

# Synthesis, Characterization, and Cure of Allyl and Propargyl Functionalized Indene as a Thermoset Composite Matrix Resin

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**ABSTRACT:** Two highly functionalized resins were synthesized by the phase transfer reaction of indene with propargyl bromide or allyl chloride in the presence of strong base. The resins consisted of a mixture of tri- and tetrafunctional indenenes with 60–80% of the product being tetrafunctional. The allylated (AL) and propargylated (PL) indene resins were thermally cured without added catalysts. Both resins exhibited a broad, highly exothermic cure with a peak energy at 320°C for AL resin and 282°C for PL resin. Thermal degradation of cured AL resin was found to begin at approximately 400°C with a carbon yield of 20% of its initial weight at 1000°C. Carbon yields for cured PL resin were excellent, with 68% retention of weight at 1000°C. Unidirectional, carbon fiber composites were fabricated from the substituted indene resins. AL–carbon fiber composites gave modulus values of 126 GPa and strength values of 967 MPa, while PL–carbon fiber composites gave modulus values of 116 GPa and strength values of 935 MPa in three-point bending tests. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 475–482, 1998

**Key words:** allylindene; propargylindene; carbon–carbon composites; high char yield resins

## INTRODUCTION

The indene ring system has been used in a variety of organic syntheses and reactions over the years. A number of researchers have studied the cationic polymerization of this cycloalkene,<sup>1,2</sup> while others have focused on its photochemical properties.<sup>3</sup> One of the unique properties of indene is its ability to react multiple times with electrophilic groups through replacement of the acidic protons on the five-membered ring. As early as 1900, researchers found that alkylation of indene could be accomplished with strong bases such as  $\text{NaNH}_2$  or

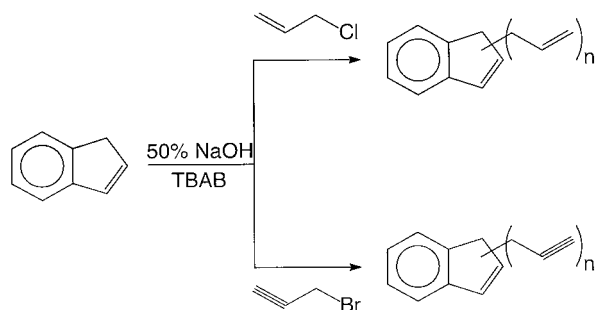
$\text{NaH}$ .<sup>4</sup> In 1966, Makosza used phase transfer conditions in the presence of aqueous  $\text{NaOH}$  to alkylate indene with dibromoalkanes.<sup>5</sup> Makosza also reported that, in the presence of highly active reagents such as allyl and benzyl halides, multiple substitution of the condensed cyclopentadiene ring took place. Similar chemistry has also been reported more recently in the tertbutylation of indene by Dehmlow and Bollmann.<sup>6</sup>

Past work in our group has focused on the development of allyl and propargyl functionalized cyclopentadienes.<sup>7,8</sup> As in the case of indene, the acidic protons of cyclopentadiene are highly susceptible to substitution under phase transfer conditions in the presence of a strong base. The multifunctional resins synthesized were thermally curable without added catalysts to give highly

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**Figure 1** Synthesis scheme for allylated and propargylated indene.

crosslinked materials. With allylated cyclopentadiene (ACP), carbon fiber composites were obtained that possessed good mechanical properties plus excellent moisture and chemical resistance. For the propargylated cyclopentadiene resin (PCP), exceptional carbon char yields (75%) were found on heating to 1000°C. Composites made with this brittle resin also showed good mechanical properties but lacked the strength of typical composite materials.

In a continuing effort to evaluate structure–property relationships in multifunctional allyl and propargyl systems, we have extended our efforts from cyclopentadiene to indene. Here, we report the synthesis, characterization, and cure behavior of allylated and propargylated indene resins and evaluation of the properties of carbon fiber composites made with them.

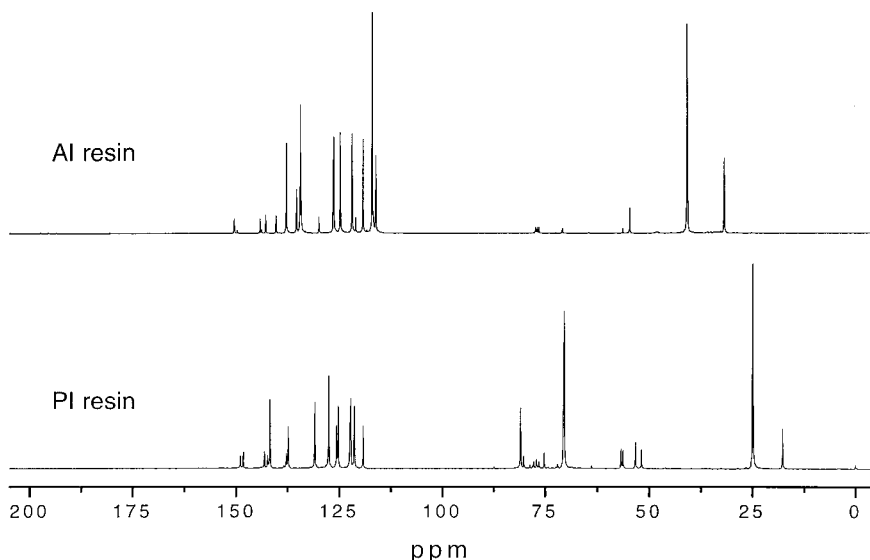
## EXPERIMENTAL

Indene, allyl chloride, propargyl bromide, and tetrabutylammonium bromide were obtained from Aldrich Chemical Company (Milwaukee, WI) and used without further purification. All solvents were obtained from Fisher Scientific (Pittsburgh, PA) or Aldrich. AS-4 unsized carbon fiber was donated by Hercules Chemical Company of Wilmington, DE.

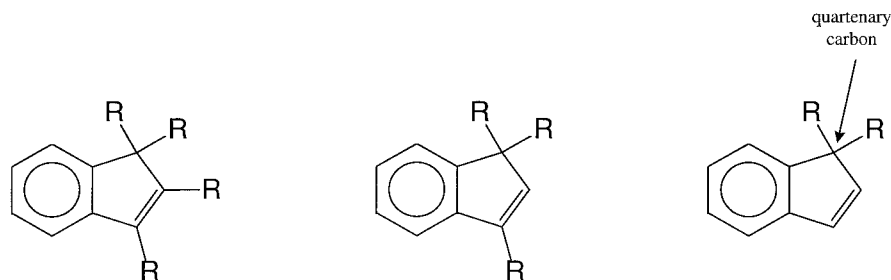
Cure analysis was accomplished using a TA Instruments DSC 2920 differential scanning calorimeter. Infrared (IR) spectra were collected on an Mattson ATI Galaxy Series Fourier transform infrared (FTIR) 5000 FTIR spectrometer. Solution  $^{13}\text{C}$  and  $^1\text{H}$  spectra were obtained on a Bruker AC-300 instrument. Three-point bending tests were carried out on a Materials Testing System (MTS) mechanical analyzer with a sample length-to-thickness ratio of 24:1 and a transverse speed of 2 mm/min. Composite cure was done in a Dake heated press.

### Synthesis of Allylated Indene (AL)

The synthesis schemes for allylation and propargylation of indene are shown in Figure 1. In the allylation reaction, a 50% aqueous NaOH solution (100 mL) was combined with tetrabutylammonium bromide (0.832 g, 2.6 mmol) in a three-necked round-bottom flask equipped with an addi-



**Figure 2**  $^{13}\text{C}$  solution NMR of substituted indene resins using allyl chloride (upper trace) and propargyl bromide (lower trace).



**Figure 3** Chemical structures of tetra-, tri-, and disubstituted indenenes.

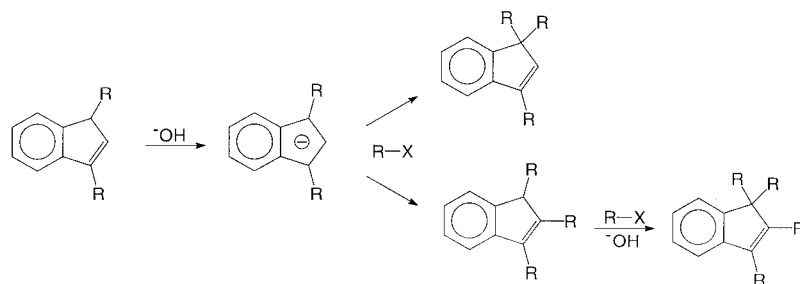
tion funnel, condenser,  $N_2$  inlet and outlet, and a magnetic stir bar. Indene (10 g, 86.0 mmol) was added to the flask dropwise with rapid stirring. As the indene was added, the mixture began to turn a bright green color believed to be associated with formation of the indenyl anion. The reaction was heated to  $50^\circ\text{C}$ , and allyl chloride (32.9 g, 430 mmol) was added dropwise over a period of approximately 60 min. The reaction mixture turned dark green during addition of allyl chloride but gradually became bright yellow as the reaction proceeded. After complete addition, the temperature was raised to  $70^\circ\text{C}$ , and the mixture was allowed to continue reacting with rapid stirring for approximately 6 h; the flask was then cooled to ambient temperature.

The product was isolated by first separating the organic and aqueous phases. The organic phase was then washed once each with dilute acid (150 ml), water (150–200 ml), and brine solution (150–200 ml). The organic phase was dried over  $\text{MgSO}_4$  for several hours,  $\text{MgSO}_4$  was filtered off, and the excess allyl chloride and allyl ether (formed during the reaction) were removed under reduced pressure. The product was a clear, golden liquid obtained in approximately 90% yield based on indene. FTIR (NaCl plate) measurements were as follows: 3075, 3006, 2977, 2900, 2834, 1833, 1639, 1465, 1434, 1413, 993, 914, 825, 754,

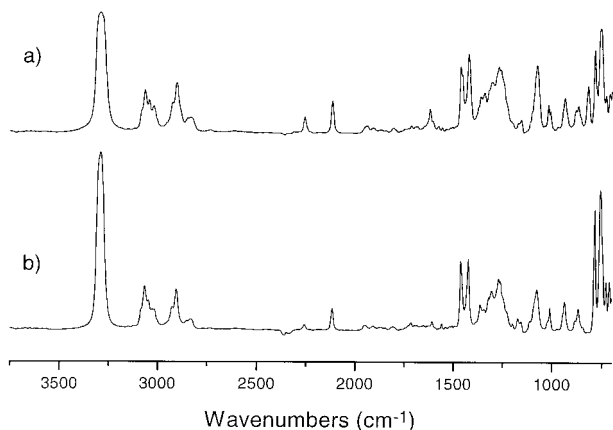
and  $705\text{ cm}^{-1}$ . Vacuum distillation of the crude mixture gave two fractions in approximately 90% purity, each with the following  $^{13}\text{C}$ -NMR peaks ( $\text{CDCl}_3$ ). Lower boiling fractions were as follows: 40.97 ( $\text{CH}_2$ ), 56.38 (C), 117.13 (vinyl  $\text{CH}_2$ ), 119.33 (CH), 121.11 (CH), 122.05 (CH), 124.82 (CH), 126.62 (CH), 129.97 (CH), 134.34 (CH), 143.00 (CH), 143.97 (C), and 149.80 (C) ppm; higher boiling fractions were as follows: 31.99 ( $\text{CH}_2$ ), 41.02 ( $\text{CH}_2$ ), 54.84 (C), 116.21 (vinyl  $\text{CH}_2$ ), 117.06 (vinyl  $\text{CH}_2$ ), 119.36 (CH), 122.03 (CH), 124.88 (CH), 126.45 (CH), 134.59 (CH), 135.48 (CH), 137.97 (CH), 140.44 (C), 144.34 (C), and 150.58 (C) ppm.

#### Synthesis of Propargylated Indene (PL)

A 50% aqueous NaOH solution (100 ml) was combined with tetrabutylammonium bromide (0.832 g, 2.6 mmol) in a three-necked round-bottom flask equipped with an addition funnel, condenser,  $N_2$  inlet and outlet, and a magnetic stir bar. Due to autoxidation in the multipropargyl system, precautions were taken to eliminate  $\text{O}_2$  from the reaction. The mixture of NaOH and TBAB was cooled in an ice bath and placed under 0.1 mm vacuum. The vessel was then sealed using a stopcock on the inlet adapter, and the vacuum hose was removed. A nitrogen gas source was attached to the



**Figure 4** Reaction pathways for continued substitution of a disubstituted indene.



**Figure 5** FTIR spectra of (a) crude PL resin and (b) PL resin vacuum distilled.

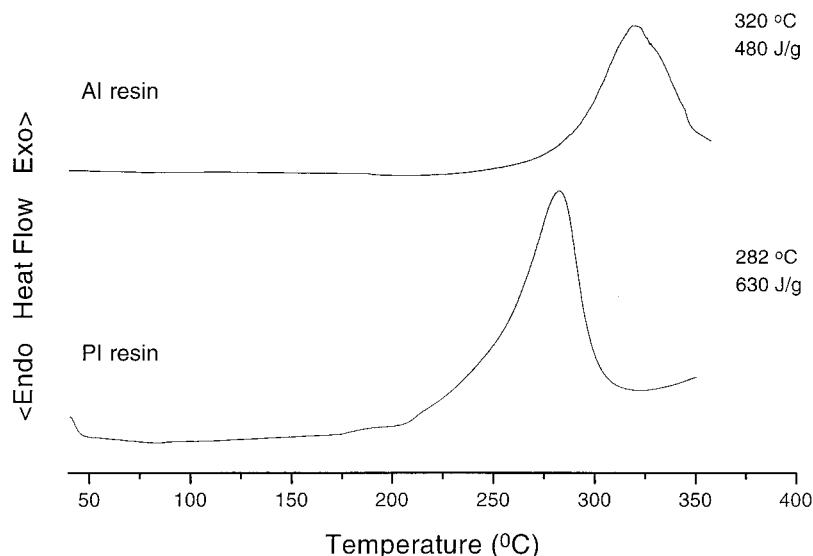
inlet adapter, the stopcock was opened, and the vessel was charged with  $N_2$ . This process was repeated to ensure complete removal of  $O_2$ . The ice bath was removed and indene (10 g, 86.0 mmol) was added to the mixture at room temperature with rapid stirring. The flask was then heated to  $50^\circ C$  with an oil bath and propargyl bromide (51.2 g, 430 mmol) was added over a period of approximately 60 min. The temperature was then raised to  $70^\circ C$ , and the reaction continued for 6–10 h.

The crude product was cooled to ambient temperature, and the organic and aqueous phases were separated in a separatory funnel. The organic phase was washed once with water (200 ml)

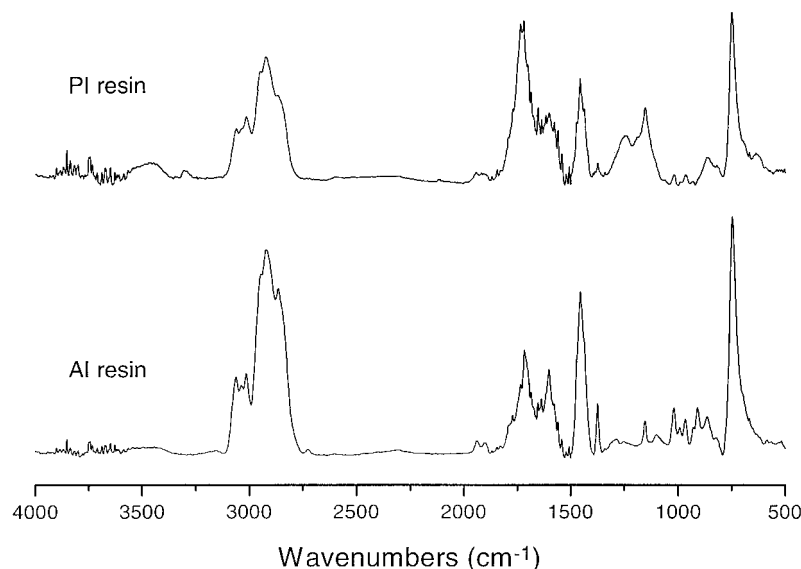
and twice with brine solution (200 ml). A small amount of hydroquinone was added to the organic phase to minimize autoxidation. The product mixture was dried over  $MgSO_4$  and filtered. Solvent, excess propargyl bromide, and propargyl ether (formed during reaction) were then removed under reduced pressure. The resulting material was an amber colored, clear liquid; vacuum distillation was unsuccessful in separating the two major products, although it did remove by-products; the yield was approximately 85%, based on indene. FTIR (NaCl plate) measurements were as follows: 3291, 3066, 3016, 2936, 2829, 2117, 1463, 1425, 1363, 1305, 1270, 1075, 1019, 939, 860, 785, 758, and  $647\text{ cm}^{-1}$ .  $^{13}C$ -NMR ( $CDCl_3$ ) measurements were as follows: 17.73, 24.95, 25.27, 51.89, 53.33, 56.32, 56.80, 70.49, 70.59, 70.74, 75.27, 80.01, 81.01, 119.23, 121.41, 122.28, 122.43, 125.27, 125.67, 127.60, 130.92, 137.41, 137.88, 141.83, 142.38, 143.14, 148.29, and 149.00 ppm.

### Composite Formation

Unidirectional composites were made in a stainless steel mold with three compartments measuring  $60.5 \times 13\text{ mm}$ . The mold surfaces were sprayed with Fluo-Kem (Aldrich) to facilitate removal of the composites after cure. Composites were formed by placing a layer of carbon fiber bundles in the mold cavities and wetting them with either AL or PL resin. The fibers were spread



**Figure 6** DSC thermograms of allyl-substituted indene resin (upper trace) and propargyl resin (lower trace) at  $10^\circ/\text{min}$ .



**Figure 7** FTIR spectra of cured allyl-substituted indene resin (lower trace) and propargyl resin (upper trace).

out to achieve homogenous distribution. This process was repeated until the desired thickness (usually 1.75–2.00 mm) was achieved. Stainless steel plugs, machined to have a small amount of clearance around the sides of the cavity, were then inserted. A heated mechanical press was used to squeeze excess resin and voids from the composite (approximately 100 psi) and then cure the materials by heating at 175°C for 6 h and at 250°C for 6 h under 500–1000 psi of pressure. Samples were then subjected to a post cure of 300°C for 4 h.

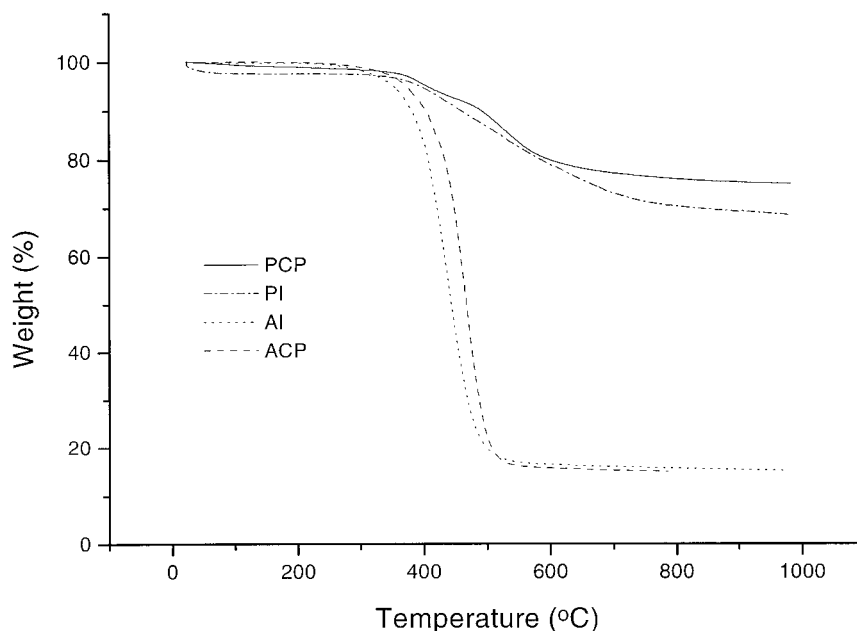
## RESULTS AND DISCUSSION

### Allylated Indene Resin Synthesis

The  $^{13}\text{C}$  solution nuclear magnetic resonance (NMR) spectrum of the washed and dried product of the phase transfer reaction of allyl chloride and indene is shown in Figure 2 (upper trace). The spectrum appears complicated on first glance but consists of peaks (discussed below) that can be assigned to two components in an approximate 1 : 4 ratio. Gas chromatography analysis (GCA) of the product confirmed that this was a mixture of the following two major products: a lower retention time material composing approximately 20% of the total, and a higher retention time product making up the remaining 80%. Because exhaustive alkylation conditions were used, residual ali-

phatic CH groups should not be present, and formation of quaternary carbons was assured. This results in only nonreactive products, such as those shown in Figure 3. The initial assumption was that the major products were the di- and trisubstituted derivatives (middle and right-hand structures in Fig. 3); i.e., reaction at the 2-position to give the left-hand structure is unlikely, based on resonance stabilization of the intermediate (benzyl) anions at the 1- and/or 3-position.

Vacuum distillation gave two fractions with the lower retention value material as the lower boiling fraction. The two purified products were easily distinguished from each other, and from possible mono- and tetrasubstituted products, by their  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra in comparison to that of indene. First, no evidence of an  $\text{sp}^3$  hydrogen was observed for either derivative (appearing at 3.26 ppm for indene), confirming formation of products with only quaternary  $\text{sp}^3$  carbon atoms. Second, the peaks at 56.4 and 54.8 ppm correspond to the quaternary carbons of the high and low boiling fractions, i.e., to the two structures shown in the middle and right of Figure 3, respectively. The peak at 40.9 ppm is the only allyl  $\text{CH}_2$  peak in the spectrum of the purified 1,1-diallyl derivative (both methylenes are chemically identical), while two allyl  $\text{CH}_2$ s were seen for the trisubstituted compound (at 41.0 and 32.0 ppm) in a 2 : 1 ratio for the two identical 1-allyls and the 3-allyl group,



**Figure 8** TGA under nitrogen atmosphere of cured AL and PL resins taken at 20°C/min compared to ACP and PCP resins.

respectively. Other peaks were assigned using DEPT  $^{13}\text{C}$ -NMR analysis (Distortionless Enhancement of Polarization Transfer) to identify CH,  $\text{CH}_2$ , and quaternary carbon peaks. The latter in the aromatic region (indene core quaternary carbons; furthest four downfield peaks in Fig. 2, upper trace) confirm the 1 : 4 ratio of products.

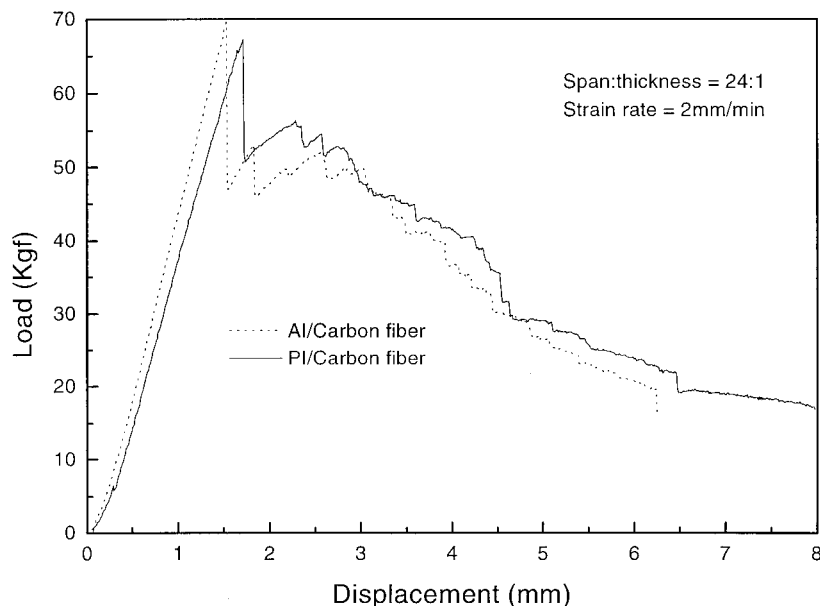
Although the reaction to form the quaternary carbon of the 1,1-diallyl derivative occurs to some extent before complete substitution (20% here), this reaction is unfavorable due to the steric hindrance caused by the first substituent. This is similar to what has been reported for the phase transfer methylation<sup>9</sup> and allylation<sup>7</sup> of cyclopentadiene and results in the majority product being trisubstituted. That is, reaction occurs at the 1- and 3-positions before disubstitution at one of these two. That is, the key intermediate is that formed in Figure 4, which then leads to the upper product in Figure 4 as the major one obtained. While it is possible for reaction to occur at the 2-position before inactivation, no evidence for tetra-substituted products was observed for either allyl or propargyl systems.

### Propargylated Indene Resin Synthesis

GCA of the product of the phase transfer reaction of propargyl bromide with indene again showed

a mixture of mostly two products. The product mixture was composed of 42% disubstituted and 50% trisubstituted product, along with about 5% of a lower retention time by-product and 3% of a higher GC-retention time material that appears to result from oxidation. The presence of more disubstituted material in the PL system is due to the higher reactivity of propargyl bromide, which reduces selectivity and allows the electrophile to overcome the steric inhibition involved in quaternary carbon formation that terminates further substitution. Similar behavior was observed with cyclopentadiene reaction where higher amounts of the lower substituted propargyl derivatives were obtained than of the allyl compounds.<sup>8</sup>

IR and  $^{13}\text{C}$  spectra of the crude materials (Figs. 2 and 5) showed peaks consistent with di- and trisubstitution. The peaks at 53.3 and 51.9 ppm in the  $^{13}\text{C}$ -NMR spectrum correspond to the quaternary carbons of the substituted indenenes and are present in an approximate 1 : 1 ratio (confirmed by the two pairs of aromatic quaternary carbon peaks furthest downfield). The peaks at 24.3, 24.9, and 17.8 ppm are due to the methylene carbons of the two main types of propargyl moieties. Again, this last peak is assigned to the unique methylene of the trisubstituted product attached to the indene double bond (at the 3-position). The peaks at 56.7 and 56.3 were determined



**Figure 9** Three-point bend analysis of unidirectional PL-carbon fiber and AL-carbon fiber composites.

to be methylene carbons by DEPT and are indicative of some type of propargyl ether formation. This was further confirmed by the peak at  $1070\text{ cm}^{-1}$  in the IR spectrum attributed to an ether moiety, while a second  $\text{C}\equiv\text{C}$  stretch at  $2250\text{ cm}^{-1}$  is indicative of a propargyl ether.<sup>10</sup> It is therefore believed that the higher retention material is due (perhaps) to oxidation of the indenyl ring and/or the attached propargyl moiety during workup, leading to ether formation with other propargyl functionalities. Vacuum distillation was used to reduce the concentration of this impurity to undetectable values (bottom spectra, Fig. 5). However, this further step of purification is not crucial since the concentration of impurity is small, even in the crude product.

### Thermal Cure and Characterization

Shown in Figure 6 are the DSC thermograms of neat AL and PL resins. Both resins showed a broad exotherm with peak cure for the AL resin occurring at  $320^\circ\text{C}$ ; the peak cure for the PL resin occurred at  $282^\circ\text{C}$ . This is due to greater reactivity of the propargyl moieties compared to the allyl moieties on bulk thermal cure. In addition, the thermal cure of the PL resin is a high-energy process, with an enthalpy of cure of  $630\text{ J/g}$ . The enthalpy of cure for AL resin is only  $480\text{ J/g}$  but is still a rather exothermic process due to the high

degree of functionality on each molecule. Similar results were seen by us for ACP and PCP resins.<sup>8</sup>

Figure 7 shows the IR spectra of cured AL and PL resins. In both cases, the peaks associated with the  $\text{C}-\text{H}$  stretch of the reactive functional group ( $3075\text{ cm}^{-1}$  for allyl;  $3290\text{ cm}^{-1}$  for propargyl) are undetectable. In addition, the broadening of the aliphatic  $\text{C}-\text{H}$  region indicates formation of new aliphatic moieties through ene rearrangements and polyaddition reactions, as previously reported for ACP and PCP.<sup>7,8</sup> Oxidation also plays a role in the cure of these materials with new peaks being seen at  $3600-3300\text{ cm}^{-1}$ , corresponding to the  $\text{O}-\text{H}$  stretch of an alcohol, and at  $1700\text{ cm}^{-1}$ , corresponding to the  $\text{C}-\text{O}$  stretch of a carbonyl. Oxidation during cure is slight and occurs to a greater degree in the PL resin than the AL material.

### Thermal Stability and Carbon Yields

Thermogravimetric analysis (TGA) results for cured AL and PL resins are shown in Figure 8 versus previously reported ACP and PCP results. AL resin behaved very similar to ACP resin, with onset of degradation occurring at approximately  $400^\circ\text{C}$  and resulting in a 15% carbon yield at  $1000^\circ\text{C}$ . PL resin, on the other hand, gave excellent carbon yields at  $1000^\circ\text{C}$ , retaining 68% of its initial weight. However, carbon yields for the PL

**Table I Flexural Storage Modulus, and Strength Values for AI–Carbon Fiber, PI–Carbon Fiber, ACP–Carbon Fiber, and PCP–Carbon Fiber Composites**

Composite	Flexural Modulus ( $E_f$ ; GPa)	Flexural Strength ( $\sigma_f$ ; MPa)
AI–Carbon	126	967
PI–Carbon	116	935
ACP–Carbon	165	965
PCP–Carbon	115	920

resin were slightly below those found for PCP resin (75%). This is counterintuitive since greater carbon yields should be obtained for systems with higher aromatic content. This demonstrates the high degrees of coalescence and crosslinking occur in the PCP system since increased aromatic content for the indene resin did little to affect the final carbon yield of structurally similar propargylated cyclopentadiene systems.

#### Carbon–Carbon Composites and Composite Properties

Three-point bending tests were used to evaluate the room temperature mechanical properties of AL and PL carbon fiber composites containing approximately 40 wt % resin. Shown in Figure 9 are typical load versus displacement curves for the composite samples. The flexural modulus and strength values for the two types of composites (given in Table I) are nearly equal, with the AL composites having only a slightly higher modulus and strength. The strength values in these composites are relatively low, indicative of poor interphase formation. This is due to hypercrosslinking and brittle failure in the matrix similar to what was seen in ACP and PCP composites. The slight reduction in reactive functionality in the substituted indene resins over the analogous cyclopentadiene resins did little to improve overall mechanical properties of their carbon fiber composites.

## CONCLUSIONS

High degrees of functionality can be obtained in substituted indenenes through the use of phase transfer conditions in the presence of a strong base and highly active electrophiles, such as allyl chloride or propargyl bromide. The higher reactivity of the propargyl bromide, however, reduces the average degree of substitution due to its reactivity overcoming steric hindrance toward quaternary carbon formation, which terminates further substitution (e.g., Fig. 4).

Cure and composite properties of the indene resins were similar to the analogous cyclopentadiene resins. The reduction of functionality did little to improve the strength of these composites due to hypercrosslinking in all the systems; i.e., the slight reduction in functionality does little to reduce crosslink density and brittleness. In addition, the reduction in functionality produced a slightly lower carbon yield in the PL resin on heating to 1000°C compared to PCP resin despite the increase in aromatic content. This demonstrates that it is the propargyl functionality that controls the ultimate carbon yields in these multifunctional propargyl systems.

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