CURE CHEMISTRY OF PHENYLETHYNYL TERMINATED OLIGOMERS

Karen H. Wood and Robert A. Orwoll
College of William and Mary
Williamsburg, VA 23187-8795

Brian J. Jensen
NASA Langley Research Center
Hampton, VA 23681-0001

and

Philip R. Young
Emory & Henry College
Emory, VA 24327

Harold M. McNair
Virginia Polytechnic Institute and State University
Blacksburg, VA 24061-0344

ABSTRACT

The ability to process high performance polymers into quality, void-free composites has been significantly advanced using oligomers terminated with reactive groups which cure or crosslink at elevated temperature without the evolution of volatile byproducts. Several matrix resin systems of considerable interest to the aerospace community utilize phenylethynyl-terminated imide (PETI) technology to achieve this advantage. The present paper addresses the cure chemistry of PETI oligomers.

The thermal cure of a low molecular weight model compound was studied using a variety of analytical techniques including differential scanning calorimetry, Fourier transform infrared spectroscopy, and liquid chromatography-mass spectroscopy. The studies indicate an extremely complex cure process. Many stable products were isolated and this paper reports current work on identification of those products. The intent of this research is to provide fundamental insight into the molecular structure of the cured PETI engineering materials so that performance and durability can be more fully assessed.

KEY WORDS: Polyimide, Cure, Phenylethynyl-terminated oligomers

1. INTRODUCTION

The need for high performance, easily processed resins for aeronautical applications has been established for decades. Recent work utilizing phenylethynyl terminated oligomers has shown great promise for improving processabilty by controlling molecular weight to lower melt viscosity and cure without the evolution of volatile byproducts.[1-2] Phenylethynyl terminated polyimide oligimers demonstrate excellent mechanical strength and solvent resistance when cured. However, the cure mechanisms and products are poorly understood. Once cured, these systems become intractable and insoluble, limiting available chemical characterization techniques to the solid state. The study of phenylethynyl terminated model compounds which have simpler structures and are soluble may provide additional insight as to the cure mechanisms of the more complex oligomers.

This paper reports examination of one such phenylethynyl terminated containing model compound, 4-phenoxy-4'-phenylethynylbenzophenone. The cure products of this model compound exhibited significant solubility when when fully cured. Initial cure studies of this compound are reported elsewhere.[3] Current work focuses on the use of reverse phase liquid chromatography in combination with mass spectroscopy to elucidate initial products and mechanisms. Numerous initial low molecular weight cure products are identified. Attempts at rationalizing cure mechanisms are presented based on these results.

2. EXPERIMENTAL

2.1 Model Compounds. Several phenylethynyl terminated model compounds were examined. 4-phenoxy-4'-phenylethynylbenzophenone (4-PPEB), molecular weight 374 amu, shown in Figure 1 was selected for the most intensive study. The synthesis of this model compound has been reported elsewhere.[4]

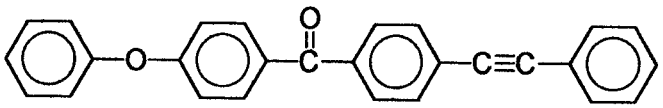


Figure 1. 4-phenoxy-4'-phenylethynylbenzophenone (4-PPEB)

2.2 Characterization. Differential scanning calorimetry (DSC) was performed on 4-PPEB in air with samples heated at 10°C/ minute to 375°C. The samples exhibited a melt temperature of 171°C and a cure exotherm between 350-400°C.
Diffuse reflectance Fourier transform infrared spectroscopy (DR-FTIR) was performed over a range of 4000-600 wavenumbers (cm^{-1}) using a Nicolet Magna-IR 750 infrared spectrometer equipped with a liquid nitrogen cooled MCT/A detector and a Praying Mantis Diffuse Reflectance Attachment (DRA).[5]

2.3 Cures. 4-PPEB was heated at 10°C/minute to 325°C, 350°C or 375°C and held for various cure times, as shown in Table 1. Samples were immediately quenched upon completing hold time. The emphasis for cure studies was to obtain initial cure products.

Table 1. Cure Scheme for 4-phenoxy-4'-phenylethynylbenzophenone

	Cure Temperatures		
Hold Times (min.)	**325°C**	**350°C**	**375°C**
	0	**0**	**0**
	5	**3**	**3**
	10	**5**	**5**
	15	**10**	**15**
	30	**15**	------

2.3.1 Cure Studies. Cured samples were examined using the DR-FTIR technique described above. Additionally, reverse phase gradient liquid chromatography in combination with mass spectroscopy (LC-MS) was performed on all cured samples using a Fisons System (Manchester, U.K.) with a VG platform. The detector wavelength was 260 nm. and the absorbance was 0.001 AU/FS. Samples were run at 85 bar pressure in a gradient going from 80:20 acetonitrile/water to 100:0 in ten minutes at 1.0 ml/min. through a Prodigy ODS-2 Phenominex C-18 column. Electron ionization (EI) cone voltage was varied from 15-50 eV depending upon the amount of fragmentation desired.

3. RESULTS AND DISCUSSION

3.1 DR-FTIR. The DR-FTIR spectra of uncured and cured 4-PPEB are shown in Figure 2. The uncured spectrum contains a weak carbon-carbon triple bond peak at 2218 cm^{-1}. After a 15 minute hold at 375°C, the ethynyl peak was greatly diminished indicating that it had either fully reacted or was in minute amounts and beyond the detection limits of the instrument.

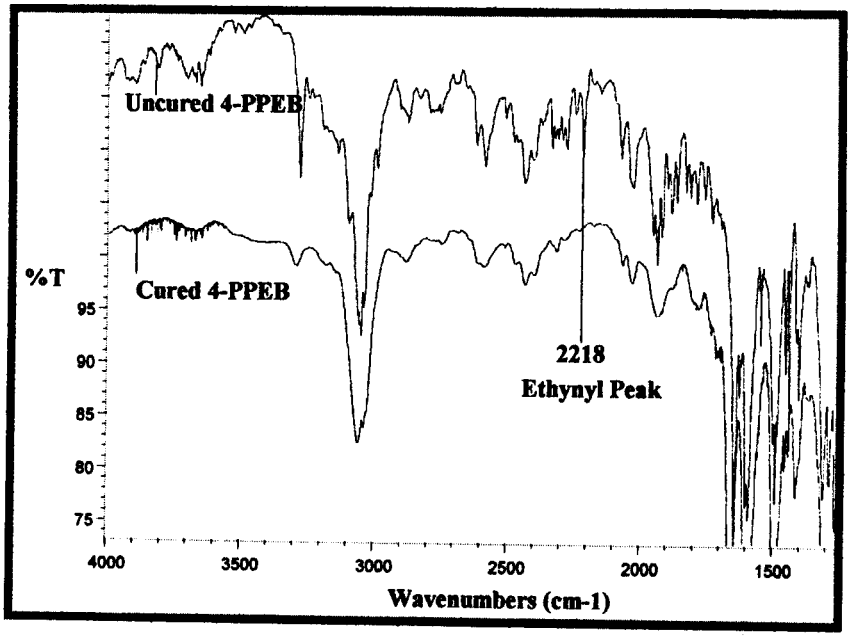


Figure 2. DR-FTIR Spectra of Ethynyl Peaks in Uncured and Cured 4-PPEB

3.2 LC-MS Initial cure products were examined using reverse phase LC-MS. While the separation achieved using the acetonitrile/water gradient was excellent, the cure products were only an average of 18% soluble in acetonitrile. Thus, while some of the cured product was could not be analyzed, many of the initial product species were available in the solution for analysis.

Example UV chromatograms are shown in Figure 3 for the 350°C cures. The chromatograms have been normalized to an arbitrary intensity and have undergone background subtraction. Each peak is noted with a retention time and a scan number which is used to obtain a corresponding mass spectrum. The chromatograms show an increasing amount of cure products with increasing hold time, however, there do not appear to be any additional types of cure products formed after a 5 minute hold. Increasing amounts of cure products with increasing hold times at temperature were also observed for samples cured at 375°C and 325°C.

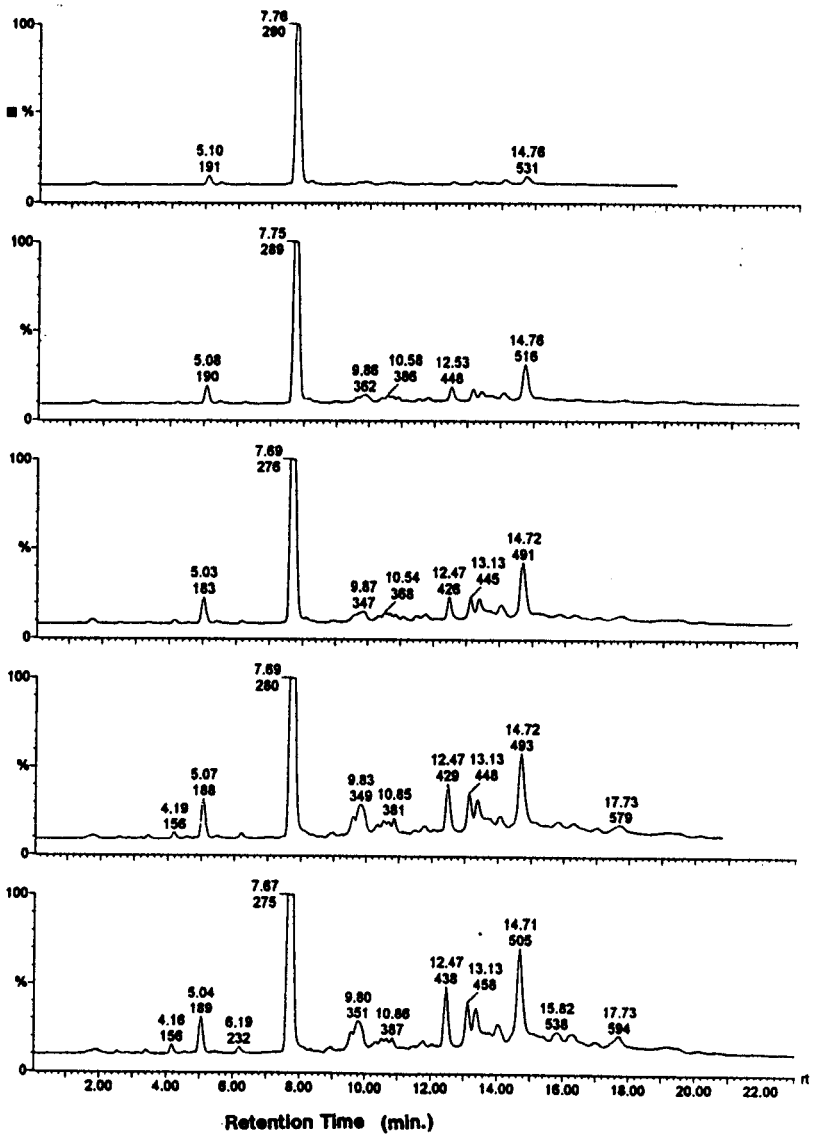


Figure 3. UV Chromatograms for 4-PPEB Cured at 350°C Held for 0, 3, 5, 10 and 15 Minutes

Each sample was also scanned for molecular weights corresponding to dimer, trimer and tetramer products. Figure 4 shows the resulting chromatograms for a sample cured at 350°C and held 15 minutes. Figure 5 presents those same results, but normalized by intensity to show the relative amounts of products. Tetramer is barely discernible on this scale compared to dimer and trimer. Numerous dimer peaks are present, each indicating multiple products with different retention times and therefore different molecular structures. Interestingly, only one trimer form was predominant. Small amounts of tetramer present gave multiple peaks. Its small amount may be due to the insolubility of the product and thus, not a true reflection of the actual quantity of tetramer formed. The dimer, trimer, tetramer chromatograms demonstrated the same trend as the UV chromatograms shown in Figure 3. As cure temperature and hold time increased, the amounts of each type product increased. However, no significant amount of tetramer was found in the samples cured at 325°C.

Mass spectra were obtained for most of the dimer, trimer and tetramer peaks found in all samples. They will be discussed in conjunction with proposed structures.

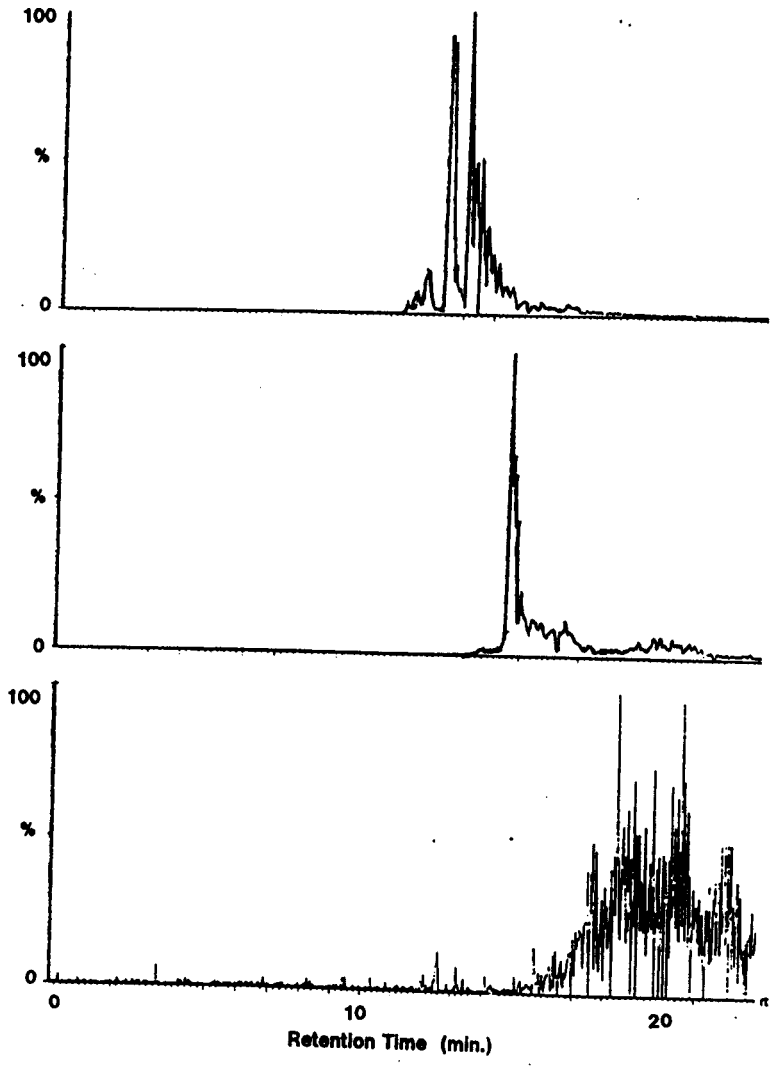


Figure 4. Chromatograms Corresponding to Dimers, Trimers and Tetramers For 4-PPEB Cured to 350°C and Held 15 Minutes

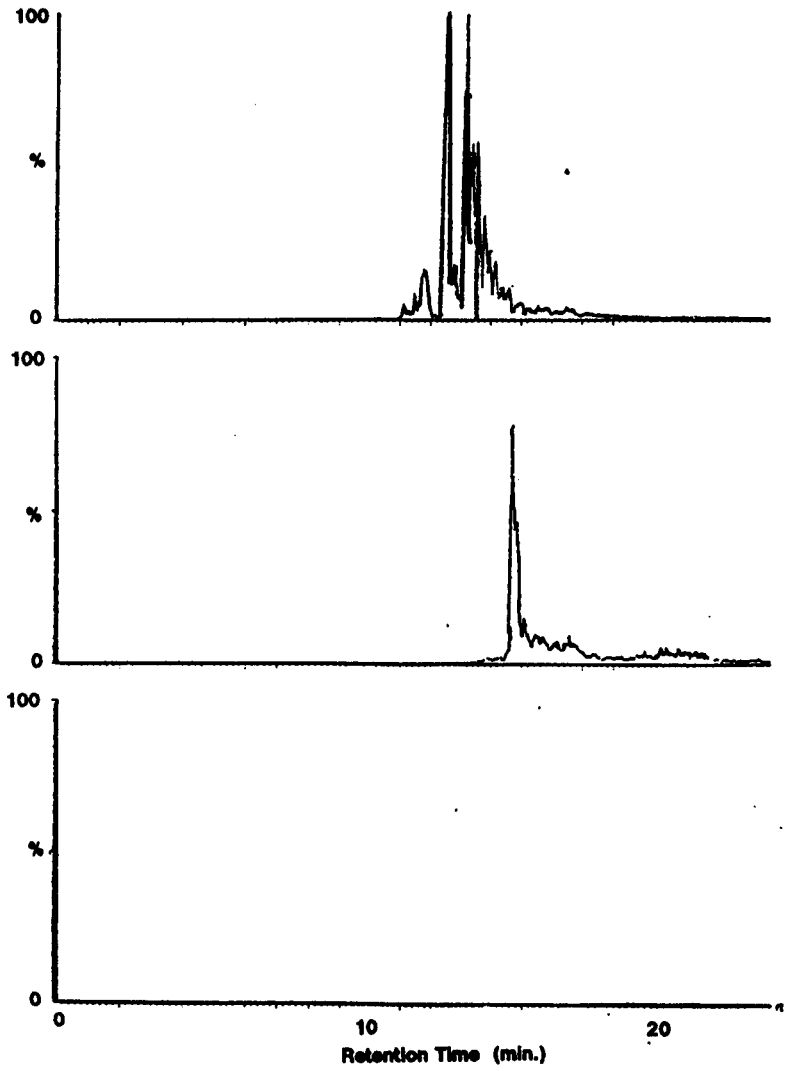
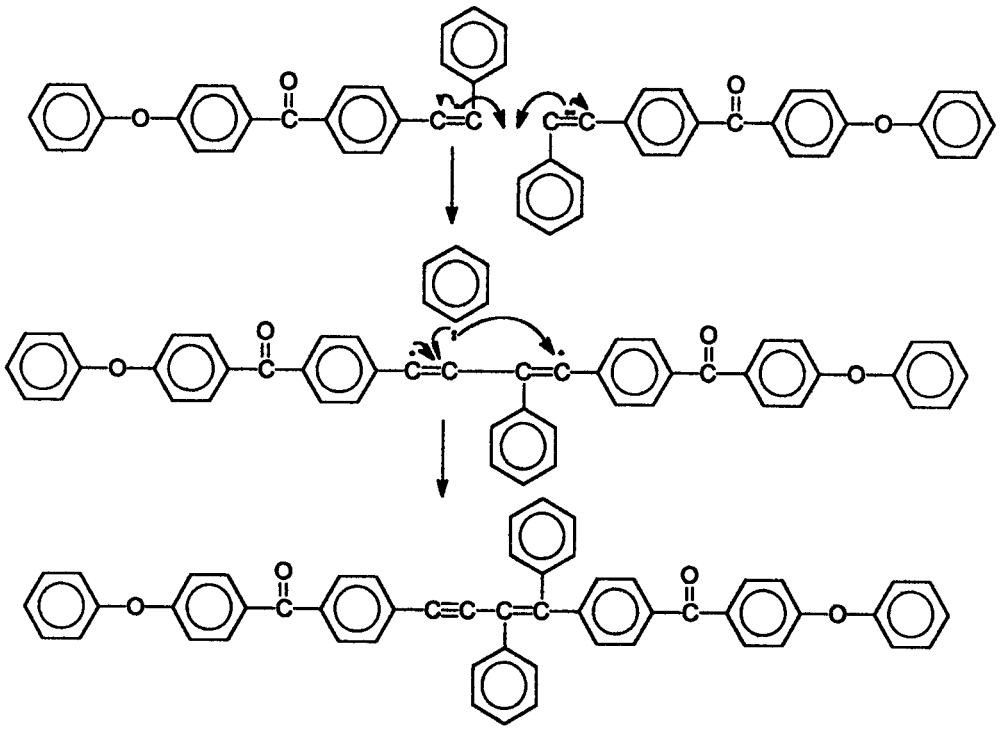


Figure 5. Normalized Chromatograms Corresponding to Dimers Trimers and Tetramer for 4-PPEB Cured to 350°C and Held 15 Minutes

3.3 Proposed Structures Chromatographic evidence revealed that the initial cure products for 4-PPEB were a complex mixture of dimers, trimers and possibly tetramers. Additional fragments were formed in the process of LC-MS analysis and were not specifically identified.

3.3.1 Dimers The chromatographic peaks that corresponded to the molecular weight of dimer, 748 amu, were numerous. The first reaction path explored was a simple tail-to-tail reaction through the phenylethynyl ends. The reaction scheme is shown in Scheme 1. Two small molecules reacting through the ethynyl endcap generates a diradical structure which is not believed to be stable at high temperatures. However, dimers remained stable and were present in all cured samples, regardless of increased temperature or hold time, indicating an enduring structure. One means of rationalizing this unexpected result is the migration of the phenyl ring on one of the ethynyl groups. Similar migrations have been reported elsewhere.[6-8] Such a migration eliminates the diradical and provides increased thermal stability. Work is ongoing using electron spin resonance (ESR) to seek more evidence to confirm or disprove the phenyl migration mechanism.

Scheme 1



Mass spectral results appear to substantiate this type of dimer structure. Figure 6 gives a mass spectrum with peaks at 202, 278, 306, and 354 that are best accounted for by addition through the ethynyl ends. This mass spectrum does not rule out the presence of a diradical structure. Addition may also take place in a head-to tail manner which may account for other structures with similar mass spectra, but different chromatographic retention times.

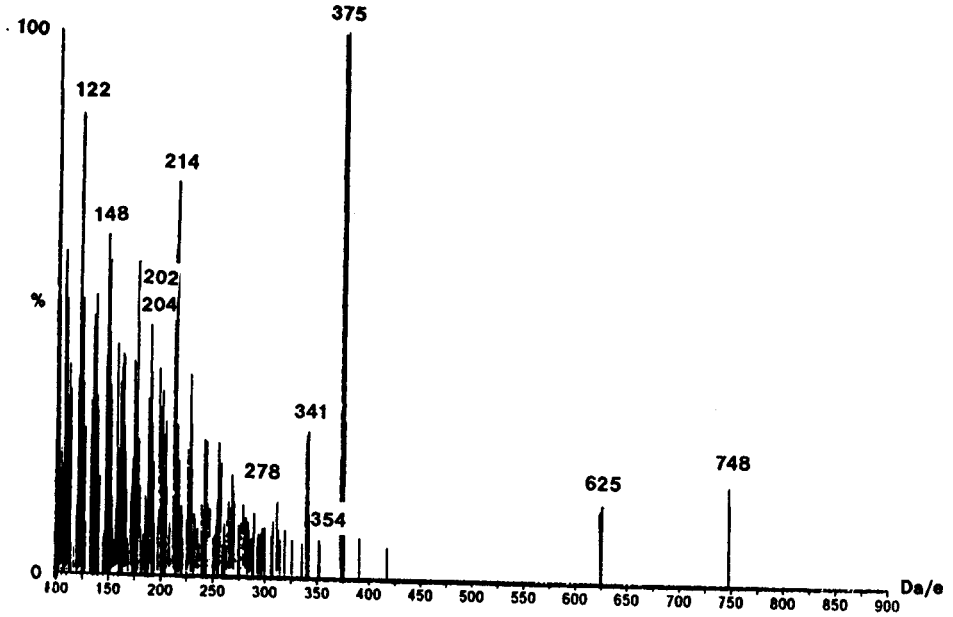
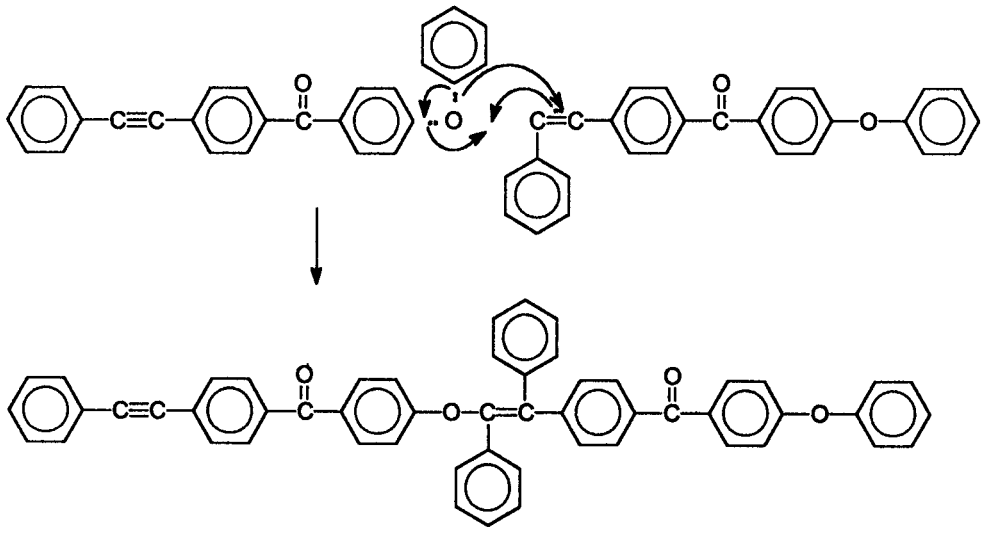


Figure 6. Mass Spectrum Supporting Monomer Reaction through Phenylethynyl Ends

Another possible reaction path supported by mass spectral results is the ethynyl end reaction with the phenoxy end of the molecule. This scheme is given in Scheme 2 and assumes the migration of the phenyl ring to give a stable structure without radicals.

Scheme 2



The mass spectrum given in Figure 7 supports this structure and contains peaks at 194, 298, 346, 390, 401 and 467 which are not expected in the previous structure and are best explained as coming from this product. The MS peak at 194 corresponds to the central portion of the dimer formed by this type of addition. A head-to-tail addition is also possible and cannot be ruled out based on the mass spectral evidence.

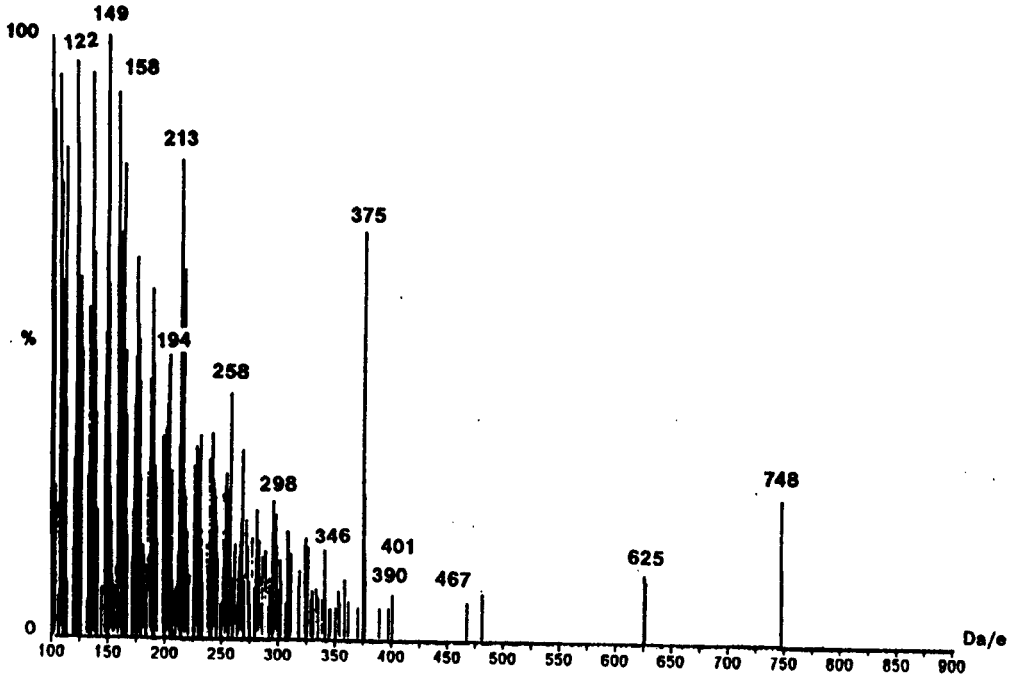
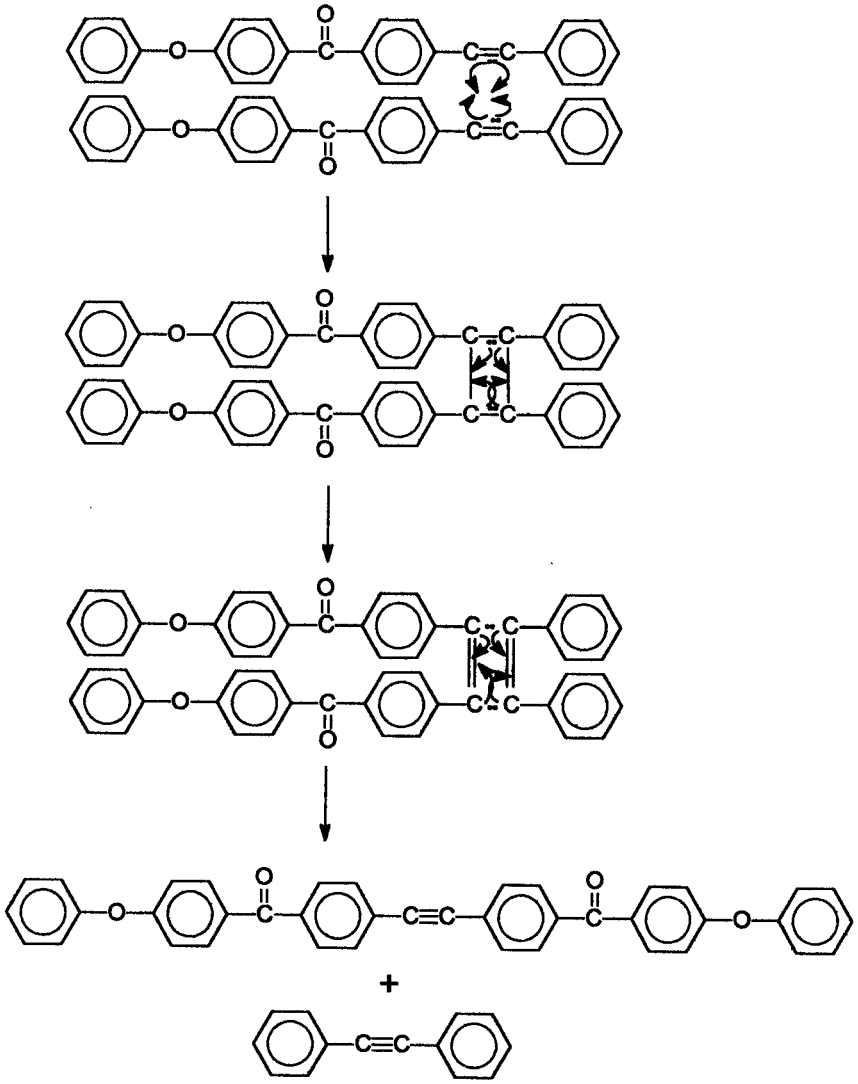


Figure 7. Mass Spectrum Supporting Monomer Reaction through Phenylethynyl and Phenoxy End Groups

Another possible addition pathway is the formation of a pseudo cyclobutadiene as proposed by Gandon, et al.[9] The intermediate cyclobutadiene could rearrange as shown in Scheme 3 to give diphenyl acetylene and a stable structure with a mass of 570 amu. A species with this molecular weight was found in all cured samples. The mass spectrum shown in Figure 8 contains peaks at 280, 373, 400, 401 and 477 amu that are best accounted for with this structure. No chromatographic evidence was found for the presence of diphenylacetylene. At cure temperatures above 300°C the diphenylacetylene apparently participated in additional reactions.

Scheme 3



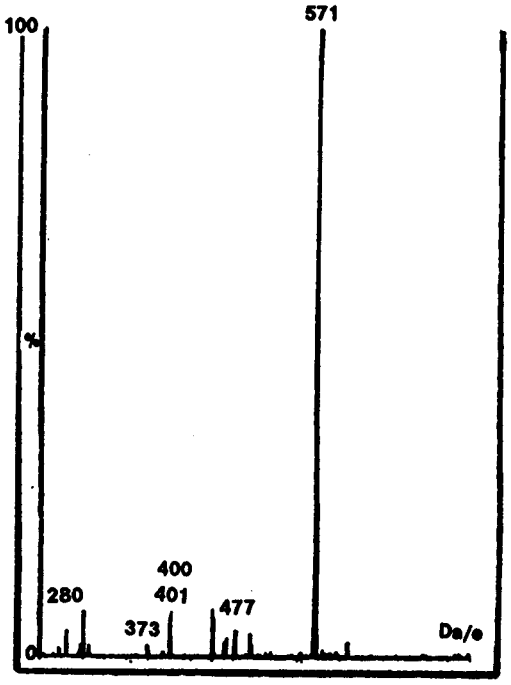
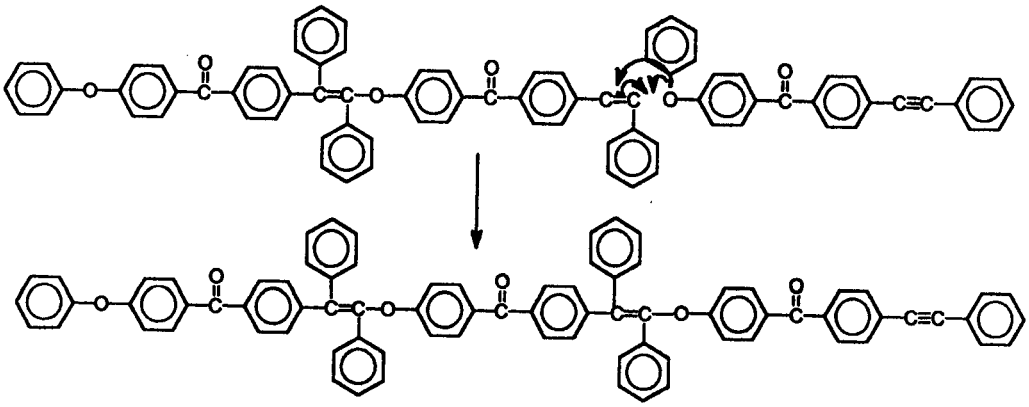


Figure 8. Mass Spectrum Supporting Formation of Cyclobutadiene Intermediate and Rearrangement

3.3.2 Trimers There appeared one major trimer peak in the chromatograms of all cured samples. These results suggest one preferred trimer structure. Of the possible combinations of monomer adding to each type dimer, the only conclusive mass spectral results obtained thus far indicate that the stable form of trimer found is the dimer formed through a phenylethynyl-phenoxy end adding to the monomer through the phenoxy end. A possible reaction is shown in Scheme 4. The mass spectrum given in Figure 9 contains peaks at 824, 917, 945, and 1022 which support this structure. Several other reaction schemes and products were analyzed, including a product formed by cyclotrimerization with three monomers reacting through the phenylethynyl ends to form an aromatic structure. No mass spectral evidence was found which supported this pathway. The trimer formed by the tail-to-tail dimer with the ethynyl end of a monomer was also extensively examined. Several mass spectra contained fragments found for this structure but none that were unique to it, making the analysis inconclusive.

Scheme 4



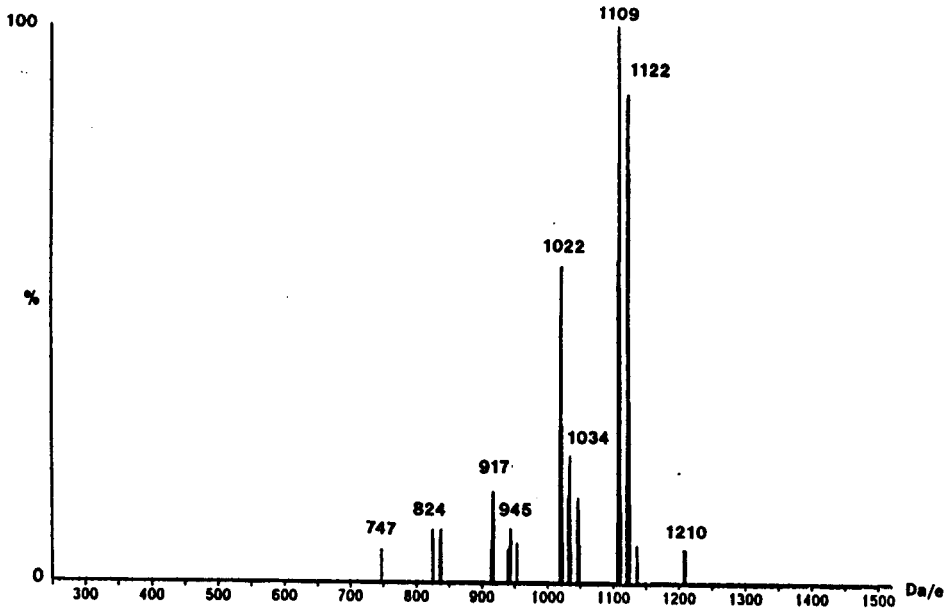


Figure 9. Mass Spectrum Supporting Trimer Scheme 4 Product

3.3.3 Tetramers Numerous chromatographic peaks shown in Figure 3 suggest many different tetramer structures exist. The possible combinations of different dimer structures and their cis-trans isomers give rise to various conceivable tetramer structures. Mass spectra obtained for tetramers were unable to distinguish among structures because few possible fragments had unique molecular weights. Additionally, the tetramers appeared to be more stable than lower molecular weight species and exhibited less fragmentation. Many of the mass spectra were very similar. The one given in Figure 10 is typical. Nearly every peak can be attributed to a tetramer structure.

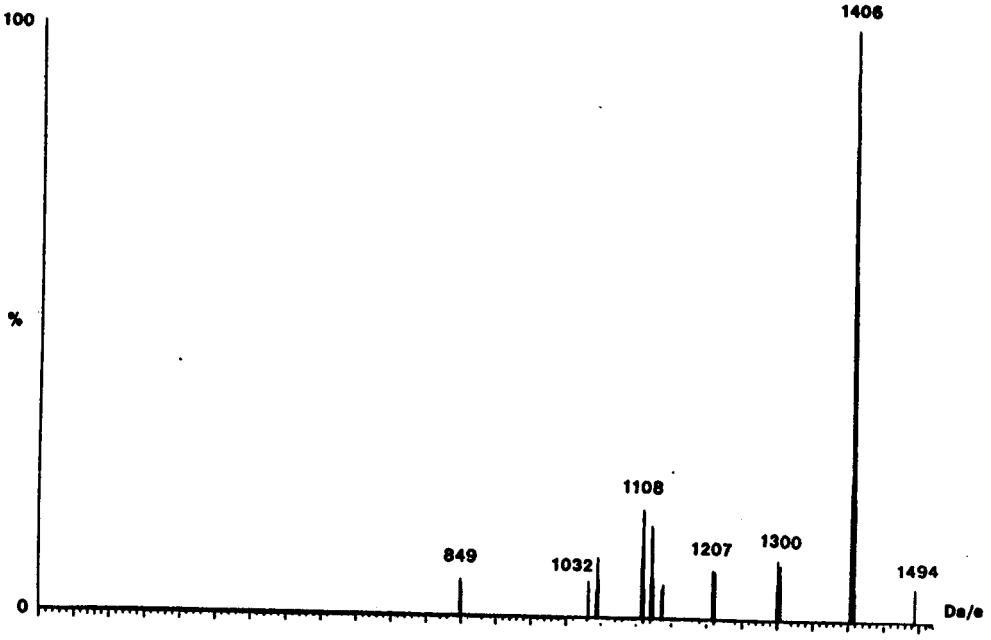


Figure 10. Typical Tetramer Mass Spectrum

4. CONCLUSION

The cure of 4-PPEB demonstrates the complexity of the cure of phenylethynyl terminated resins. Many initial cure products were separated and attempts at identification and possible cure mechanisms were made. This system appears to react at both the phenylethynyl and the phenoxy ends at these temperatures. Additional work is ongoing to determine if an ethynyl phenyl ring migrates to provide additional thermal stability or if low molecular weight diradical structures are actually stable at high temperature.

5. REFERENCES

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