The effect of solvent to the kinetics of imidization of poly(amic acid)

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ABSTRACT

Kinetics of the imidization reaction of poly (amic acid) (PAA) film based on pyromellitic anhydride (PMDA) and 4,4′-diaminodiphenyl ether (ODA) was studied by infrared spectroscopy. Attention is paid to the effect of solvent content inside the sample to the reaction kinetics. The results show that the presence of solvent favors the imidization reaction, rendering a much higher reaction kinetics than the case of without solvent. The data indicates that there is almost one NMP solvent molecule lost per imidization reaction. The kinetics of isothermal imidization reaction exhibits huge heterogeneity and is well-fitted by the Kohlraush-Williams-Watts (KWW) equation, from which the characteristic reaction time and the stretching exponent are determined. Both of them decrease with the increasing of the imidization reaction temperature, demonstrating the reaction is retarded with the proceeding of the reaction together with the creation of bigger dynamical heterogeneity.

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1. Introduction

Polyimide (PI) is a type of excellent high performance polymers with high resistance to heat, chemical exposure and radiation, etc. It also has relatively low dielectric constant and outstanding mechanical properties and has been widely used in the microelectronics, semiconductor and aerospace industries [1,2]. One of the major features of PI is the strong inter-chain interaction, especially due to the charge transfer interaction and the strong van der Waals force. This results in its poor solubility and infusibility, which brings about tremendous challenges for manufacturing [3,4]. One popular method for PI fabrication is the classical two-step method: Firstly, the precursor, poly (amic acid) (PAA), is synthesized using equimolar tetracarboxylic acid dianhydride and diamine in a polar aprotic solvent. Afterwards, PI is prepared by treatments at elevated temperatures or with chemical dehydrating agent, i.e. the thermal and chemical imidization process. For the thermal imidization, PAA is converted to PI at the extent of 90% of conversion at 200 °C and 100% conversion is reached at higher temperatures, typically 300–450 °C, depending on the chemical structure [5–8].

The structure and properties of PI are strongly dependent on the imidization history, making the imidization progress the key issue of manufacturing advanced PI materials [9–15]. Multiple factors are involved in the imidization process, including solvent evaporation, chemical conversion, water loss, thickness reduction, polymer chain orientation and reduction of molecular chain mobility. Clearly, this is rather complicated because all these processes take place simultaneously along with the chemical reaction, and they are affecting each other. For example, the loss of solvent can bring about a reduction of chain mobility due to the increase of concentration. This change, in turn, can slow down the kinetics of imidization reaction due to the retarded diffusion. Consequently, it is rather difficult to predict the effect of these factors on the final properties of PI materials [16–18].

Kinetic of imidization has long been a very important topic attracting extensive research efforts, in which various techniques and methods are employed to investigate, such as thermogravimetric analyzer, differential scanning calorimetry, Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, ultraviolet spectroscopy and fluorescent spectroscopy [19–25].1 However, the detailed reaction mechanisms are still not completely understood. It is proposed that the reaction process is a first-order reaction, in which only the adjacent CONH and COOH groups are involved [26]. Although the reaction kinetics has been considered as one-mode process, it is getting more popular to consider it as multiple process of different kinetics. For example, it is considered to be composed of two consecutive first-order processes, in which the rate constant of the first process remains invariable and the second one has a continuously decreasing rate constant with the increase of the degree of imidization [27–30]. This is mainly

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attributed to the decrease in polymer chain mobility with the proceeding of the imidization reaction.

Solvent content inside the reaction system has a significant influence on the imidization kinetics, and attention has been paid to the solvent-PAA interaction [31—33]. It is found that PAA molecules can form complexes with the polar solvent molecules via hydrogen bonding — the 4:1 and 2:1 (solvent: PAA repeat unit) complex can form based on the two carboxylic acid groups and two amide groups, depending on the processing conditions, such as thickness of film casting and the temperature [34]. For thermal imidization, it was found that no obviously imidization reaction occurred below ~86 °C, at which point PAA films contain 30—50% bound solvent. Taking imidization via the ring closure reaction in dimethylformamide (DMF) as an example, the reaction can complete in 10 min at 150 °C, while with the absence of solvent, it takes several hours to reach the same state, even at 180 °C. The rate of imidization also depends on the solvent used to dissolve the PAA, following the order of NMP > DMAc > DMSO (NMP = 1-methyl-2-pyrrolidinone, DMAc = dimethylacetamide, DMSO = dimethyl sulfoxide). The effect of the solvent to imidization kinetics is believed to originate from the change of chain mobility and as a result, the change of the glass transition temperature of the system because the solvent can have a plasticizing effect. Although the imidization reaction has been investigated in many studies, the relation between imidization kinetics and the solvent is still unclear [35,36]. There are a number of open questions related such as: how many solvent molecules are really correlated with the imidization reaction? How does the presence of solvent affect the reaction kinetics? What is a reliable way to describe the kinetics of imidization process, which is not supposed to have a uniform kinetics?

Motivated by these open questions, a detailed investigation into the kinetics of the imidization reaction of PAA inside its films is conducted by infrared spectroscopy (IR) in the current study. Attention is paid to the variation of the reaction kinetics with the proceeding of the imidization and the correlation between the solvent content and the imidization extent.

2. Experimental section

2.1. Materials and sample preparation

All materials were purchased from TCI. Pyromelliticdianhydride (PMDA) and oxydianiline (ODA) was purified by vacuum sublimation. NMP was dried with phosphorus pentoxide and then vacuum-distilled before use.

PAA were polymerized by adding an equi-molar amount of PMDA (2.1812 g, 0.01 mol) powder into the ODA (2.0024 g, 0.01 mol)/NMP (40 g) solution with continuous mechanical stirring under dry nitrogen flow. An ice water bath was used. The reaction mixture was further under stirring at room temperature for 12 h continuously so that a uniform PAA solution formed. The solid content of the obtained PAA solution was 9.46 wt%. The PAA solution was characterized by an Ubbelohde viscometer and the results show its intrinsic viscosity of PAA of 0.201 L/g in NMP at 25.0 °C. The viscosity average molecular weight was deduced to be 60,700 by the Mark-Houwink relationship [1]. Thin films of PAA (10 μm thick) were prepared by casting from diluted PAA solution (wt 2%) onto KBr windows. All of the PAA films were incubated under vacuum at 80 °C over 12 h. Without specific explanation, PAA film represents the PAA films prepared under this condition in later text. As a comparison, thin films without solvent (denoted as NMP-free PAA) were prepared, by casting from solutions of NMP onto glass slides and subsequently immersing in distilled water for 4 h, followed by incubation under vacuum at 30 °C to remove residual water. The removal of NMP solvent is evidenced by the absence of

absorbance band of NMP in FTIR spectra (Fig. 1), although a sample with complete removal of NMP solvent is rather hard to define as it depends not only the detection sensitivity but also the experimental condition such as temperature, segmental density and possible surface hindrance.

2.2. Measurements

IR spectra were acquired in a transmission mode using an FTIR spectrometer (EQUINOX 55) equipped with a DTGS detector. A heating stage (INSTEC, HCS402) was equipped for the control of sample's temperature at the precision of ±0.05 °C. To conduct IR measurements, a KBr substrate coated with a 10-μm-thick PAA film was mounted in the heating stage and the spectra were collected in a temperature swap manner up to 300 °C with at a heating rate of 2.0 °C·min^{-1}. To finish one run of spectrum collection, 32 s is needed for 16 scans at a resolution of 2.0 cm^{-1}. For the study of the kinetics of isothermal imidization reaction, the sample was quickly heated from room temperature to the targeting temperature at a high heating rate of 50 °C·min^{-1}.

3. Results and discussion

3.1. Non-isothermal imidization reaction

The correlation of the loss of NMP solvent and imidization degree in investigated. To determine the imidization degree, a sample of full imidization was prepared by annealing at 300 °C for 2 h. The weight loss of the PAA film due to full imidization is determined by the weight difference of the PAA film before and after annealed at 300 °C for 2 h. Such a weight loss contains the weight of water generated from the imidization as well as the evaporation of solvent. Therefore, the solvent content (ϕ_s) was determined according to $\phi_s = \frac{W_{PAA} - W_{PI} - W_{H_2O}}{W_{PAA}} \times 100\%$, where W_{PAA}, W_{PI} and W_{H_2O} is the weight of PAA film before imidization, the weight of PAA film with

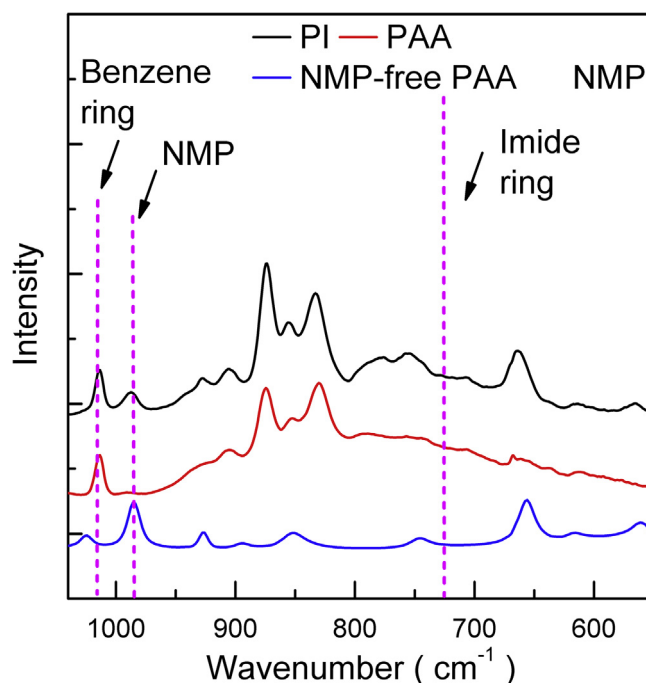**Fig. 1.** IR spectra in the range 1040-550 cm^{-1} of PI film, PAA film vacuum-dried for 12 h at 80 °C, NMP-free PAA film together with the spectra of the solvent, NMP.