DMI/Langley

TOUGHENING OF BIS MALEIMIDE RESINS:

SYNTHESIS AND CHARACTERIZATION OF MALEIMIDE TERMINATED

POLY(ARYLENE ETHER) OLIGOMERS AND POLYMERS

IN-27

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FINAL REPORT

TASK 1-17000

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to

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ABSTRACT

Amine functional poly(arylene ether) sulfones were previously reported. They were synthesized via aromatic nucleophilic substitution step growth polymerization using the novel monofunctional reagent 2,2'(4-amino-phenyl, 4'-hydroxyphenyl) propane. Among other things, these oligomers and polymers were successively utilized to toughen epoxy resin networks. Additional studies have shown them to be also suitable for toughening epoxy-graphite composites. In the present task, the chemistry was extended to amorphous poly(arylene ether) ketones because of their higher fracture toughness values, relative to the polysulfones. Interestingly, we have demonstrated that the amino functional oligomers undergo a self-crosslinking reaction at temperatures above about 220°C. This produces an insoluble, but yet quite ductile network that has excellent chemical resistance. A ketamine structure hypothesis was proposed and subsequently verified using solid state magic angle NMR. In most cases, the water generated upon ketamine formation is too low to produce porosity and solid networks are obtained. The stability of the ketamine networks towards hydrolysis is remarkably good. For example, they have been boiled in water for over 80 hours with no loss of integrity. The chemistry was further demonstrated to be able to crosslink preformed nonfunctional poly(arylene ether) ketones if a difunctional amine was utilized. This concept has the possibility of greatly improving the creep resistance of thermoplastics. In a related area, we have developed a new technique for converting the amine functional oligomers cleanly into maleimide structures. This method involves reacting maleic anhydride with either monomeric aminophenols or oligomeric species in the presence of solvent mixtures based upon N-methyl pyrollidone (NMP) and N-cyclohexyl pyrollidone (CHP). Suitable monofunctional reagents can be used directly in polymerizations to produce the desired maleimide functional oligomers. Such materials can be molded above Tg into useful films prior to initiating the free radical crosslinking reaction at higher temperatures. Basic chemistry and some physical processes utilized thus far will be described. Further work is planned to verify and expand upon these initial results.

INTRODUCTION

The objectives of NASA Task 1-17000 were to synthesize novel
poly(arylene ether ketones) of controlled molecular weight and controlled
functionalities. One of the preferred end groups was to be a primary amine
group. One goal of these studies was to develop methods for derivatizing the
amine group cleanly to a bismaleimide functionality. The recognition is that
transformation reactions at the ends of polymer chains have to be nearly
quantitative to be successful. Earlier studies of this reaction were thought
to involve some loss of maleimide functionality as a result of fumaric acid
generation in the first step. The oligomers were to be characterized by end
group analysis using titration methods developed in our own laboratories:
GPC, NMR, FT-IR, differential scanning calorimetry, thermogravimetric analysis
and thermal mechanical analysis. The objectives also included an
investigation of curing behavior of these end functionalized oligomers and
some assessment of their solvent resistance and mechanical properties.

Earlier work in our laboratories demonstrated that one could cleanly
prepare aromatic amine functional poly(arylene ether sulfone) oligomers such
as outlined in Scheme 1. The key intermediate here was the monofunctional

Scheme 1. Polysulfone Oligomer Synthesis
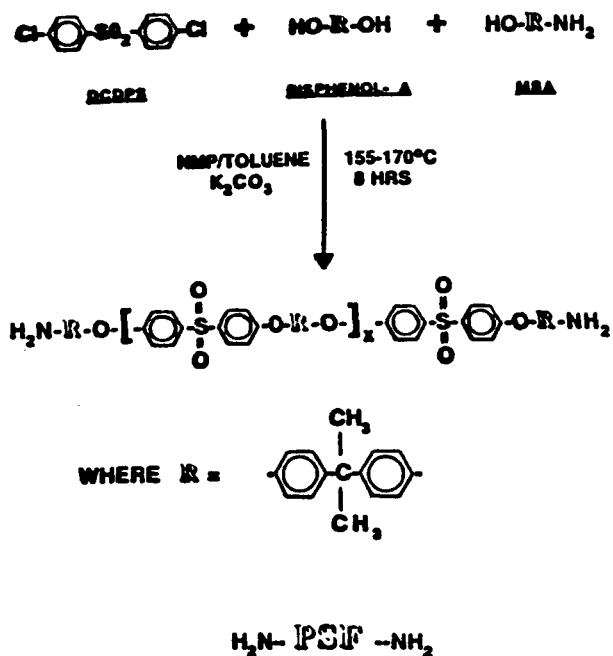
termed MBA. The synthesis of MBA has been described earlier. Alternatively, hydroxy amine which we have recently considered analogous structures based upon meta m-aminophenol. The meta orientation is preferred due to the deactivation of undesirable processes such as oxidation of the phenol group. Under the conditions indicated in Scheme 1, and indeed related conditions using other aprotic dipolar solvents, one can generate the desired poly(arylene ether sulfones). The molecular weight, or the value of X in this case, is limited by the concentration of the monofunctional hydroxy amine that one utilizes in the synthesis. Such materials have already been utilized to significantly toughen epoxy networks. The reason for their improvement is believed to be related to the formation of a highly dispersed, ductile engineering thermoplastic in the presence of the crosslinked matrix network. Typical SEM micrographs of an epoxy network modified with 15% of a 13,000 molecular weight amino terminated sulfone are provided in Figure 1.

SYNTHESIS AND CHARACTERIZATION

Having demonstrated that it was possible for the functionalized ether sulfones to significantly toughen the epoxy resins, it was of interest to also consider synthesizing analogous amino functional poly(arylene ether ketones). The most studied polymer of this type to date are the commercially available semicrystalline "PEEK"-type systems based upon hydroquinone and 4,4'-difluorobenzophenone. However, crystalline materials would be very difficult to use as toughening agents for either epoxies or maleimide systems per se. Therefore, we demonstrated that the somewhat analogous bisphenol-A derived poly(ether ketones) were indeed amorphous with Tg's in the range of 160 or a little higher. Independent measurements of fracture toughness showed that the amorphous bis-A ether ketones showed very good fracture toughness behavior. It then was desirable to extend the synthesis scheme to prepare the analogous amino functional amorphous poly(ether ketones). The first route to such an
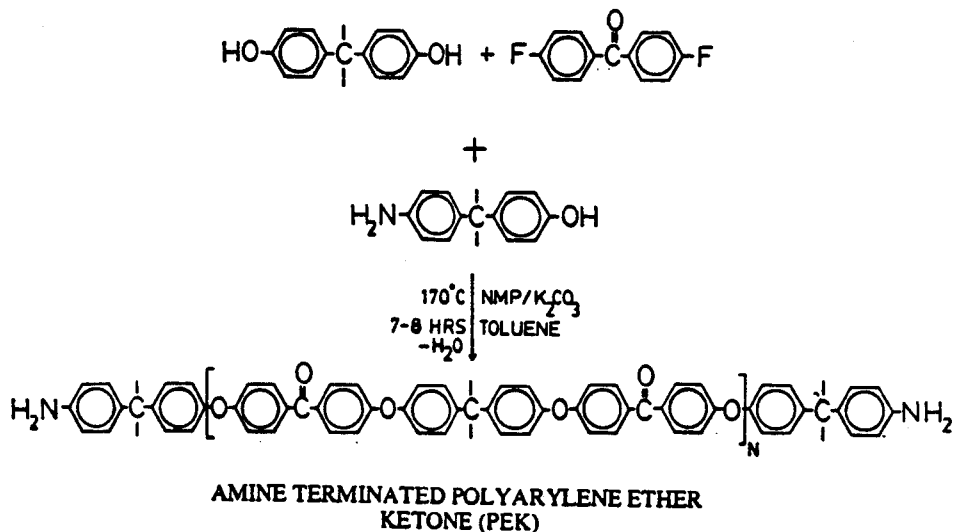
Figure 1. SEM Micrographs of Epoxy Network Modified with 13,100 <Mn> Amine

Terminated Polysulfone

oligomer is outlined in Scheme 2. The resulting materials were prepared in a

straightforward manner, where again the value of n could be controlled as a

function of the concentration of the mono-hydroxy, mono-amino compound employed

in the synthesis. Simple fabrication studies, however, identified an unusual

crosslinking reaction that took place in the case of the amine functional

poly(arylene ether ketones) that was not observed in the analogous sulfone

oligomers. For example, as illustrated in Scheme 3, we observed a self-

crosslinking behavior of the amino terminated PEEKs if they were molded at

temperatures higher than about 220°C. The resulting materials as indicated

Scheme 2. Synthesis of Amine Terminated PEK

HO-⬡-C-⬡-OH + F-⬡-C-⬡-F

+

H₂N-⬡-C-⬡-OH

170°C | NMP/K₂CO₃
7-8 HRS | TOLUENE
-H₂O ↓

H₂N-⬡-C-⬡[O-⬡-C-⬡-O-⬡-C-⬡-O-⬡-C-⬡-O]ₙ⬡-C-⬡-NH₂

AMINE TERMINATED POLYARYLENE ETHER KETONE (PEK)

Scheme 3. "Self Crosslinking" Behavior of Amine Terminated PEK

H₂N-⬡-C-⬡[O-⬡-C-⬡-O-⬡-C-⬡-O-⬡-C-⬡-O]ₙ⬡-C-⬡-NH₂

BULK | 220°C
2 HOURS ↓

CROSSLINKED POLYMER
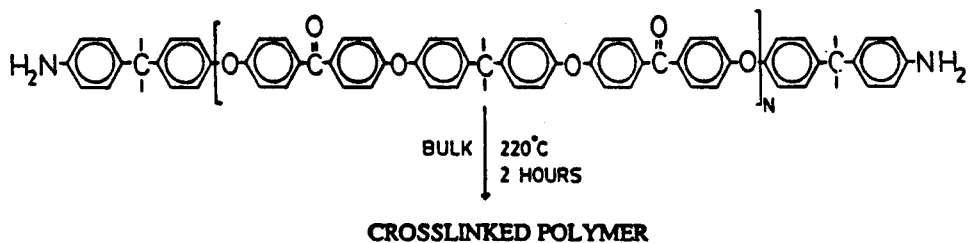
__INSOLUBLE IN__

- THF
- CHCl₃
- THF / AcOH (50/50)
- DMSO

were insoluble in a variety of solvents. Glass transition temperatures were also determined on the oligomers and it was observed that typically, Tg's could increase by as much as 20° after some of these reactions. In general, at intermediate oligomer molecular weights of 5 or 10,000, the Tg increase was only on the order of 10°C or less. We immediately sought explanations for this self-crosslinking behavior and proposed that one would generate imine or ketamine type structures of the type shown in Scheme 4. Since the resulting networks were insoluble, we decided to investigate solid state magic angle NMR

(S-S-NMR) as a route to identifying the possible ketamine structures. To develop appropriate assignments, we synthesized a model compound derived from

Scheme 4. Chemistry of "Self Crosslinking" Behavior


INTER AND INTRAMOLECULAR IMINE
FORMATION
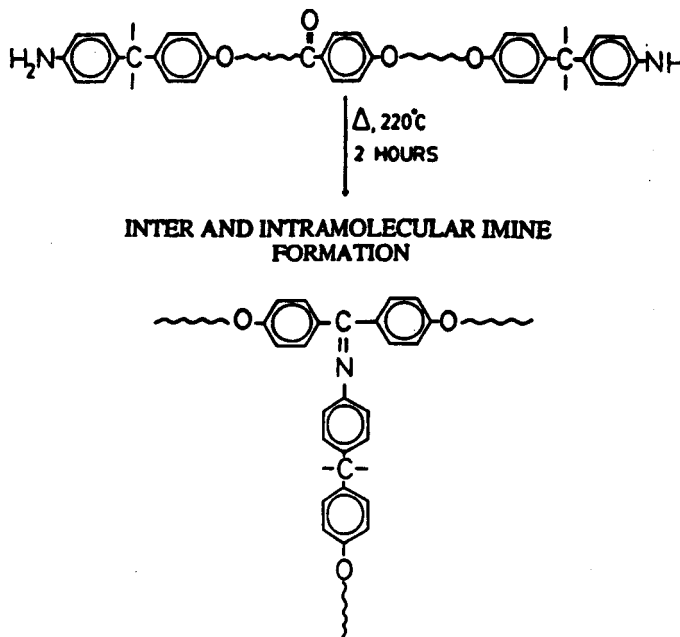
benzophenone and aniline. The model compound was examined by S-S-NMR, and a clearly defined ketamine resonance at about 176.2 ppm was observed and assigned to the ketamine structure. This structure is shown in Figure 2. The analogous magic angle NMR spectra of a 5,000 molecular weight poly(arylene ether ketone) which had been exposed to temperatures of 220°C for two hours was examined. As can be seen in Figure 3, the identical ketamine structure at about 176.5 ppm is observed and appears to thus convincingly show that one can generate a ketamine structure in these materials as a function of thermal processing. The ketamine structure produced therein was quite different than the solution spectra of the amine terminated oligomer of 5,000 molecular weight prior to the 220°C thermal treatment. Indeed, the precursor material was completely soluble in deuterated

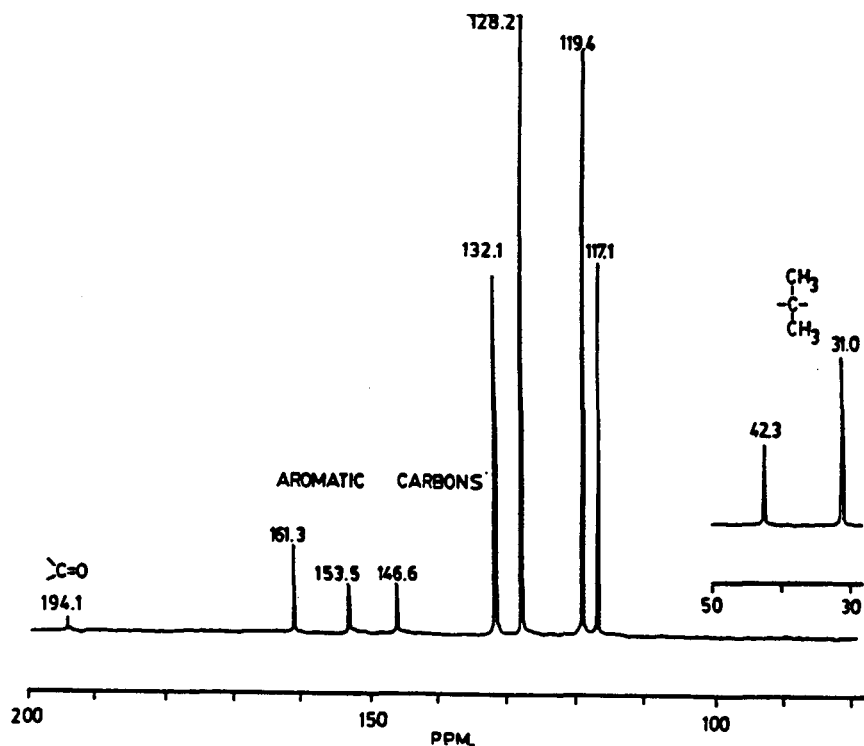**Figure 2. Solid State Magic Angle NMR of Benzophenone Imine**
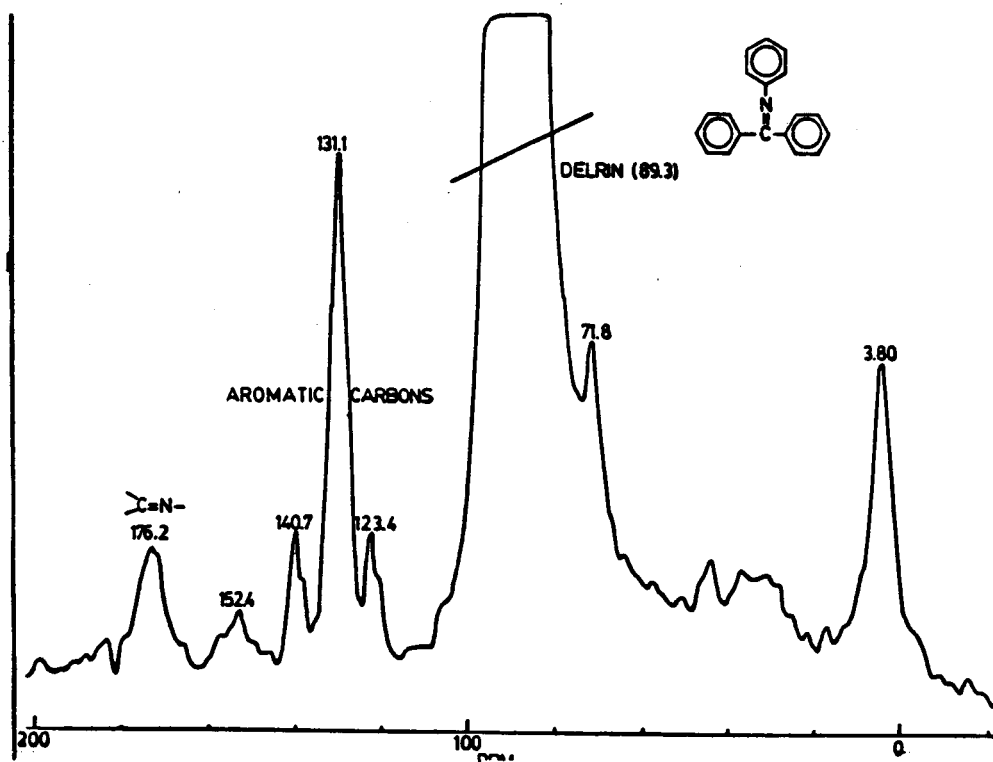
Figure 3. Solid State NMR of Crosslinked Amine Terminal PEK (5K)
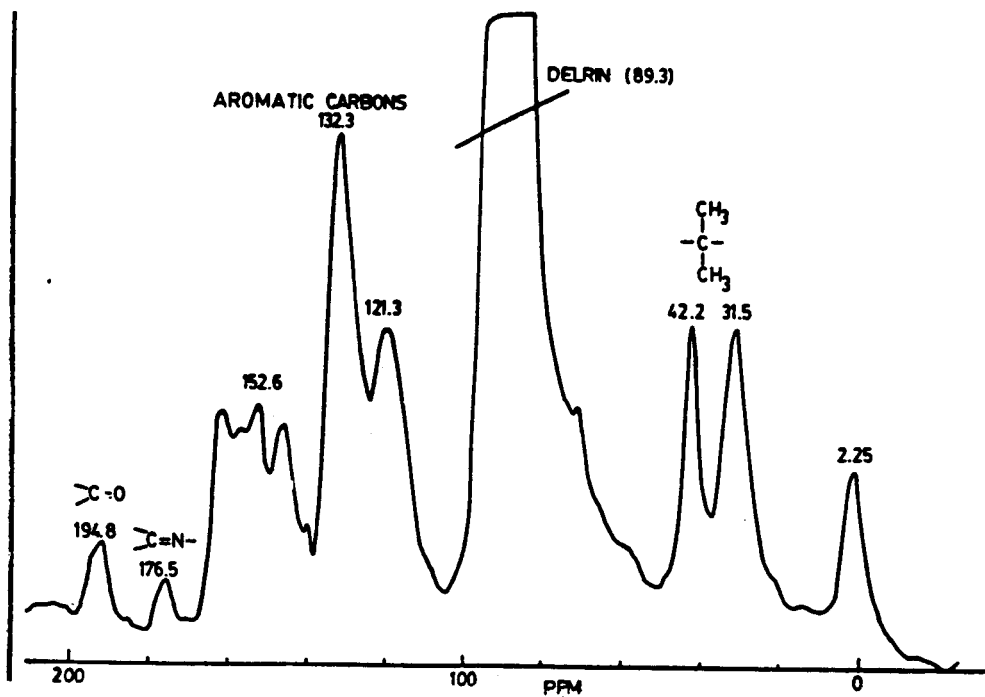
chloroform and a well-defined NMR spectra could be produced as shown in Figure

4. The effect of curing time on the glass transition temperatures of either

Figure 4. ^{13}C Solution NMR of Amine Terminal PEK (5K) in CDCl$_3$

linear or crosslinked materials is also illustrated in Figure 5. As mentioned

earlier, an increase of about 8°C is observed for the 10,000 molecular weight

crosslinked oligomer after two hours. As shown in Figure 6, higher temperatures

clearly produce a much higher gel content. The variable of curing temperature

was investigated and, as shown in Figure 7, the percent insolubles can reach

well over 90% if the curing temperature is conducted up to 280°C or higher.

Interestingly, the materials are quite ductile, after even becoming insoluble.

Most likely this is due to the fact that the crosslink density is quite low

under these conditions. An example of the stress-strain behavior is shown in

Figure 7. Clearly, a yield elongation at 5 or 10% can be identified with

resulting ultimate elongations being remarkably high for glassy materials.

Ketamines are known in small compounds to be relatively hydrolytically unstable.

However, in the macromolecular system, the material appears to be hydrolytically

Figure 5. Effect of Curing Time on the Glass Transition Temperature

[Amine Terminal PEK (10K) Cured at 220°C]

No exotherm in the first run — 3 minutes — $T_g = 426$ K
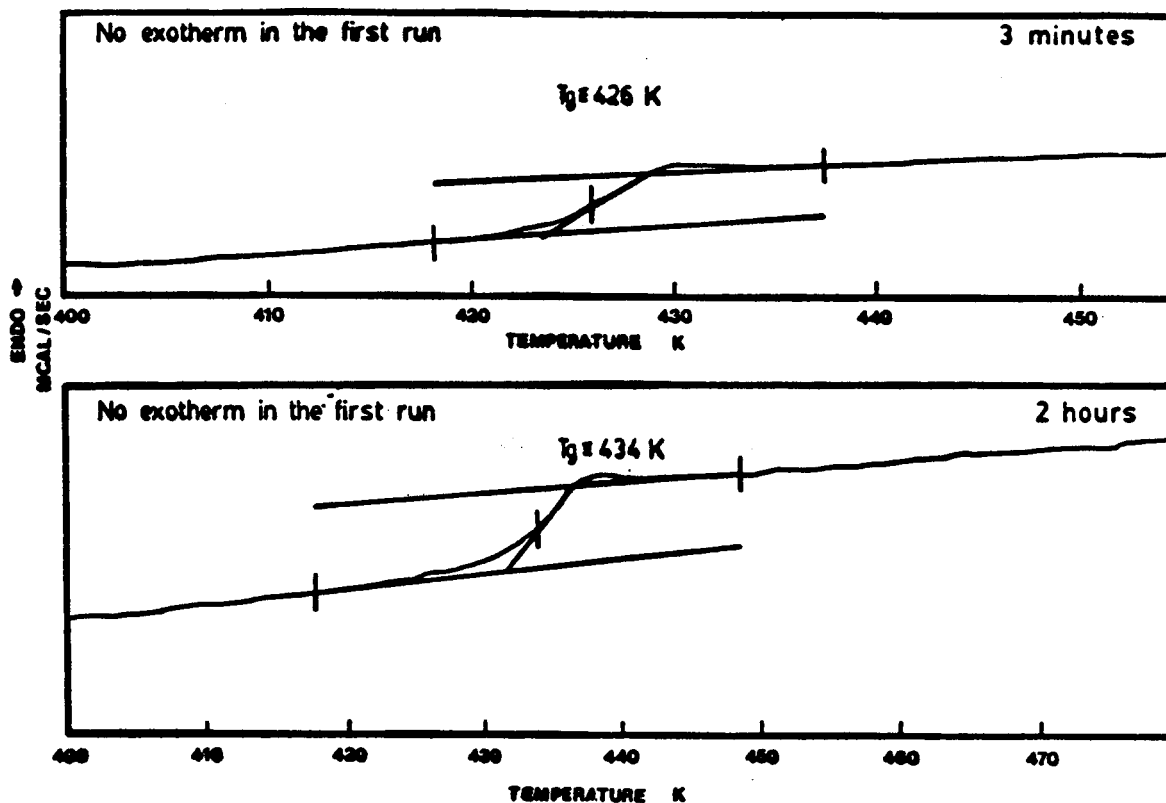
No exotherm in the first run — 2 hours — $T_g = 434$ K

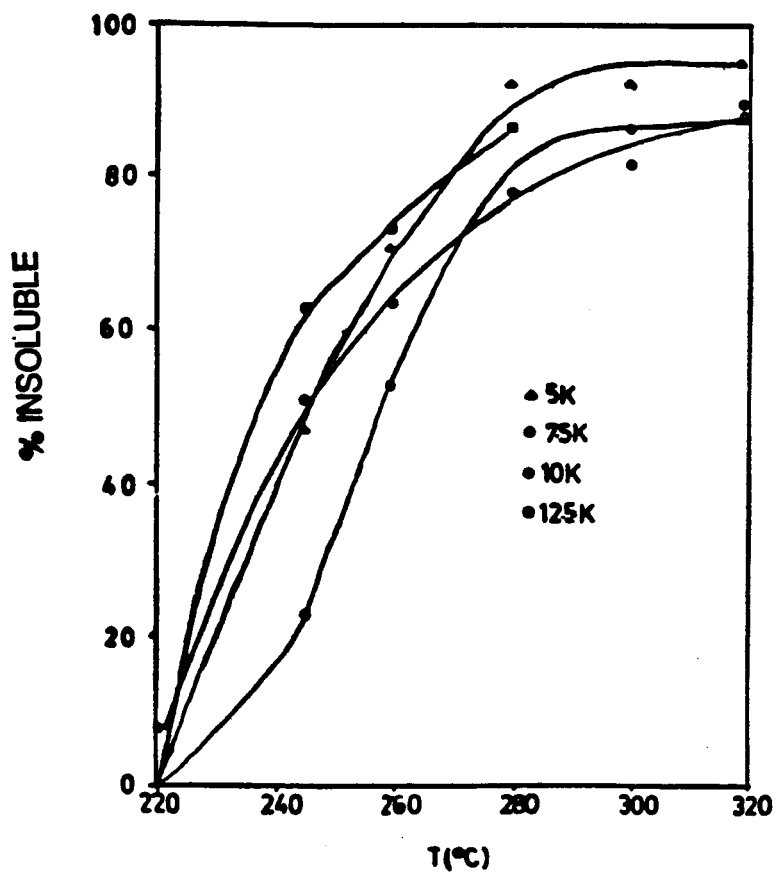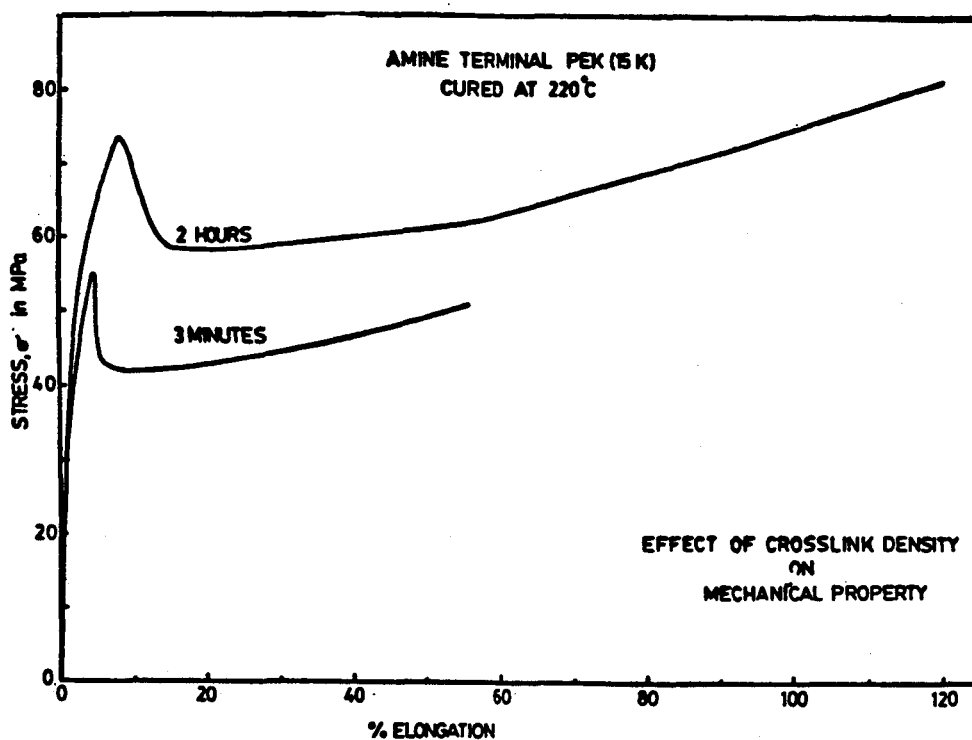## Figure 6. % Insoluble vs. Cure Temperature of Amine Terminal PEKs

Figure 7. Amine Terminal PEK (15K) Cured at 220°C

stable as judged by the fact that it retained its integrity and strength after

boiling in water for up to 80 hours. Indeed, the stress-strain curve of a

10,000 molecular weight material thermally crosslinked through ketamine

formation and subjected to boiling water treatment for 80 hours is shown in

Figure 8. After the material was boiled in water for this length of time, it

was dried and retested and shown, in fact, to be remarkably similar to the

original specimen. Therefore, one must conclude that the ketamine crosslinks

are stable, at least under neutral conditions, for relatively long periods of

time. The films produced were also free of voids, which implies that the water

eliminated during the crosslinking step must be in low enough concentrations

that the resulting polymer film can absorb the material without developing

voids. Rough calculations suggest that the amount of water produced is well

under 0.1%, which is probably soluble in the matrix and explains the basic

result. Further influence of the structure's end groups was investigated by

Figure 8. Stress-Strain Diagram of Cured and Water Soaked Ketimine Networks

A --- CURED PEK (M̄n-10K)

B --- 'A' BOILED IN H₂O FOR 80 Hrs
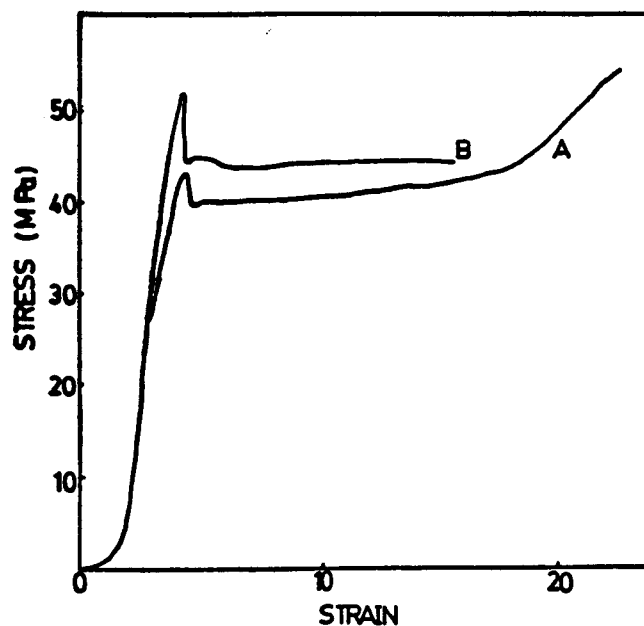
preparing poly(arylene ether ketones) that do not have amine end groups and poly(arylene ether sulfones) that did have amine end groups. As indicated in Scheme 5, the structures shown demonstrated absolutely no crosslinking

Scheme 5. Effect of End Groups on "Self Crosslinking" Behavior

I, II, III (M̄ₙ ₌₁₀ K) ──220°C──→ SOLUBLE
                        2 HOURS

tendency after up to 2 hours at 220°C. This appears to confirm that both the amine groups and ketone groups are necessary in order to produce the crosslinking behavior. Preliminary experiments have been done, however, to show that difunctional amines are capable of crosslinking poly(arylene ether ketones) as indicated by the fact, as shown in Scheme 6, oxydianiline was able to produce an insoluble material which was still fairly tough and ductile after

Scheme 6. Reaction of F-Terminated PEK With ODA

$$F\text{—}\bigcirc\text{—}\overset{O}{\underset{C}{\parallel}}\text{—}\bigcirc\text{—}O\text{—}PEK\text{—}O\text{—}\bigcirc\text{—}\overset{O}{\underset{C}{\parallel}}\text{—}\bigcirc\text{—}F$$

$$\bar{M}_n = 10K$$

$$+$$

$$H_2N\text{—}\bigcirc\text{—}O\text{—}\bigcirc\text{—}NH_2 \quad \text{(STOICHIOMETRIC)}$$

$$\downarrow \begin{array}{l} 220°C \\ 2\ Hrs \end{array}$$

INSOLUBLE POLYMER
CREASABLE FILM
% INSOLUBLE IN CHCl₃ ≈ 90%

2 hours exposure to temperatures of about 220°C. This suggests a possible route for the crosslinking of even commercially available PEEK. Such a treatment may be of some interest to reduce the creep behavior in thermoplastics.

While the phenomenon described thus far would seem to be of great fundamental interest, it did not address the tests outlined in this original proposal. To reiterate, our original goals were to synthesize the amine terminated poly(ether ketones) of controlled molecular weight, which was entirely possible as illustrated thus far. A major goal, though, was to
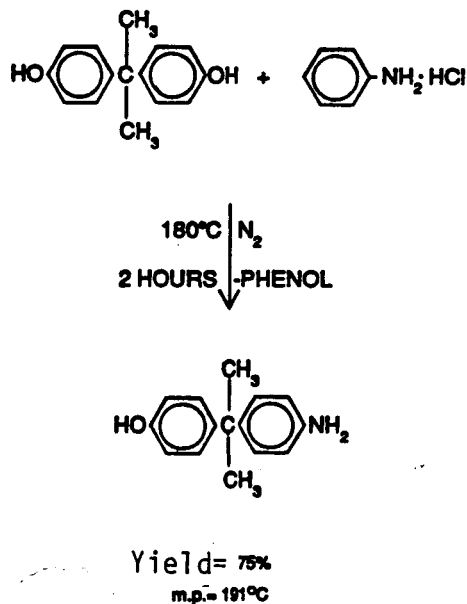
convert these amine groups into maleimide functional oligomers or, optionally, to possibly directly synthesize maleimide functional poly(ether ketone) materials which could be subsequently cured into somewhat toughened matrix resins for composite materials. To address this issue directly, we synthesized the monomer shown in Scheme 7.

Scheme 7. Synthesis of Bis-1,4-(4-Chlorobenzoyl) Benzene


YIELD = 48%   m.p. = 256°C
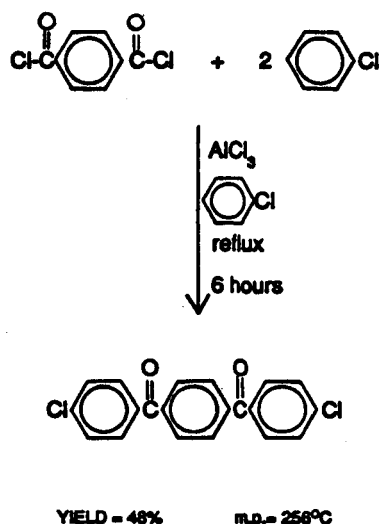
The synthesis of one of the desired monomers was achieved in a straightforward fashion in quite high yields. After crystallization, we obtained about a 50% yield of materials showing a melting point of 256°C. The diketone monomer (CBB) was utilized then to first prepare high molecular weight poly(arylene ether ketone) structures as shown in Scheme 8. Very high molecular weight materials with intrinsic viscosities over one were achieved by following the sequence shown. Interestingly, this procedure works much better with DMAC than it does with the previously utilized NMP as the reaction solvent; reasons for this are not yet clearly apparent. The initial diamine functional oligomers were prepared after first synthesizing additional 4-amino phenyl, 4'-hydroxy phenyl, 2,2 propane as shown in Scheme 9. Utilizing the

Scheme 8. Synthesis of Poly(Arylene Ether) Ketone

DMAC/TOLUENE

K_2CO_3 | 155°C

N_2 | 8 HOURS

$T_g = 165°C$
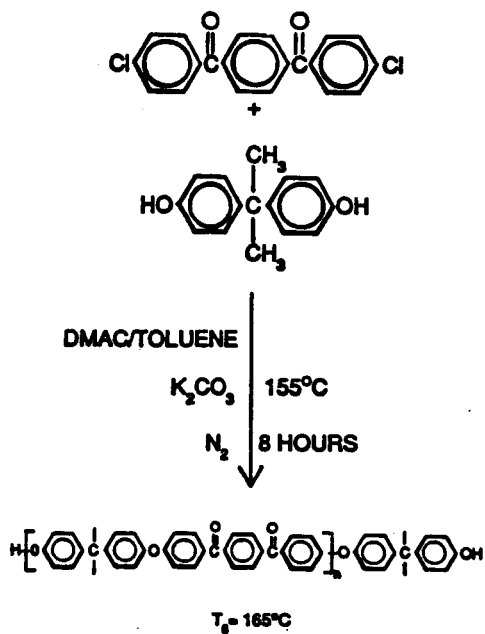
Scheme 9. Synthesis of 4-Aminophenyl-4'-Hydroxyphenyl-2,2-Propane

180°C | N_2

2 HOURS | -PHENOL

Yield= 75%
m.p.= 191°C

mono functional constituent as shown in Scheme 10, we were able to prepare a range of molecular weights of the poly(arylene ether ketones) shown with functional amine end groups.

Scheme 10. Synthesis of Amine Terminated Poly(Arylene Ether) Ketone
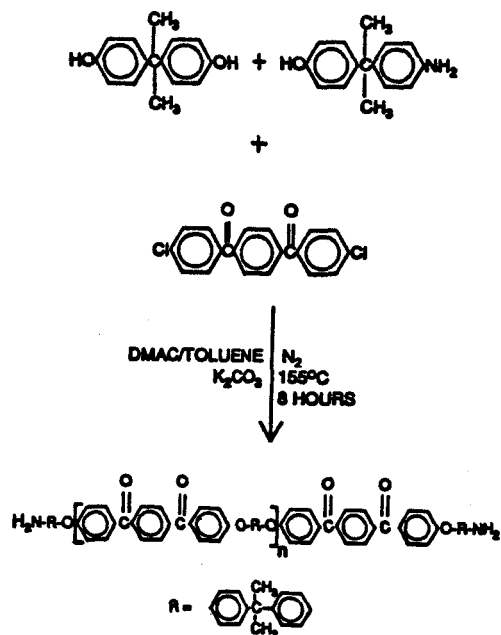
Two possibilities existed then for conversion of the amine group to a maleimide. One could convert the amine oligomers or, alternatively, it might be possible to synthesize a mono functional material which could be used as a direct end blocker. In fact, the latter approach is becoming increasingly attractive after proper developments of methods to prepare this unique material. In Scheme 11 we show the synthesis of a mono functional maleimide phenyl derivative of bisphenol A. The scheme appears to go quite well as outlined. The key step, perhaps, is the use of the co-solvent, approximately 80:20 ratio, of N-methyl pyrrolidone/N-cyclohexyl pyrrolidone (NMP/CHP). We have used CHP earlier in, for example, solution imidization studies. It has the unique feature that it is extremely miscible with water at ambient temperatures but becomes progressively less miscible as one increases the temperature. Thus, it serves as a fairly effective cyclo dehydration agent, perhaps under milder conditions than are usually employed. In any event, we have prepared a white crystalline solid possessing the right NMR structure to

/

e

f

f

o

r

t

18

Scheme 11. Synthesis of 2,2'-(4-Hydroxyphenyl, 4'-Maleimidophenyl) Propane

YELLOW CRYSTALLINE SOLID   m.p.=162°C
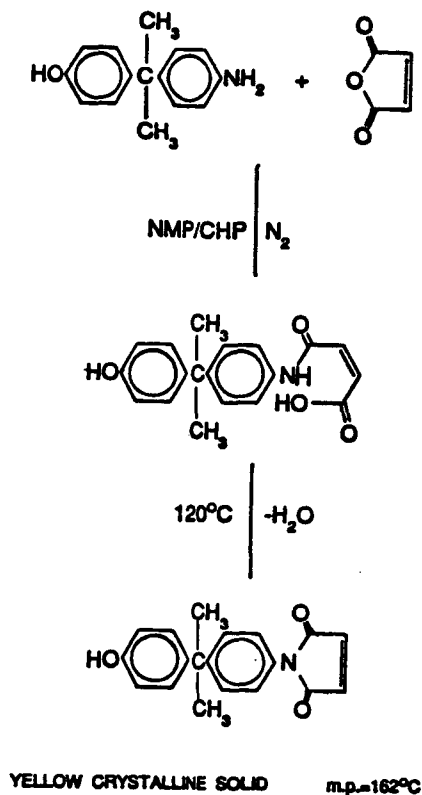
be considered a mono-maleimidophenyl, mono-hydroxy phenyl derivative of bisphenol A. This appears to be a breakthrough in the organic synthesis of compounds of this type. Further work is required, but the initial results are promising indeed. For example, the NMR spectra shown in Figure 9 of the amino hydroxy derivative, and the corresponding NMR structure, shown in Figure 10, of the maleimido structure, appear to give the right integrations for the proposed structures. In addition, the FT-IR assignments are also consistent with this structure as shown in Figure 11 for the amine precursor, and Figure 12 for the maleimide derivative. In particular, the sharp carbonyl expected for the maleimide derivative is readily apparent. Initially, we synthesized what we believed to be quite highly functionalized maleimide materials. The reaction appeared to proceed, to considerable extents, as judged by the infrared spectra

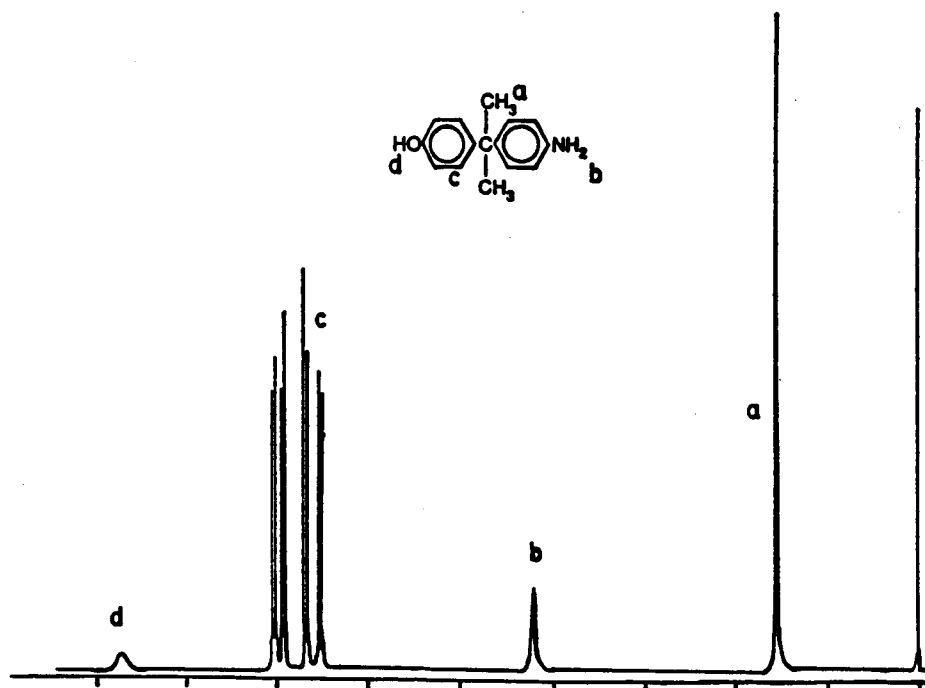**Figure 9. H' NMR Spectra of 4-Aminophenyl, 4'-Hydroxyphenyl-2,2-Propane**

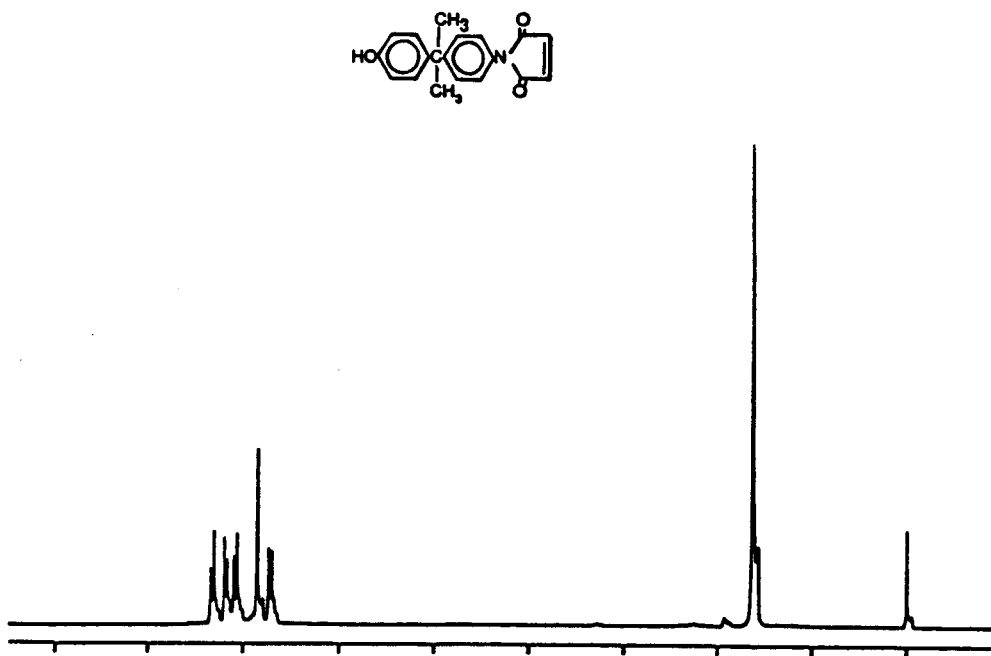**Figure 10. H' NMR Spectra of 4-Hydroxyphenyl, 4'-Maleimidophenyl-2,2-Propane**

of the precursor amine derivative and Figure 12, the maleimide derivative of

the amine systems. Nevertheless, the possible synthesis of a maleimide

terminated poly(ether ketone) in one step is very attractive for both practical

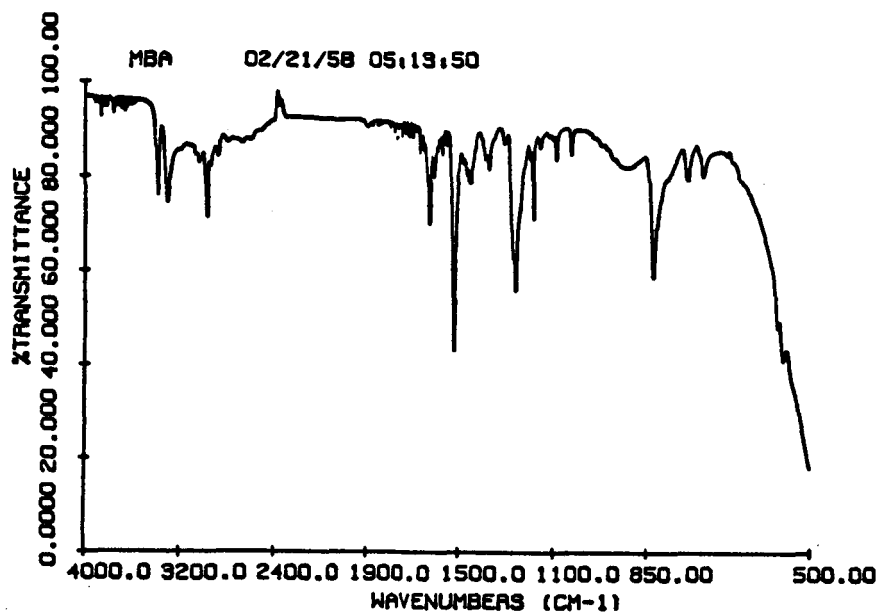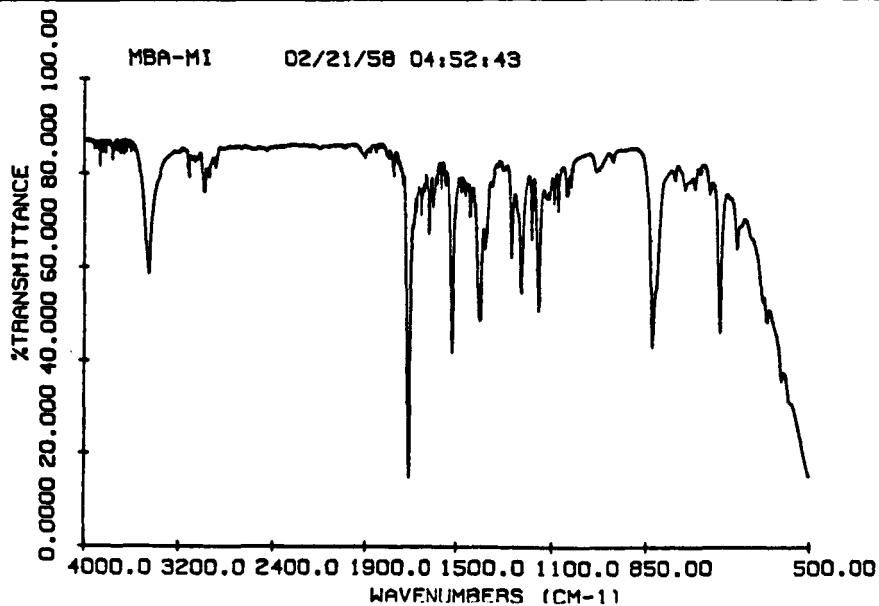**Figure 11. FT-IR Spectra of 4-Aminophenyl, 4'-Hydroxyphenyl-2,2-Propane**

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%TRANSMITTANCE

WAVENUMBERS (CM-1)

Figure 12. FT-IR Spectra of 4-Hydroxyphenyl, 4'-Maleimidophenyl-2,2-Propane

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%TRANSMITTANCE

WAVENUMBERS (CM-1)
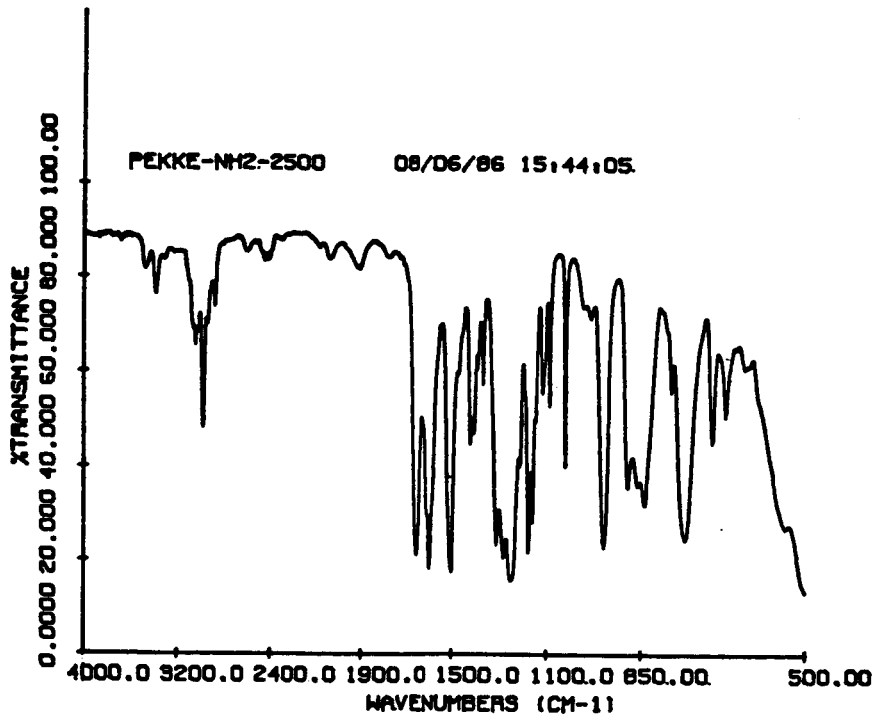
and theoretical reasons. The preliminary experiments conducted have been

considered to be quite successful. For example, in Scheme 12 we were able to

maintain the unsaturated imide end group under the conditions of a weakly basic

potassium carbonate catalyzed polymerization under typical DMAC toluene-type

conditions. Oligomers of 3,000 to 7,000 molecular weight have been prepared

Scheme 12. Synthesis of Maleimide Terminated Poly(Arylene Ether) Ketone

$$H_2N\text{---}(\text{PEK})\text{---}NH_2$$

Maleic Anhydride

N_2 NMP/CHP

110°C $-H_2O$
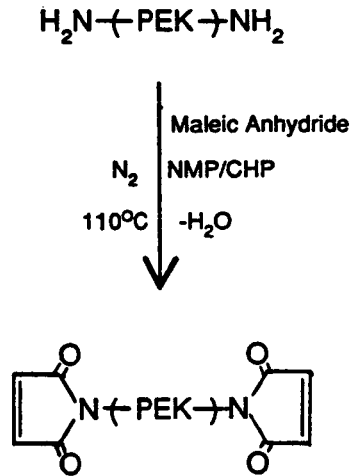
which appear to have the appropriate functionalities. For example, in Figure

13 the infrared of the PEKKE oligomer functionalized with the bismaleimide

Figure 13. FT-IR Spectra of Amine Terminated Polyether Ketone

PEKKE-NH2.-2500   08/06/86 15:44:05.

XTRANSMITTANCE

0.0000 20.000 40.000 60.000 80.000 100.00

4000.0 3200.0 2400.0 1900.0 1500.0 1100.0 850.00   500.00

WAVENUMBERS (CM-1)

produces a reasonably consistent spectra. One important but indirect proof of

the functionalization is the idea that the maleimide capped oligomers can be

thermally crosslinked. Thus far, in our initial experiments, we exposed what we believed to be the bismaleimide functional oligomer of from 3 to 7,000 molecular weight to temperatures of 195° for one hour, followed by 220° for two hours. We were able to produce a crosslinked insoluble, and the spectra are consistent with the maleimide being polymerized by radical mechanism. Thermal analysis has been explored, and in Figure 14 a 5,000 molecular weight maleimide

Figure 14. FT-IR Spectra of Maleimide Terminated Polyether Ketone

NICOLET DX: PEKKE-MI-2500   08/06/86. 15.11:03
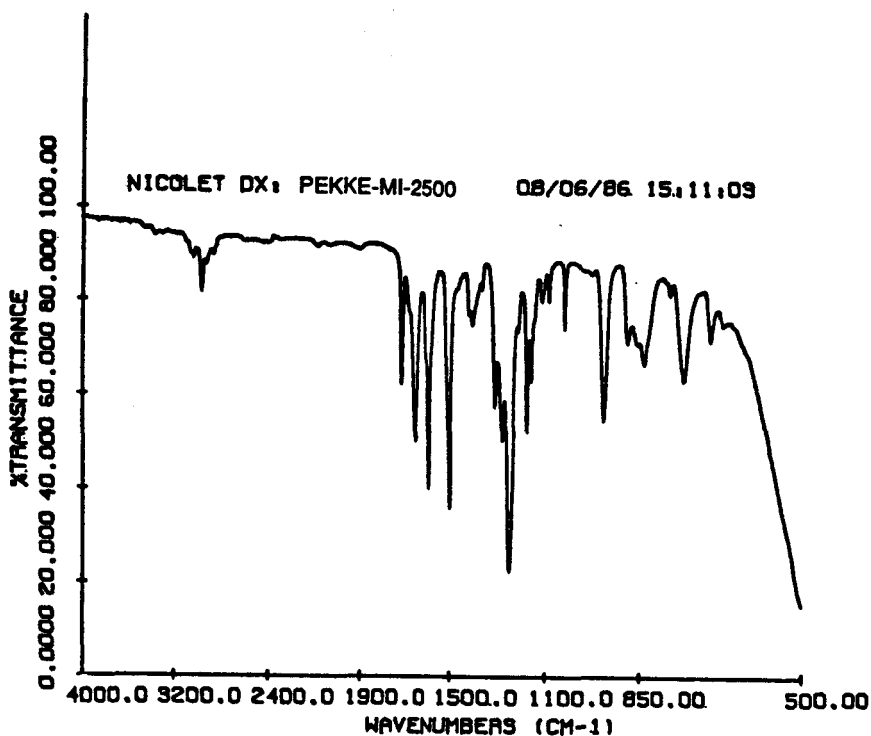
functional oligomer was examined by DSC at 10° per minute. The glass temperature was consistent with the other oligomer values of about 162°C. Upon heating the material further, one could both transform it from a soluble system to an insoluble network and at the same time the Tg value was increased significantly by about 11°C to about 173°C. Again, we feel this increase is consistent with the degree of crosslinking expected for a 5,000 molecular weight oligomer. 7,000 molecular weight oligomers were treated similarly and produced reasonably ductile films after their curing step. This was considered

very encouraging indeed. Lower molecular weight poly(ether ketone) maleimides

have also been prepared, for example, at 2,500 number average molecular weight.

These materials show initial Tg of about 126. After thermally crosslinking,

the Tg is increased fairly dramatically to 177°C, which is consistent with the

higher degree of crosslinking possible with these lower molecular weight, more

highly functional oligomers.

Some preliminary characterization on the various poly(ether ketones) and

derivatives have been already achieved, and in Table 1 we summarize typical

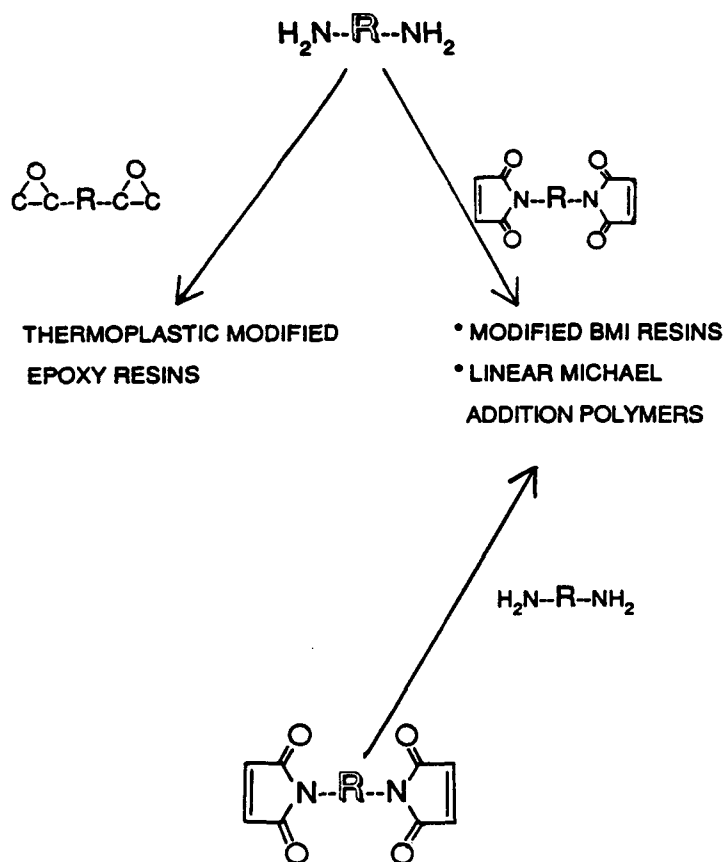Table 1. Intrinsic Viscosities and Tg's of Polyether Ketone for Varying

Molecular Weights

END CAP	MW	$[\eta]_{CHCl_3}^{25°}$	$T_g$init	$T_g$cure
CONTROL	25000	1.30	165°	
NH$_2$	3200	0.19	132°	183°
NH$_2$	6800	0.33	148°	168°
MI	3200	0.13	119°	177°
MI	6800		162°	173°

10°C/Min

intrinsic viscosity and glass temperature values for the materials which have

possessed different types of end group functionalities. For example, the high

molecular weight linear control which produced a tough, ductile, transparent

film with about 165° Tg. The neutralized chlorine or hydroxyl end groups do

not undergo any particular reaction, therefore the material remains soluble

even after molding at higher temperatures. The amine terminated polymers as

indicated earlier do undergo the somewhat novel ketamine types of crosslinking

steps, and as a function of molecular weight their glass temperatures after

curing at 220° or higher may be increased significantly. For example, the

3,200 molecular weight oligomer, which initially has a Tg of 130, is increased

to 180° after curing. By contrast, the similar structure that is about 7,000

molecular weight shows a Tg of +148 is only increased to 168 due no doubt to

the lower degree of crosslinking possible with these lower functionality

oligomers. The identical maleimide structures have been prepared and

crosslinked. They were observed to undergo similar types of increase in Tg

after their free radical curing step. For example, the low molecular weight

material increases over 50%, whereas the 7,000 molecular weight oligomer

increases about 11%. Many other possible post-reactions could be envisioned

for these interesting oligomers. These are summarized in Scheme 13. One could

<u>Scheme 13. Possible Post Reactions</u>

THERMOPLASTIC MODIFIED
EPOXY RESINS

* MODIFIED BMI RESINS
* LINEAR MICHAEL
  ADDITION POLYMERS

also use these oligomers to toughen epoxy resins, and indeed some of this work

has been done and already published. In addition, it may be possible to form

relatively linear molecular addition products by reacting the oligomeric diamines with bismaleimides. In contrast, the bismaleimide functionalized materials discussed in this report may also be chain extended with diamines by similar type microprocesses to produce linear or possibly crosslinked materials.

CONCLUSIONS

Work under this program has demonstrated that several types of poly(arylene ether ketone) oligomers possessing amine end groups can be prepared. These were utilized with either difluorobenzophenone or the chlorobenzoylbenzene, the bis(chlorobenzoyl) benzene ketone monomer. Also, functional end groups have been obtained either from aminohydroxy derivatives of bisphenol A or from meta-aminophenol. The latter would be no doubt more economical and more readily available.

It appears that it is possible to convert the terminal amine end groups of the oligomers substantially to maleimide functionalities through the use of the interesting co-solvent dehydration agent NMP/CHP. Our current studies and future plans are focused on preparing test specimen from the maleimide reactive oligomers, generating K_{1C} and flexural modulus data and providing suitable materials to NASA for further evaluation.