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Two-dimensional correlation analysis study of the curing process of phenylethynyl end-capped imide model compounds

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ABSTRACT

The phenylethynyl end-capped imide model compounds 6F-PDA-PEAP and 6F-ODA-PEAP were prepared for detailed investigation of the thermal cure process. To probe the spectral changes of ethynyl C≡C moieties as well as imide rings and phenyl rings in PDA and ODA units during the thermal curing, we applied two-dimensional (2D) correlation analysis to the infrared spectra of 6F-PDA-PEAP and 6F-ODA-PEAP films. Thermal curing of 6F-PDA-PEAP and 6F-ODA-PEAP was influenced by molecular structure, and it induced spectral changes of C≡C moieties as well as imide rings and phenyl rings in PDA and ODA units. The thermal curing of 6F-PDA-PEAP and 6F-ODA-PEAP films induces the intensity changes of bands of imide and phenyl rings in PDA and ODA units before that of C≡C moieties.

1. Introduction

Ethynyl end-capped polyimide systems have attracted attention because of their ease of processing, good material properties, and potential applications [1,2]. In particular, phenylethynyl end-capped polyimide compounds exhibit processing characteristics (thermal and mechanical properties) that are superior to those of ethynyl end-capped polyimide systems [3]. Thus, much effort has been exerted to better understand the cure process of these materials.

Several different methods have been applied to investigate cure kinetics and cure products as a function of molecular structure. Fang et al. [4] intensively studied the cure kinetics of phenylethynyl end-capped imide model compounds using Fourier-transform infrared (FTIR) spectroscopy and thermal analysis. In addition, the cure products of these materials were analyzed using solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy [5]. Takekoshi et al. [6,7] evaluated the cure kinetics and cure product by high performance liquid chromatography (HPLC) and field desorption mass spectroscopy. These results suggested that the molecular structure of phenylethynyl end-capped imide compounds influenced the reaction order as well as the cure product. The phenylethynyl end-capped imide compounds with relatively simple molecular structures had a higher reaction order and induced the complicated cure reaction. The phenylethynyl end-capped imide compounds with bulk functional groups reduced the reactivity of the ethynyl moiety and induced the ethynyl to ethynyl addition reaction.

Based on these results and other research results, several reaction pathways were proposed to elucidate the thermal cure mechanism of phenylethynyl end-capped imide compounds [5,8]. In addition, it has been proposed that thermal curing of these compounds induced molecular rearrangement to form stable cure products [5]. However, the detailed segmental motion in these compounds has not been fully investigated.

Two-dimensional (2D) correlation spectroscopy is a well-established analytical technique that has considerable utility and benefits in various spectroscopic studies [9–12]. In particular, 2D correlation spectroscopy is a powerful technique for studying the inter- and intra-molecular interactions between spectral peaks and for determining the sequence of spectral changes. Several researchers have been applied 2D correlation spectroscopy to understand the detailed reaction pathway during thermal reaction such as crosslinking of polyurethane, epoxy curing reaction, imidization of poly(amic acid) [13–15]. However, specific sequence of spectral changes related to cure kinetics and cure mechanism of phenylethynyl end-capped imide compounds has not been fully examined.

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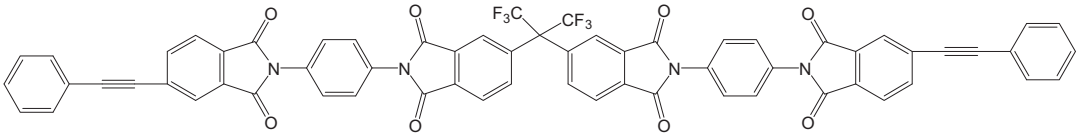
6F-PDA-PEAP 1:4



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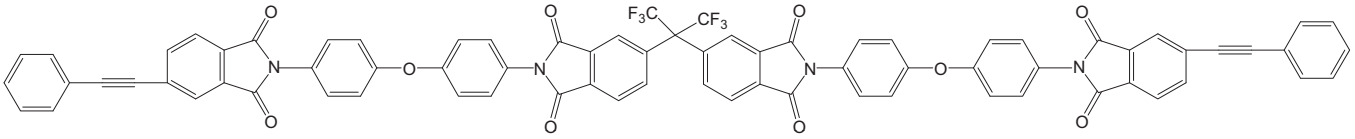

Fig. 1. Chemical structure of imide model compounds.

In this study, we examined the thermal curing of phenylethynyl end-capped imide model compounds (Fig. 1) prepared from 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6F) with two different diamines (e.g. 4,4-oxydianilline (ODA) and 1,4-phenylenediamine (PDA)) using FTIR spectroscopy. In particular, 2D correlation analysis of FTIR spectra was used to better understand the spectral changes of phenylethynyl and imide moieties in a phenylethynyl end-capped imide model compound during thermal curing.

2. Experimental details

2.1. Materials

4,4′-(Hexafluoroisopropylidene)diphthalic anhydride (6F) was supplied by Chriskev Company and purified by recrystallization from acetic anhydride. ODA, PDA, isoquinoline, and 4-(dimethylamino)pyridine (DMAP) were purchased from Aldrich Company, and 4-phenylethynylphthalic anhydride (PEAP) was purchased from TCI and used without purification. *N*-methyl-2-pyrrolidinone (NMP) was purchased from Aldrich Company and distilled over calcium hydride in a nitrogen atmosphere.

2.2. Synthesis of model compounds

The thermal curable model compound 6F-PDA-PEAP was synthesized as follows. First, 10 mmol (4.44 g) of FDA and 50 mmol (5.41 g) of PDA were dissolved together with 20 mmol (2.58 g) of isoquinoline and a catalytic amount of DMAP in dry NMP. The solution was gently heated with stirring at 70 °C for 2 h and refluxed with stirring for 12 h. The reaction solution was poured into water with vigorous stirring, giving 6F-amido-N,N′-4,4′-dianilline (6F-PDA) in the form of a precipitated powder. The precipitated powder was filtered and dried. The crude product was purified by recrystallization from the methanol/H_2O mixture and by drying *in vacuo*. Second, the thermal curable model compound with ethynyl groups, 6F-PDA-PEAP, was synthesized from the 6F-PDA and PEAP. A mixture of 5 mmol (3.12 g) of 6F-PDA and 11 mmol (2.73 g) of PEAP with 10 mmol (1.49 g) of isoquinoline and a catalytic amount of DMAP in dry NMP was stirred at 70 °C for 2 h; refluxed with stirring for 12 h; and poured into methanol. The precipitated solids were separated by filtration and washed thoroughly with methanol, leading to a precipitated model compound product. The precipitated polymer powder was filtered and dried, producing 6F-PDA-PEAP. Yield: 87.4%. ^{1}H NMR (δ, DMSO-*d*6): 8.24–8.22 (d, 2H, Ar*H*), 8.13 (s, 2H, Ar*H*), 8.10–7.98 (m, 6H, Ar*H*), 7.78 (s, 2H, Ar*H*), 7.69–7.58 (m, 12H, Ar*H*), and 7.52–7.44 (m, 6H, Ar*H*).

In the same manner, the 6F-ODA-PEAP compound was prepared from the reaction of 6F, ODA, and PEAP. Yield: 81.5%. ^{1}H NMR (δ, DMSO-*d*6): 8.24–8.18 (d, 2H, Ar*H*), 8.13 (s, 2H, Ar*H*), 8.10–7.96 (m, 6H, Ar*H*), 7.78 (s, 2H, Ar*H*), 7.70–7.64 (s, 4H, Ar*H*), 7.58–7.46 (m, 12H, Ar*H*), and 7.32–7.22 (m, 6H, Ar*H*).

2.3. Film preparation and measurement

The 6F-PDA-PEAP films (Fig. 1) were obtained by dropping 1 wt% solutions of these imide model compounds in *N*-methyl-2-pyrrolidone (NMP) on Si wafers for FTIR spectra. These films were dried at 60°C for 12 h under vacuum.

FTIR spectroscopic measurements were carried out on a Bruker IFS 66/v spectrometer equipped with #2000-A (Aabspec, Fig. 2). IR spectra were recorded at 4 cm^{-1} resolution with a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector under vacuum. The imide model compound films were cured at 330°C for 60 min. Thermal cure behaviors were estimated by the following equation [3,4]:

$$\text{The extent of cure } \alpha = \left(\frac{\left(\frac{A_{C\equiv C}}{A_{imide\ C=O}} \right)_t}{\left(\frac{A_{C\equiv C}}{A_{imide\ C=O}} \right)_{t=0}} \right) \quad (1)$$

The 2D correlation spectra were obtained using an algorithm based on a numerical method developed by Noda [9–12]. The 2D correlation analyses were carried out after baseline correction of the FTIR spectra. A subroutine, named KG2D and written in Array Basic language (GRAMS/386; Galactic Inc., NH), was employed in the 2D correlation analyses [16].

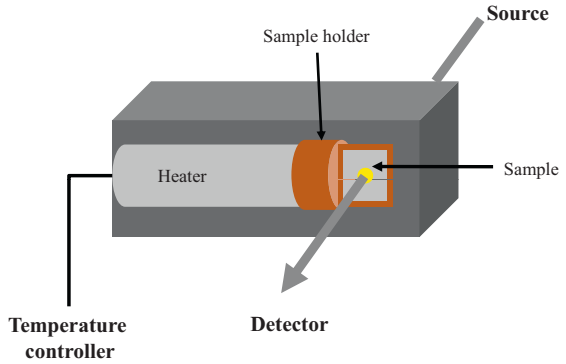

Fig. 2. Schematic diagram of the heating cell used for IR study.