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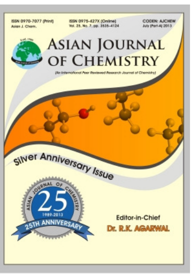

Study of Cure Kinetics of Vinyl-*tri*(phenylethynyl)silane Monomer†

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An isothermal cure kinetics of vinyl-*tri*(phenylethynyl)silane ($(ph\text{-}C{=}C)_3\text{-}Si\text{-}C{=}CH_2$) (VTPES) was investigated by differential scanning calorimetry in the temperature range 345-370 ºC. The results showed that the shapes of the conversion curves were all similar and all of the cure reactions could be described by an autocatalytic kinetic model.

Key Words: Vinyl-*tri*(phenylethynyl)silane, Differential scanning calorimetry, Cure kinetics, Autocatalytic reaction.

INTRODUCTION

In 1968, Luneva first reported the synthesis of diethynyldiphenylsilane in nitrogen atmosphere[1]. This kinds of silicon-containing arylacetylenic monomers can be cured thermally without volatiles. The polymers' high-temperature properties and high char yield resulted in a rapid development because of their potential applications in biomaterials, optoelectronics, ceramic precursors, *etc.*[2-7]. The thermal polymerization of arylacetylene compounds, in particular, phenylacetylene, had been studied for several years and mechanism and structures for these systems had been proposed in the literature[8-11]. It is interesting to these monomers stems from the fact that they could be processed into void-free components and the cured resins possessed excellent thermal stability as well as good mechanical properties. In general, the dielectric and mechanical properties of thermoset matrices were dependent on the degree of cure. Because the degree of cure was defined by the reaction kinetics, understanding the cure kinetics of these matrices became essential for defining final properties, process development and quality control. The cure chemistry of some of these monomers had been addressed earlier from a molecular structure and cure activation energy standpoint[12-15].

EXPERIMENTAL

Vinyl-*tri*(phenylethynyl)silane (VTPES) was prepared according to the literature[16].

Cure kinetics analysis: The differential scanning calorimetry (DSC) study was performed on Mettler-Toledo-DSC 821^e/400 in nitrogen atmosphere. Before measurements, the temperature and heat flow calibrations were done by a recommended procedure with pure indium metal (m.p. = 156.6 ºC). Then, the DSC cell was preheated to ambient temperature and approximately 8.5 mg of monomer was inserted as quickly as possible. During measurements, nitrogen, at a flow rate of 50 mL/min, was used as purge gas to minimize oxidation of the sample. The isothermal DSC analyses of the vinyl-*tri*(phenylethynyl)silane monomer were performed at different temperatures at the fastest heating rate (100 ºC/min). After measurement, the total area under the exothermic curve, based on the extrapolated baseline at the end of the reaction, was used to calculate the isothermal heat of cure (H_T) at a given temperature.

RESULTS AND DISCUSSION

The generation of accurate time-temperature-degree of conversion curves was of great practical importance for establishing optimum cure schedules[17]. The DSC curves from the isothermal mode at different temperatures were given in Fig. 1. The maximum of heat flow was highest when t = 30s and decreased with increasing cure time. The peak value of heat flow increased with increasing temperature and the time needed to get to the endpoint of the cure reaction shortened with increasing temperature. The area under the isothermal curve up to any time t represented the heat of the reaction at time t (H_t). α and $d\alpha/dt$ could be obtained according to literature[18].

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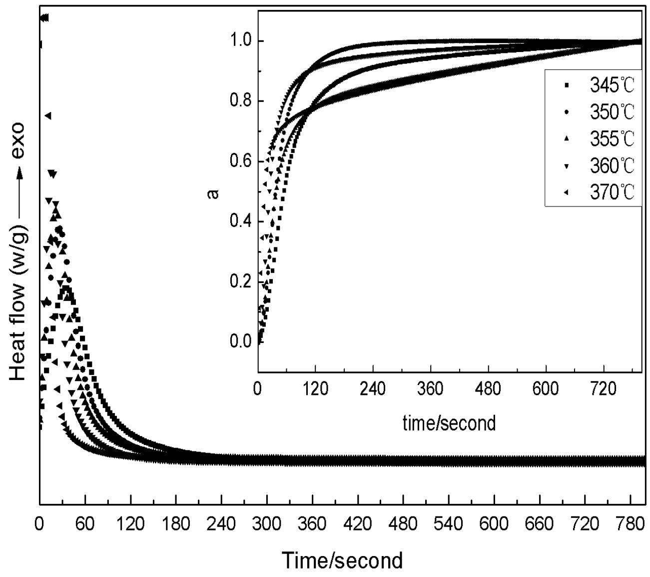

Fig. 1. DSC curves from the isothermal mode at different temperatures

The isothermal time-conversion profiles and the time-cure rate profiles for the VTPES monomer at different temperatures were given in Fig. 1. Conversion rate (a) increased with increasing cure time. The time to reach a = 0.6 at 345, 350, 355, 360 and 370 ºC were 65, 50, 45, 30 and 21 s, respectively. Therefore, respective cure rates at 350, 355, 360 and 370 ºC were 1.12, 1.22, 1.35 and 2.03 times faster than the cure rate at 345 ºC. It also showed that the time needed to achieve the highest a decreased with increasing temperature. This indicated that a complete cure could be obtained when the reaction temperature was above 370 ºC and that lower temperatures clearly necessitated longer reaction time to drive the reaction to completion. The initial steep rise in the time-conversion plot, followed by a very gradual increase, was suggestive of the kinetic behaviour of a diffusion-limited system[12]. At the initial stage of the cure reaction, the viscosity of the medium increased dramatically with the initial reaction of reactive groups of the monomer. When the effects of the decrease in both the concentration of the reactive ends and the ability for diffusive movement of those ends were combined, the rate of the reaction should have begun to diminish once these effects became substantially inhibiting. The effect of the viscosity increase could be minimized and a higher degree of conversion could be achieved as the cure temperature was raised.

The cure rate, represented by da/dt, shown as a function of cure time at different isothermal exposure temperatures from 345 ºC to 370 ºC was given in Fig. 2. With the increment of cure temperature, the maximum point appeared at shorter time and the value of differential cure rate at this point was increased. The maximum in the cure curve meant that the nature typically autocatalytic in all cases with the maximum rate of conversion after the start of the reaction, cure rates appeared about at t = 30s and the maximum da/dt occurred at a = 0.3 conversion, which was also a characteristic of the autocatalytic reaction[18].

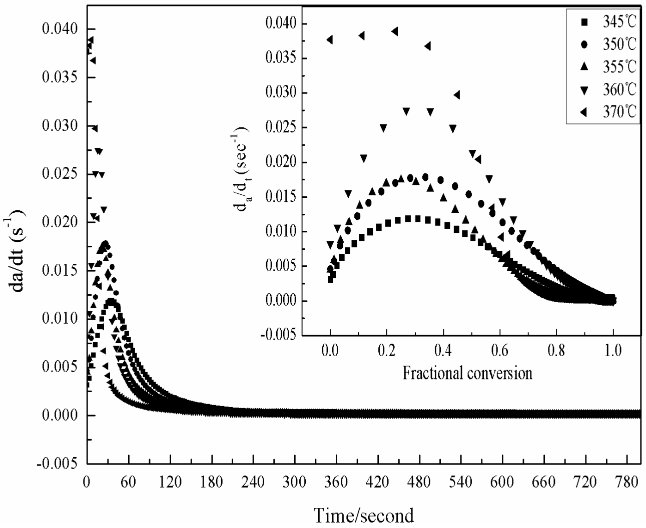

Fig. 2. Isothermal cure rate-time profiles for the VTPES monomer at different temperatures

Conclusion

The isothermal DSC study was carried out in the temperature range 345-370 ºC and all of the cure curves were typically sigmoid shape and cure reactions could be described by an autocatalytic kinetic model, which were in good agreement with the values calculated by non-isothermal cure kinetics analysis. Thus, it can be said that the cure reaction of silicon-containing arylacetylenic monomer was a first-order kinetic reaction.

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