

Synthesis and Characterization of Cyclic and Polycyclic Structures

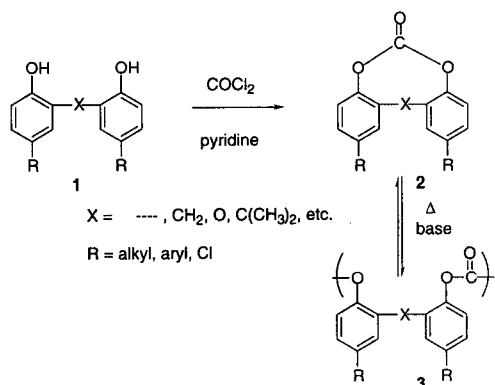
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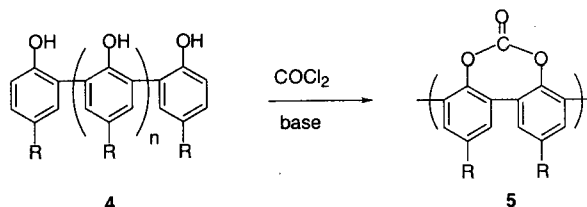
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In a series of US Patents Prochaska¹⁻⁵ described the synthesis of cyclic carbonates from 2,2'-dihydroxybiphenyls (I; X = -) 2,2'-dihydroxydiphenylmethanes (**1**; X = CH₂, C(CH₃)₃) and 2,2'-dihydroxydiphenyl ethers (**1**; X = O). The cyclic carbonates **2** could be formed by reaction of **1** with phosgene in the presence of pyridine or by depolymerization of the polymer **3**. Heating the cyclomers with a catalytic amount of potassium carbonate gave the polymer **3**. Very little information on the properties of the resulting polymers was presented. Inherent viscosities of several of the polymers were in the 0.5 dec. /g. range. Subsequently Kricheldorf⁶ studied the polymerization of 2,2'-dihydroxybiphenyl carbonate (**2**; X = -, R = H) and was unable to form high molecular weight polymers.

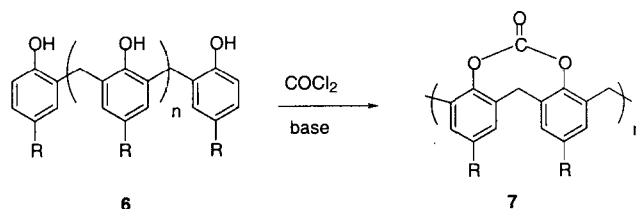


We initially became interested in the possibility of forming polycyclic carbonate structures from polyphenols **4** prepared by enzymatic oxidation of phenols⁷⁻⁹ and manufactured by Enzymol International Inc.. Based on Prochaska's results we thought it might be possible for these resins to react with phosgene to prepare resins **5** containing multiple cyclic carbonate moieties. The odd numbered species would of course have to undergo intermolecular reactions if complete functionalization were to occur. We found that when the reaction was carried out under high dilution conditions soluble resins were produced indicating very little intermolecular reaction had taken place. However, because of steric crowding, only a



relatively small percentage of the phenolic hydroxyl groups were reacted. Molecular modeling confirmed the severe crowding in these molecules.

We then turned our attention to Novolac resins **6**. Molecular models indicated that the methylene bridge in these resins should allow the formation of polycyclic structures **7** that are not strained.



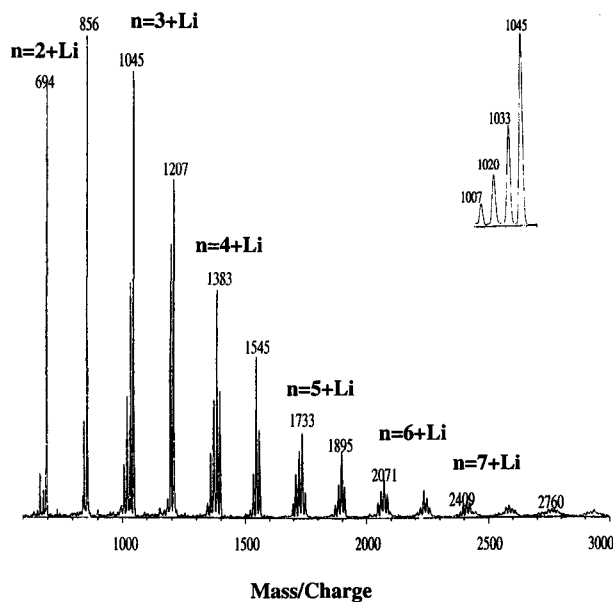
This is an idealized structure since odd numbered species would be expected to undergo intermolecular condensation reactions, or if the odd numbered hydroxyl group was not terminal it would be expected to remain unreacted because of steric hindrance.

Phenolic resins are the oldest known synthetic polymers, first reported by Bayer¹⁰ and later developed and commercialized by Baekland.¹¹ The early efforts in characterizing phenolic resins have been covered by Walker¹² in his classic text. Novolac resins, linear structures connected primarily through the ortho-positions, have been characterized by synthesis and isolation of the individual oligomers. Recent efforts¹³⁻¹⁶ have relied heavily on ¹H and ¹³C NMR using specific oligomers as models. More recently we,¹⁷ and others,¹⁸ have demonstrated that the use of MALDI-TOF mass spectrometry provides an excellent method for detailed examination of Novolac resins.

RESULTS AND DISCUSSION

A. Polycyclic polycarbonates.

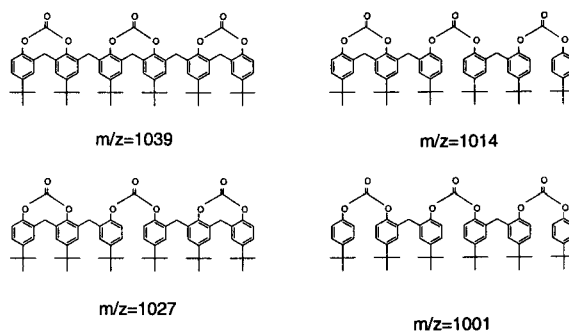
Low molecular weight novolac resins were prepared in isolated yields of 90-95% by reacting 4-t-butylphenol with formaldehyde in a 1/0.85 molar ratio in chlorobenzene solution using a cation-exchange resin as catalyst by following the procedure previously described.¹⁷ A mixture of this resin and excess triphosgene in dry THF was added slowly to a reaction flask containing THF and pyridine over 3-4 hours (final concentration of the resin about 0.25M). The solid residue remaining after removal of pyridine.HCl by filtration and rotavapping the THF was dissolved in CHCl₃, washed once with 10 % HCl and three times with water. Removal of chloroform gave the polycyclic carbonate resin in about 45 % yield.^{19, 20} The MALDI-TOF spectrum of this material showed clusters of peaks which correspond to the various oligomers.



Each mass peak in a cluster, using the tetramer as an example, could be assigned to a specific structure.

Figure 1. MALDI-TOF spectrum of polycyclic polycarbonate

Oligomer $m/z = 1039$ corresponds to a tricyclic structure obtained from a hexamer; $m/z = 1027$ derives from trimer involving one intermolecular reaction and two intramolecular reactions with triphosgene; $m/z = 1014$ one trimer, one dimer and one monomer, and $m/z = 1001$ derives from 2 monomers and 2 dimers. Analysis by gradient HPLC gives no detailed information on the composition of the oligomeric clusters. Similar results were obtained from novolacs prepared



from 4-phenylphenol.

The polycyclic carbonates are polyfunctional and would be expected to undergo ring opening reactions in the presence of a transesterification catalyst and therefore perform as thermoset resins. We found that, by addition of 10% of a polycyclic carbonate to a commercial linear polycarbonate in the presence of 1% lithium stearate at 350°C for 30 minutes, a cross-linked structure with no Tg was obtained that was now insoluble in all common solvents.^{19, 20} At 300°C complete curing did not take place and a Tg was still observable. The novolac resins derived from 4-phenylphenol behave in a similar fashion.

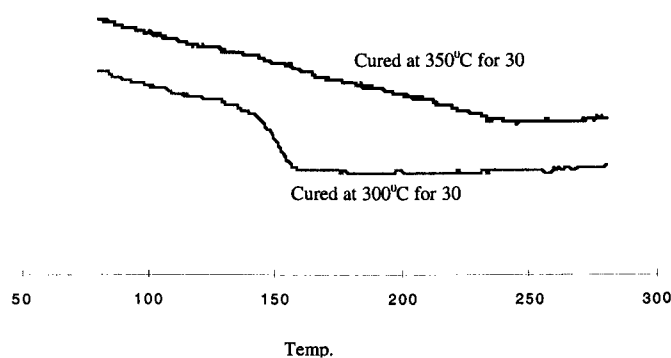


Figure 2. DSC of a 10% mixture of polycyclic carbonate in commercial polycarbonate resin

B. Polycyclic Siloxanes

The novolac resins can also be reacted with dichlorosilanes to give similar polycyclic structures.²¹ The product from the reaction with dimethyldichlorosilane is shown in Fig. 3. The principal structure formed corresponds to the tetramer that is fully functionalized. Similar products are obtained from the reaction with diphenyldichlorosilane.

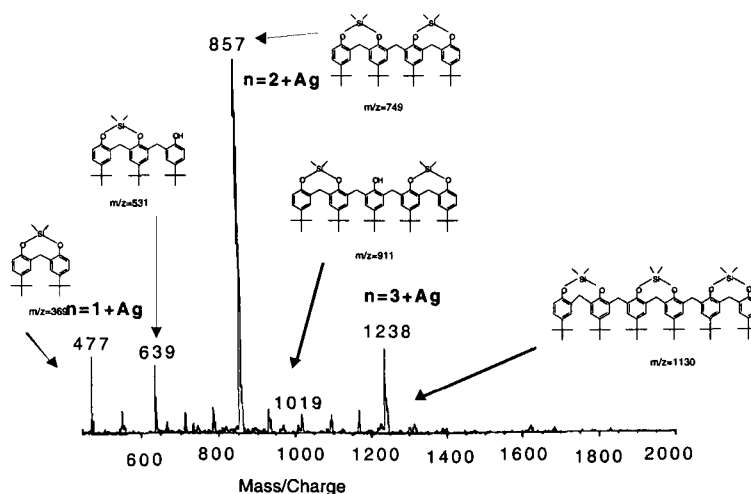


Figure 3. MALDI-TOF MS of polycyclic siloxanes

When this product mixture is combined with a silicone gum and a catalytic amount of potassium hydroxide the mixture can be cured at 300°C to give a silicone rubber. Therefore these polycyclic siloxane structures may be useful as a new curing system for silicone rubbers (Figure 4).

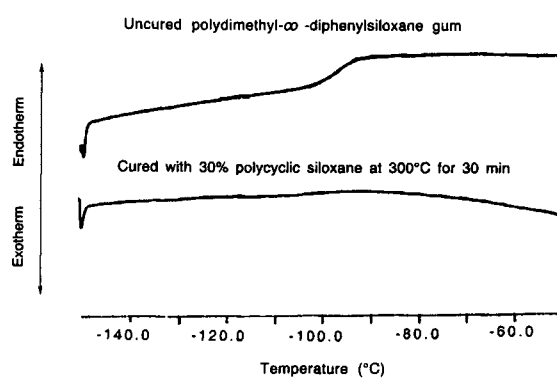
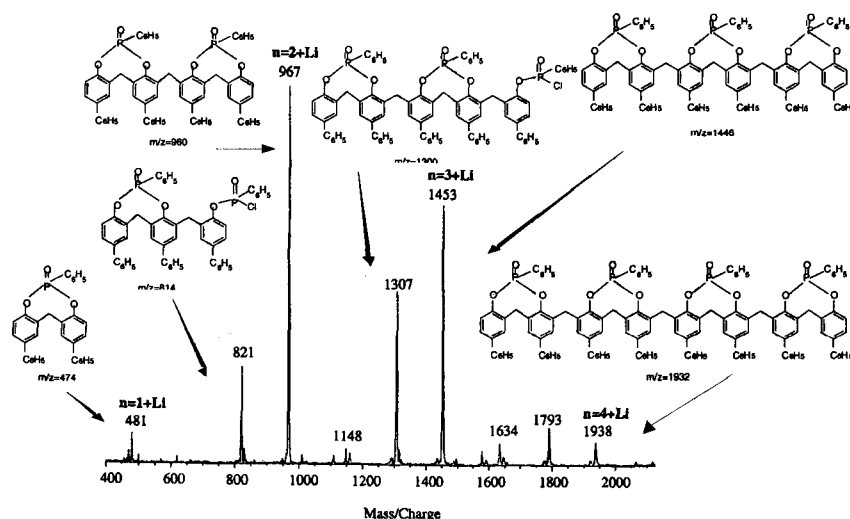


Figure 4. DSC of uncured and cured polydimethyl-co-diphenylsiloxanes

C. Polycyclic phosphonates

Very similar reactions occur between the novolac resins and various phosphorous



dihalides.²² Analysis of the product by MALDI-TOF from the reaction with methylphosphonous dichloride is shown in Fig. 5. Molecules containing residual chloride groups are prepared.

Figure 5. MALDI-TOF analysis of a polycyclicphosphonate

These byproducts can be further identified by reaction of the product with diethylamine. The chloro-compounds are converted to amides as shown in the MALDI-TOF spectrum in Fig. 6. This demonstrates the power of the MALDI technique for analysis of complex mixtures and the identification of unwanted byproducts which therefore allows one to optimize the reaction conditions.

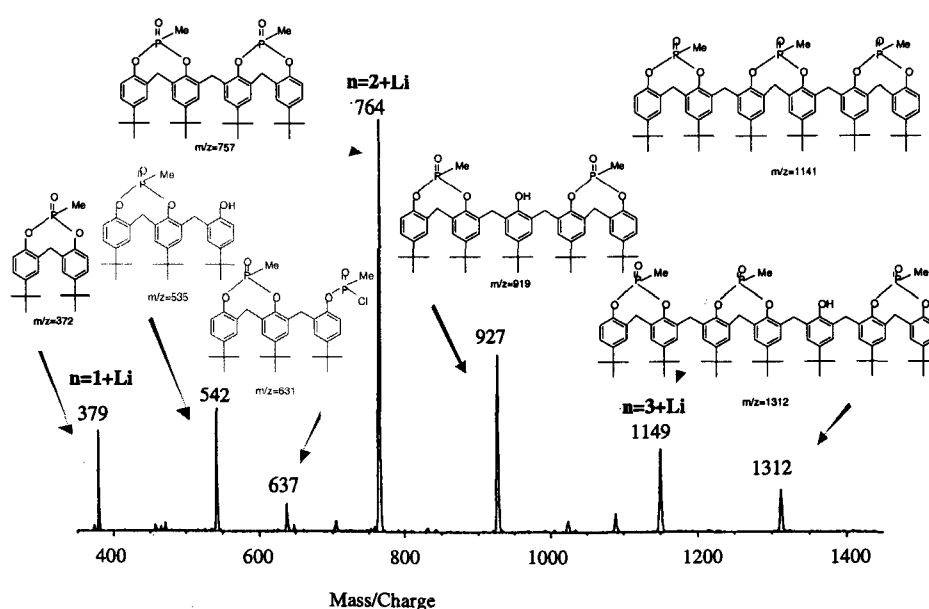


Figure 6. MALDI-TOF analysis of a polycyclic phosphonate treated with diethylamine.

The phosphorus containing polycyclics can also act as curing agents for polymers such as polycarbonate. They also act as flame retardants when added to polycarbonate. If added simply as an additive the flame retarding capability as indicated by the char yield is modest. However if the polyphosphonate is first incorporated into the polycarbonate by transesterification the char forming capability is dramatically increased as shown in Table 1.

Table 1. Char yields of polycarbonate containing cyclic phosphonates.

Wt % of poly cyclic phosphonate	phenylphosphonate Char yield % ^a	phenylphosphonate Char yield % ^b	methylphosphonate Char yield % ^c
0	18	18	18
5	45	27	28
10	48	28	40
15	50	28	44

^a: Cured 1 hour at 350°C & heated to 600°C under oxygen

^b: Heated to 600°C under oxygen

^c: Cured 1 hour at 350°C & heated to 600°C under oxygen

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