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A Fast Thermally Curing Naphthyl−Ethynyl Imide

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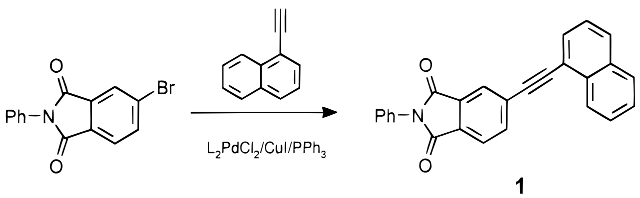
Phenyl−ethynyl terminated imide oligomers can be thermally cured to afford a final resin that possesses excellent mechanical and chemical properties pivotal to high-performance composite applications.[1,2] Typical curing temperatures for the neat oligomer are generally near 350 °C, and the chemical reaction or reactions leading to the final resin appear to be multifaceted.[3] The entire cure process appears to follow a complicated rate law.[4] Some of the most recent studies have suggested that first-order (*pseudo*) kinetics are followed for the initial 90% of the reaction for both an oligomeric material and a bis(phenylethynyl) model compound.[5] Other mechanistic studies have demonstrated the complexity of the curing process.[6,7] It is interesting to note that in each study performed to date, there is reasonably good agreement between the kinetic data observed for oligomeric material and their model compound analogues.[3,5] This latter point would appear to validate the use and study of small molecules to probe both the mechanism and products for at least a majority of the curing reaction(s).

We have recently initiated a research program to design and prepare new aryl−ethynyl model compounds and end-capped oligomeric materials. Our research effort is directed at developing prepolymers which can be cured at lower temperatures yet produce a final material that possesses the excellent chemical, thermal, and mechanical properties associated with NASA's thermally cured PETI-5.[2] In the present study we present the synthesis, thermal curing, and kinetic analysis of a naphthyl−ethynyl imide model compound, which cures at a significantly faster rate than the phenyl−ethynyl analogue.

We recognized from review of the literature that no previous studies had explored the use of polycyclic aromatic rings as end-capping groups. This substitution would appear to provide the necessary thermal stability and provide a significant change in stereoelectronics (to be discussed further below). The naphthyl−ethynyl model (**1**)[8] was prepared in high yield using standard ethynylation techniques.[9]



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Thermal curing of **1** was carried out in sealed Pyrex vessels under a nitrogen atmosphere. A set of eight samples were placed in a calibrated aluminum heating block, and at selected reaction times, a sample was removed and then analyzed by proton NMR spectroscopy. The entire sample was dissolved in $CDCl_3$ that contained an integration standard of 1,2-dichloroethane. The concentrations were determined directly by integration of the NMR signals for the phthalimide singlet at δ 8.20 ppm to the dichloroethane singlet at δ 3.73 ppm. It is important to note that all reaction samples were completely soluble in the NMR solvent (both products and reactants) for all data points. In addition, we observed an induction period for each sample that we attribute to the time needed for the sample to equilibrate to the heating block temperature. Applying first-order data analysis (i.e. $\ln(C/C_o)$ vs time) we obtained uniformly good line fits and used the observed rate constants (k) in Arrhenius plots to determine the apparent energy of activation (E_a). To strike a better comparison we also performed a kinetic analysis on the phenyl−ethynyl imide model compound: *N*-phenyl-4-(phenylethynyl)phthalimide (**2**) (Figure 1).

The E_a values found for naphthyl−ethynyl **1** and phenyl−ethynyl **2** model compounds are 45 ± 1.7 kcal/mol and 42.5 ± 1.0 kcal/mol, respectively. The activation energy we measure for the phenyl-ethynyl compound is somewhat higher than that determined previously (36.5 kcal/mol).[6] The value of 42.5 kcal/mol for **2** is similar to a related model compound, 3,4′-bis[4-(phenylethynyl)phthalimido]diphenyl ether, which also follows first-order kinetics ($E_a = 40.7 \pm 2.7$ kcal/mol).[5] The fact that the apparent energy of activation is similar for the naphthyl−ethynyl compound yet the reaction rate is faster at normal curing temperatures is intriguing and useful. Hence, we can obtain similar cure rates for the naphthyl−ethynyl analogue at a temperature ~30 °C below that needed for the phenyl−ethynyl system. Preliminary studies of the thermal cure of naphthyl−ethynyl-terminated imide oligomers have also revealed a similar rate acceleration.

We have analyzed the curing model reactions using size exclusion chromatography (SEC)[10] to better understand the products and help in confirming that the curing reaction of the naphthyl and phenyl systems are similar (Figure 2). In each kinetic run studied, we find a low molecular weight material forming (~1000) with no indication of oligomeric or polymeric products forming. These data support the premise that the naphthyl system is undergoing a curing chemistry similar to that of the phenyl−ethynyl model compound. Thermal gravimetric analysis under a nitrogen atmosphere also showed the two systems to possess similar thermal stability (>300 °C).

The significant increase in the rate of curing for the naphthyl-ethynyl system must be due to a difference in the Arrhenius constant. Hence, there are reaction parameters (e.g. stereoelectronic factors, collisional parameters, etc....) that enable the naphthyl−ethynyl system to produce more successful results (i.e. curing of the ethynyl group) for a given amount of applied external energy. A brief examination of molecular orbital calculations[11] suggests indeed that there are significant differences between the highest occupied molecular orbitals (HOMO) of **1** and **2**. Notably, the HOMO orbital shows a great deal of "movement" from the alkyne in **2** to the naphthyl ring (carbon-4 in particular) in **1**.

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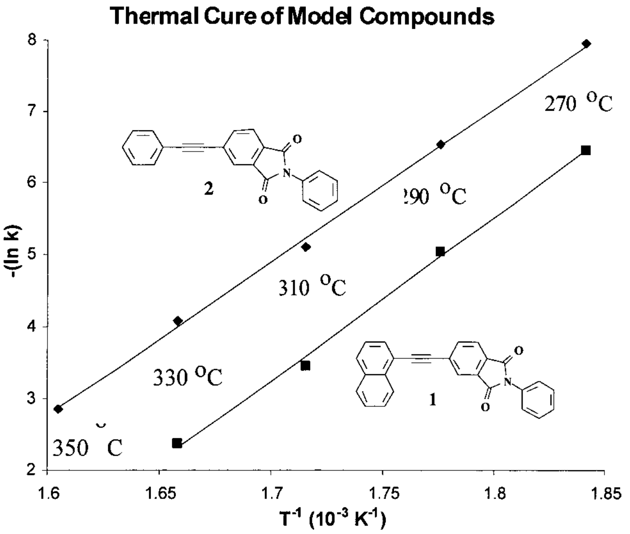

Figure 1. Arrhenius plot of thermal cure of model compounds: ■ = model compound **1**, $R^2 = 0.998$; ◆ = model compound **2**, $R^2 = 0.997$.

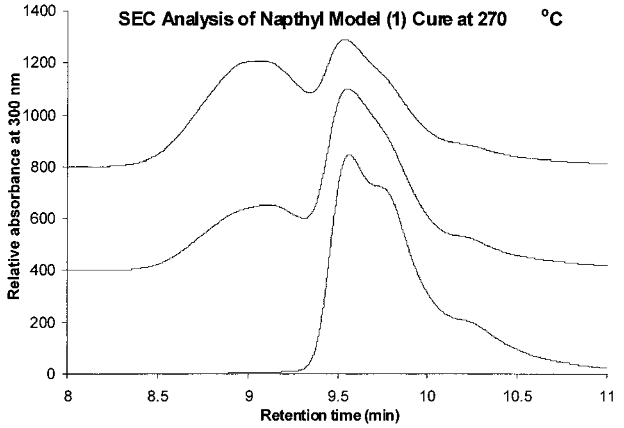

Figure 2. SEC trace of cured model compound **1** samples in relative absorbance units: top, cure time = 360 min, mol/mol$_0$ = 0.56; middle, cure time = 180 min, mol/mol$_0$ = 0.80; bottom, cure time = 0 min, mol/mol$_0$ = 1.00.

In summary, the present study reveals a successful approach to increasing the rate of curing for aryl–ethynyl compounds by simply changing from a phenyl– to a naphthyl–ethynyl system. Currently, we are exploring the utility of this enhanced reactivity and building additional ethynyl analogues in order to probe the reasons behind this newly discovered curing efficiency.

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References and Notes

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(8) Compound **1** was isolated in 55% overall yield as a yellow crystalline solid. Selected physical, spectroscopic, and analytical data: mp 176–178 °C; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.40–7.68 (m, 8 H), 7.83 (d, $J = 7.2$ Hz, 1 H), 7.91 (dd, $J = 6.5, 4.7$ Hz, 1 H), 7.98 (d, $J = 7.8$ Hz, 1 H), 8.03 (d, $J = 7.5$ Hz, 1 H), 8.20 (s, 1 H), 8.42 (d, $J = 8.4$ Hz, 1 H); ^{13}C NMR (CDCl$_3$) δ 92.7, 92.9, 119.8, 124.0, 125.5, 126.1, 126.69, 126.72, 126.9, 127.4, 128.4, 128.7, 129.4, 130.1, 130.2, 130.5, 131.3, 131.8, 132.2, 133.32, 133.35, 137.3, 166.8. Anal. Calcd for $C_{26}H_{15}NO_2$: C, 83.63; H, 4.05. Found: C, 83.67; H, 4.12.

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(10) SEC analyses of reaction samples were performed by dilution in THF (2 mg/mL) and then injection onto a Hewlett-Packard 1100 HPLC (column: PL 300 × 7.5 mm, 5 μm particle size). Molecular weights are calculated relative to polystyrene standards.

(11) Both MINDO and ZINDO molecular orbital calculations (CAChe Scientific Inc. calculation package, version 3.7, 1994) were used in this preliminary evaluation.

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