed to the cleavage of phenyl–phenyl bonds, generating a phenyl radical and leaving behind a reactive phenylene radical on the polymer chain. The relative ease of cleavage of the phenyl–phenyl bond as compared to that exhibited for biphenyl, for example, was ascribed to lack of conjugation between phenyls as a result of the crowding of five phenyl groups around a phenylene in the backbone. The placement of six equivalent phenyls on a backbone phe-

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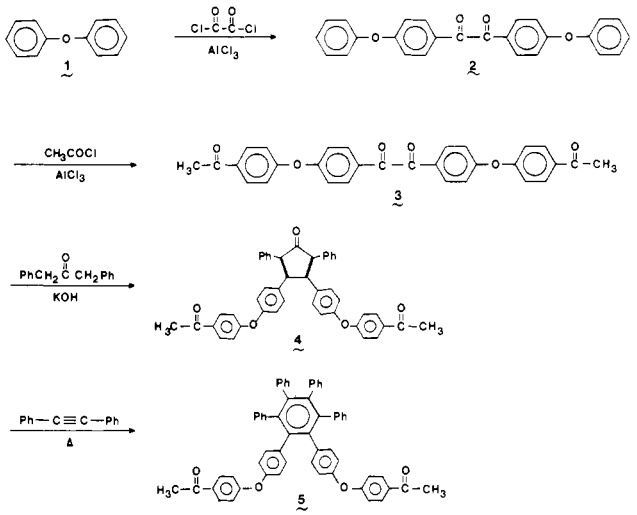
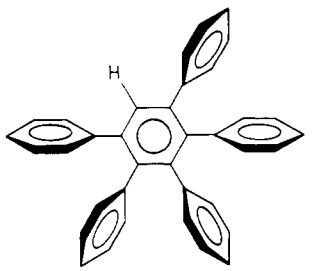
Scheme I



nylene, therefore, should serve to enhance the cross-linking reaction. Thus the incorporation of a suitable monomer



unit containing the hexaphenylbenzene nucleus appeared to be a likely method for the preparation of polymers that could be cross-linked near 400 °C. In the present study, the effects of including such a unit and the cross-linking reaction were explored.

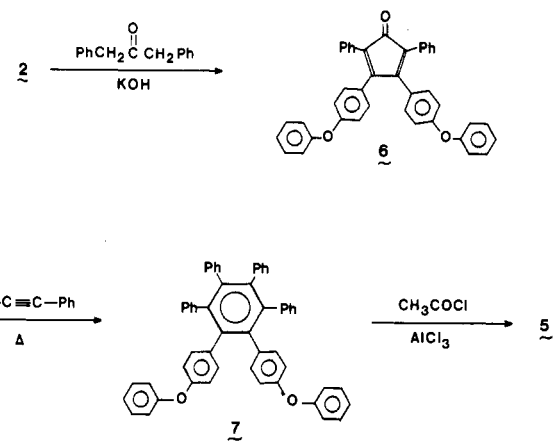
Results and Discussion

Monomers. The synthesis of the desired diacetyl monomer **5** was approached by two closely related routes. In the first, 4,4′-diphenoxybenzil was acylated with acetyl chloride in carbon disulfide to give the diacylated product **3** in 72% yield. The condensation reaction of **3** with dibenzyl ketone with potassium hydroxide as base gave the highly substituted cyclone **4** in 61% yield. The yields for the condensation reaction were highly variable, in part due to the presence of the methyl ketone functionalities. Both are susceptible to base-catalyzed condensations. A complicated mixture of products resulted in most cases, requiring preparative liquid chromatography for separation. Treatment of **4** with diphenylacetylene over a free flame until carbon monoxide evolution ceased gave the desired monomer **5** (Scheme I). This Diels–Alder reaction could also be effected in diphenyl ether at the reflux temperature, but the reaction time was extremely long, and yields were comparable to the 78% obtained in the first method.

The monomer proved difficult to purify since it could only be crystallized from solvents such as 2-methoxyethanol and phenyl ether. The lower boiling aromatic solvents such as benzene and toluene and chlorinated solvents proved to be poor solvents for use in crystallization owing to the high solubility of the monomer in them.

Synthesis of **5** by an alternate route was less satisfactory even though its immediate precursor could be obtained quite readily. Treatment of diphenoxybenzil with dibenzyl ketone and potassium hydroxide gave cyclone **6** in 87%

Scheme II



Scheme III

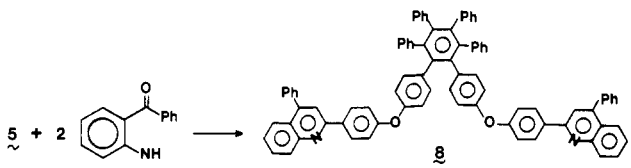


Table I
Properties of Polyquinolines 11-13

	11	12	13[a]
$[\eta]$ ($CHCl_3$)	0.56	1.56	1.80
T_g (DSC)	256	248	266
(Rheovibron)	285	275	271
TGA break (N_2)	555	540	565
loss at 800 °C, %	27	36	16
E' below T_g, dyn/cm^2	2×10^{10}	3.5×10^{10}	2.3×10^{10}
E' above T_g, dyn/cm^2	$<10^7$	$<10^7$	2.4×10^7
E' below T_g after curing, dyn/cm^2		4.0×10^{10}	
E' above T_g after curing, dyn/cm^2		3×10^8	

[a] From ref 8 and 11.

yield. The absence of the reactive methyl ketones made purification of this compound straightforward. The Diels–Alder reaction of **6** with diphenylacetylene, carried out as before, gave **7** as white powder in 75% yield. The Friedel-Crafts acylation of this compound to give **5** proved troublesome. In all cases a tan product which could not be further purified was obtained. It did exhibit, however, the same spectral characteristics as **5** obtained in the alternate scheme (Scheme II).

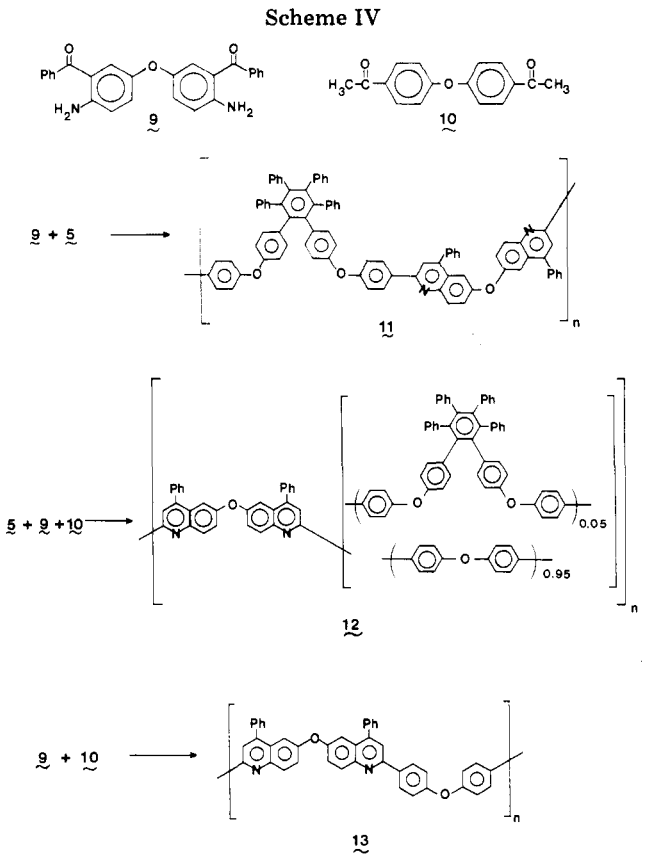
Model Compound and Polymer Synthesis

Both the model compound **8** and polymers **11** and **12** were synthesized by the acid-catalyzed Friedlander reaction. The best catalyst for this reaction has been found to be di-*m*-cresyl phosphate.[7] In all cases quantitative yields are obtained.

The inclusion of a hexaphenylbenzene unit into a compound appears to enhance the solubility of that compound. Whereas aromatic diacetyl compounds are often poorly soluble in most solvents, both **5** and **8** were very soluble in benzene, toluene, and chlorinated solvents. Even acetone proved to be a suitable recrystallization solvent for **8**. The molecular weight of **8** is over 1100; a distinct T_m was not observed, but rather a transformation from the solid to a thick clear viscous liquid took place gradually near 170 °C.

Both polymers **11** and **12** exhibited a high solubility in chloroform. Polymer **12**, containing only 5% of the

Scheme IV



hexaaryl cross-linking agent, showed solubility behavior similar to that of the parent polymer 13,[8] allowing suitable films to be cast from chloroform or chlorobenzene.

The viscosities of the polyquinolines indicate that inclusion of the hexaaryl unit tends to decrease the intrinsic viscosity. This could be due to the unit providing a highly flexible site in the polymer chain, or more likely it is caused by trace impurities in the monomer which limit the molecular weight to an intermediate value. Polymer 12 containing 5% of the cross-linking agent has a viscosity only slightly less than that of 13, which has been found to have a number average molecular weight greater than 72 000.[8] Thus 12 is expected to show substantially similar properties.

Thermal Behavior of the Polymers

The values of T_g for polymers 11 and 13 are very similar, differing by only 10 °C. In copolymer 12, the plasticizing effect of the added comonomer is exhibited by a T_g which is lower than that of either polymer. The values of T_g obtained by thermal mechanical analysis cannot be directly compared since it is possible that some cross-linking occurs in polymers 11 and 12 as T_g is reached, effectively increasing the value of T_g.

The uncross-linked samples of the polymers show similar values for E' before T_g is reached and nearly complete loss of mechanical properties above T_g. However a cross-linked sample of 12 showed enhanced mechanical properties above T_g after curing for 2 h at 400 °C. Polymer 11 as expected formed a highly cross-linked polymer which became too brittle for further analysis and would not swell in all solvents tested. Polymer 12 remained quite flexible after cross-linking and showed few signs of decomposition.

Polymer 13 modified to contain 5% biphenylene units in the chain showed behavior similar to that of 12.[4] A 6-h cure at 350–380 °C was required to effect a similar level of cross-linking to that shown by 12. Thus polyquinolines can be cured at higher temperatures and with efficiency comparable to that shown by biphenylene.

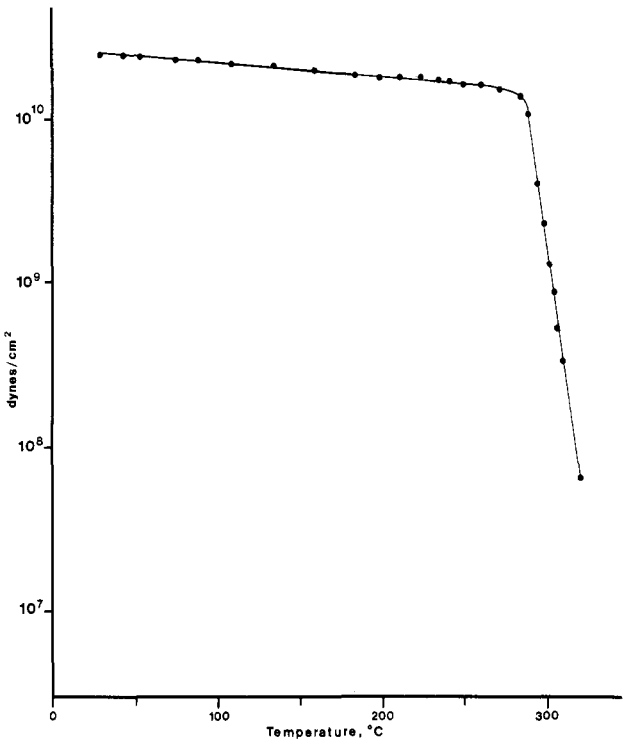


Figure 1. Dynamic modulus vs. temperature for polymer 11.

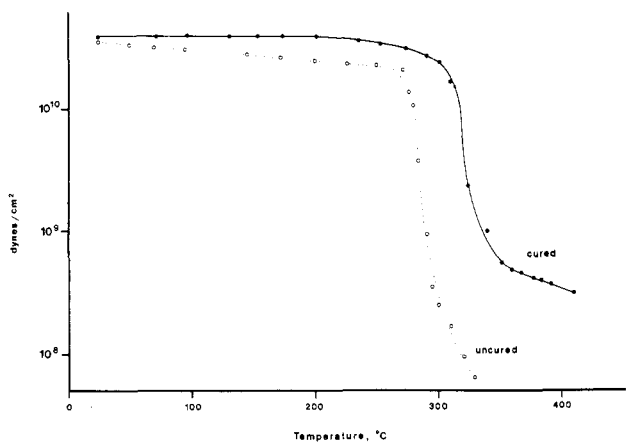


Figure 2. Dynamic modulus vs. temperature for polymer 12.

Conclusions

As expected, the hexaarylbenzene unit serves as an efficient cross-linking site for polyquinolines. The cross-linking reaction proceeds well with a 5% inclusion of the unit to give an insoluble polymer with enhanced thermomechanical properties, especially above T_g. The cross-linking reaction proceeds well above the T_g of the parent polymer, allowing a greater temperature range for processing than was obtained for biphenylene-containing polymers.

Experimental Section

Thermal transitions were measured using a Differential Scanning Calorimetry Cell attachment for a DuPont 990 differential thermal analyzer under 40 mL/min flow of nitrogen and at a heating rate of 20 °C/min.

Thermal gravimetric analyses were carried out on thin films using a DuPont 950 thermal balance and a 990 thermal analyzer (recorder). Samples were heated at a rate of 5 °C/min under a nitrogen atmosphere.

All reported melting points are uncorrected.

4,4′-Diphenoxybenzil (2). To 136.0 g (800 mmol) of phenyl ether, 66.8 g (500 mmol) of aluminum chloride, and 250 mL of dry carbon disulfide in a three-necked flask equipped with mechanical stirring was added dropwise at 0 °C 25.2 g (200 mmol) of oxalyl chloride. The solution was stirred 12 h at 0 °C and was then allowed to warm to room temperature. The reaction mixture was poured into a beaker containing 500 mL of concentrated hydrochloric acid and 500 g of crushed ice. The resulting yellow organic oil was separated from the water layer, and the carbon disulfide was removed by distillation. Upon cooling, a yellow solid formed which was recrystallized from 95% ethanol to give 60.0 g (75%) of pale yellow needles, mp 110–116 °C (lit.[9] mp 116 °C).

The product could be further purified by column chromatography on silica gel with benzene as elutant to remove the byproduct 4,4′-diphenoxybenzophenone. Upon recrystallization from 95% ethanol, pure material with a melting point of 119.5–121.0 °C was obtained as pale yellow needles.

Bis(4′-acetyl-4-phenoxyphenyl)ethanedione (3). To a mechanically stirred slurry of 35.2 g (0.264 mol) of aluminum chloride in 500 mL of carbon disulfide was added 15.8 g (0.040 mol) of 4,4′-diphenoxybenzil. After cooling to 0 °C, 6.91 g (0.088 mol) of acetyl chloride dissolved in 100 mL of carbon disulfide was added dropwise in 1 h. The cooling was removed and the reaction was allowed to warm to room temperature. After 12 h, the reaction was heated to the reflux temperature for 1 h and then quenched in a slurry of 500 mL of concentrated hydrochloric acid and 500 g of crushed ice. The carbon disulfide was removed by distillation and the yellow solids were collected by suction filtration. The filter cake was taken up in benzene and chromatographed on silica gel with benzene as the elutant. After changing to ethyl acetate, the ethyl acetate band was concentrated to give 16.8 g of nearly pure product. After recrystallization from ethanol 14.0 g (72%) of very pale yellow needles were isolated: mp 142.5–143.5 °C; ^{1}H NMR ($CDCl_3$) δ 2.55 (6 H, s), 7.0 (8 H, d, J = 9 Hz), 7.9 (8 H, d, J = 9 Hz); ^{13}C NMR ($CDCl_3$) δ 196.1, 192.2, 161.6, 158.9, 133.2, 130.5, 128.1, 119.0, 118.4, 26.5; IR ν(max) (KBr) 1690, 1595, 1260 cm^{-1}.

Anal. Calcd for $C_{30}H_{22}O_6$: C, 75.30; H, 4.63. Found: C, 75.01; H, 4.68.

2,5-Diphenyl-3,4-bis(4′-acetyl-4-phenoxyphenyl)-2,4-cyclopentadien-1-one (4). To a solution of 0.479 g (1.00 mmol) of **3** and 0.210 g (1.00 mmol) of dibenzyl ketone in 25 mL of 95% ethanol at the reflux temperature was added 5 mL of an enthanolic solution containing 0.1 mmol of potassium hydroxide. After heating at the reflux temperature for 1 h, the reaction mixture was cooled in an ice bath and then filtered. The product was chromatographed on neutral alumina with chloroform as elutant. The first band was collected giving 0.401 g (61%) of a dark purple product. Recrystallization from ethanol–benzene gives the pure cyclone: mp 200.0–200.5 °C; ^{1}H NMR ($CDCl_3$) δ 2.55 (6 H, s), 7.0 (8 H, d, J = 9 Hz), 7.9 (8 H, d, J = 9 Hz); ^{13}C NMR ($CDCl_3$) δ 199.4, 196.2, 160.6, 155.7, 152.9, 132.2, 131.0, 130.4, 130.3, 129.8, 128.7, 127.9, 127.4, 125.2, 119.0, 117.6, 26.4; IR ν(max) (KBr) 1740, 1685, 1600, 1250 cm^{-1}.

Anal. Calcd for $C_{45}H_{32}O_5$: C, 82.80; H, 4.94. Found: C, 79.07; H, 5.20.

1,2-Bis(4′-acetyl-4-phenoxyphenyl)-3,4,5,6-tetraphenylbenzene (5). (1) To 0.687 g (1.05 mmol) of **4** in a thick-walled test tube was added 0.500 g (2.81 mmol) of diphenylacetylene. The test tube was heated over a free flame until carbon monoxide evolution from the dark liquid ceased. Upon cooling, the solidified product was dissolved in chloroform and coated on silica gel. Elution with hexane removed diphenylacetylene. The desired product was collected upon elution with ethyl acetate. Removal of the solvent gave 0.658 g of **5** (78%) as an off-white powder. The product was purified by repeated crystallizations from phenyl ether and 2-methoxyethanol to give pure **5**: mp 263–264 °C; ^{1}H NMR ($CDCl_3$) δ 2.45 (6 H, s), 6.4–7.0 (32 H, m), 7.85 (4 H, d, J = 9 Hz); ^{13}C NMR ($CDCl_3$) δ 196.2, 162.1, 152.2, 140.3, 140.1, 140.0, 139.9, 139.2, 137.4, 132.7, 131.1, 130.1, 126.5, 126.4, 125.1, 119.0, 116.0, 26.3; IR ν(max) (KBr) 3070, 1685, 1600, 1510, 1250 cm^{-1}.

Anal. Calcd for $C_{58}H_{38}O_2$: C, 86.76; H, 5.27. Found: C, 86.19; H, 5.27.

(2) To a solution of 5.3 g (40 mmol) of aluminum chloride in 250 mL of dry nitrobenzene in a three-necked flask equipped with a dropping funnel and magnetic stirrer was added 7.189 g (10 mmol) of **7**. The reaction mixture was cooled to 0 °C, and 10 mL of a stock solution of 17.27 g of acetyl chloride in 100 mL of dry nitrobenzene (22 mmol) was added dropwise in 1 h. Upon completion of the addition, the cooling was removed and the reaction mixture was allowed to warm to room temperature. After 17 h, the mixture was heated to 60 °C for 21 h and then quenched by pouring the dark brown solution into a beaker containing 100 mL of concentrated hydrochloric acid and 100 g of crushed ice. After removing the nitrobenzene by steam distillation, the product was chromatographed on silica gel. After elution with 5 L of benzene, the solvent was changed to 70/30 hexane–ethyl acetate allowing the isolation of 2.6 g (32%) of **5** as a tan amorphous powder, which resisted further purification.

Table II
Elemental Analyses of Polyquinolines 11 and 12[a]

	11	12
C	88.55 (86.41)	85.69 (83.94)
H	4.78 (4.80)	4.47 (4.62)
N	2.46 (2.33)	4.52 (4.35)

[a] The first numbers represent calculated analyses; numbers in the parentheses indicate found analyses.

2,5-Diphenyl-3,4-bis(4-phenoxyphenyl)-2,4-cyclopentadien-1-one (6). To a solution of 11.8 g (30 mmol) of 4,4′-diphenoxybenzil and 6.3 g (30 mmol) of dibenzyl ketone in 350 mL of 95% ethanol at the reflux temperature was added 3 g of potassium hydroxide dissolved in 30 mL of 95% ethanol in three portions. After 1 h, the solution was cooled in an ice bath and filtered yielding 14.0 g (87%) of fine dark purple crystals: mp 222.5–225.5 °C; ^{1}H NMR ($CDCl_3$) δ 6.5–7.4 (m); ^{13}C NMR ($CDCl_3$) δ 199.7, 157.5, 155.8, 153.3, 130.9, 130.5, 129.8, 129.6, 127.8, 127.2, 124.8, 123.6, 119.2, 117.4; IR ν(max) (KBr) 3080, 1715, 1595, 1245 cm^{-1}.

Anal. Calcd for $C_{41}H_{28}O_3$: C, 86.60; H, 4.96. Found: C, 86.27; H, 4.95.

1,2-Bis(4-phenoxyphenyl)-3,4,5,6-tetraphenylbenzene (7). To 5.4 g (10 mmol) of the cyclone **6** in a thick-walled test tube was added 2.5 g (14 mmol) of diphenylacetylene. The test tube was heated over a free flame until carbon monoxide evolution from the dark purple solution ceased. Upon cooling, the product solidified and was then stirred twice with 50-mL portions of glacial acetic acid. After filtration and drying, a 5.9-g (82%) yield of a snow-white powder was isolated: mp 257–258 °C; ^{1}H NMR ($CDCl_3$) δ 6.3–7.3 (m); ^{13}C NMR ($CDCl_3$) δ 157.4, 153.7, 140.0, 139.5, 135.9, 132.4, 131.0, 129.1, 126.4, 126.3, 124.9, 122.2, 117.8, 117.5; IR ν(max) (KBr) 3060, 1600, 1240 cm^{-1}.

Anal. Calcd for $C_{54}H_{38}O_2$: C, 90.22; H, 5.33. Found: C, 90.06; H, 5.44.

1,2-Bis[4′-(2-phenyl-4-quinolyl)-4-phenoxyphenyl]-3,4,-5,6-tetraphenylbenzene (8). To a mixture of 6.7 g of di-*m*-cresyl phosphate and 12 g of *m*-cresol was added 0.394 g (2 mmol) of *o*-aminobenzophenone and 0.803 g (1 mmol) of **5**. The solution was heated to 137 °C for 24 h under a nitrogen atmosphere. The reaction was then quenched by pouring the solution into a mixture of ethanol and triethylamine. The precipitated product (quantitative) was dissolved in chloroform and reprecipitated in ethanol–triethylamine. After chromatography on silica gel with chloroform as the elutant, the product was isolated as a pale yellow solid. Recrystallization from acetone gave pale yellow crystals. The product showed a transition to a highly viscous glassy liquid near 170 °C: ^{1}H NMR ($CDCl_3$) δ 6.5–8.2 (m); ^{13}C NMR ($CDCl_3$) δ 159.1, 155.5, 153.3, 148.5, 148.3, 140.0, 139.5, 137.9, 136.5, 133.4, 132.5, 131.6, 129.5, 129.1, 128.6, 128.1, 127.9, 126.4, 125.7, 125.1, 118.4, 117.4; IR ν(max) (KBr) 3050, 1595, 1550, 1500, 1235 cm^{-1}.

Anal. Calcd for $C_{84}H_{56}N_2O_2$: C, 89.65; H, 5.02; N, 2.49. Found: C, 88.15; H, 4.85; N, 2.26.

Polymerizations. The polymerization and copolymerization of **5** with **9** and **10** was carried out as described elsewhere.[7] The polymers were dissolved in chloroform and reprecipitated in an ethanol–triethylamine mixture. Films were cast from either chlorobenzene (**11**) or chloroform (**12**) for thermal analyses and were vacuum dried prior to use (Table II).

Thermomechanical Analyses. The dynamic mechanical properties of samples were determined as follows using the

Rheovibron (Model DDV-II): Samples were cut into narrow strips aproximately 3 cm in length, 0.3 cm in width, and 0.002 cm in thickness. Runs were made at a frequency of 35 Hz at a heating rate of 5 °C/min in an inert atmosphere. The dynamic moduli of films were calculated using the following equation:

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

where A is a constant given by the instrument manual,[10] DF is the value of the dynamic force dial when measuring tan δ, L is the length of the sample, S is the cross-sectional area in cm^2, and K is an error constant due to the displacement of the stress gauge. Values of the dynamic storage modulus E' were obtained as follows: $E' = |E^*| \cos \delta$.

Acknowledgment. This research was supported by the Army Research Office, Research Triangle, N.C.

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D_2-m-Carborane Siloxanes. 7. Synthesis and Properties of Ultra-High Molecular Weight Polymer

Donald D. Stewart,* Edward N. Peters, C. D. Beard, G. B. Dunks, E. Hedaya, G. T. Kwiatkowski, R. B. Moffitt, and J. J. Bohan

Union Carbide Corporation, Chemicals and Plastics, Bound Brook, New Jersey 08805, and Tarrytown Technical Center, Tarrytown, New York 10591. *Received September 1, 1978*

ABSTRACT: A new two-step synthesis of linear, ultra-high molecular weight D_2-m-dodecacarborane siloxane was developed based on the preparation of a carborane silanol terminated prepolymer which was subsequently advanced in molecular weight to >10^6. This was the result in part of an improved synthesis for the bis(ureido)silane monomers of >98% purity and the development of a reverse addition heterophase polymerization technique. The ultra-high molecular weight polymers exhibited improved thermal mechanical properties as a result of increased chain entanglement of the polymer chains. Superior thermal stability in air was exhibited up to 800 °C.

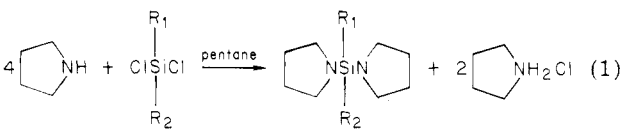
Recently we described the synthesis of linear, high molecular weight D_2-m-carborane siloxanes based on the condensation reaction between bis(ureido)silanes and carborane disilanol.[1-3] These polymers have unusual thermal stability and have potential utility as high-temperature elastomers.[1,4,5]

In previous work, polymers with molecular weights up to 250 000 were prepared.[1-3] Within the range of 50 000 to 250 000, an increase in the molecular weight of the polymer resulted in improvements in the mechanical properties for both polymer and vulcanizates.[4] Similar improvements in properties with increasing molecular weight were noted for poly(dimethylsiloxane).[6] Thus, a rapid improvement in the tensile strength was noted for poly(dimethylsiloxane) with increasing molecular weight up to 500 000.[6] Therefore, further advances in the molecular weight of D_2-m-carborane siloxane were desirable.

This paper describes the development of a synthetic route to ultra-high molecular weight (>10^6) D_2-m-carborane siloxane polymers[7] and the evaluation of their unique properties. In addition, this paper describes the improved synthesis of bis(ureido)silane monomers and the techniques used for the synthesis of consistantly high molecular weight carborane siloxane polymers using these monomers.

Experimental Section

Synthesis of Monomers. The bis(amino)silane intermediates used for the synthesis of bis(ureido)silanes were originally prepared using n-butyllithium to deprotonate the appropriate amine.[3] An improved synthesis was developed which involved the direct reaction of 4 equiv of amine with a dichlorosilane.



(1)

The preparation of a bis(pyrrolidinyl)silane is described below:

Bis(pyrrolidinyl)dimethylsilane. A three-necked, 2000-mL flask was equipped with a mechanical stirrer, a reflux condenser, a nitrogen inlet, and an addition funnel. Dichlorodimethylsilane (129 g, 1 mol) and heptane (200 mL) were placed in the reaction vessel. Pyrrolidine (284.5 g, 4 mol) was added dropwise over a period of 2 h with stirring and cooling in an ice bath. The reaction was slightly exothermic, and solid amine hydrochloride began to separate immediately.

After completion of the addition, the cooling bath was removed and the reaction mixture was stirred at ambient temperature for 12 h. The solid was removed by filtration under nitrogen and washed with three 50-mL portions of heptane. The solvent was removed by distillation through a 12-in Vigreaux column at atmospheric pressure under nitrogen. Distillation of the residue gave 174 g (87 percent) of bis(pyrrolidinyl)dimethylsilane, bp 59–60 °C (0.025 mm).

Bis(pyrrolidinyl)methylphenylsilane was prepared in a similar manner in 92% yield, bp 114–8 °C (0.05 mm).

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