

Imidization processes of aromatic polyimide by temperature modulated DSC

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Abstract

Processing of polyimide (PI) from precursor polyamic acid (PAA) involves simultaneous imidization, evaporation of residual solvent and crystallization. These overlapped processes were analyzed by temperature modulated differential scanning calorimetry (T-MDSC). Glass transition temperature (T_g) of precursor PAA was manifested by T-MDSC, and it was 107°C for pyromellitic dianhydride–oxidianiline (PMDA–ODA) PAA cast from *N*-methyl-2-pyrrolidone (NMP) solution. The thermal cyclization reaction from PAA to PI is considered to progress randomly. The solvent system for casting PAA, influenced the conversion to PI, which is found to affect the T_g of PAA. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Temperature modulated DSC; Imidization process; Glass transition

1. Introduction

Thermal properties are one of the most important properties for polymeric materials. Aromatic polyimides (PI) have not only excellent thermal stability but also good mechanical properties, high chemical resistance and low electric constant; so they are widely used in many applications as semiconductor devices, printed circuitry boards and so on. As PI is generally insoluble in any solvent, it is thermally or chemically converted from precursor polyamic acid (PAA) dissolved in aprotic polar solvents such as *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc) and *N,N*-dimethylformamide (DMF) [1]. Their boiling temperatures are relatively high, so cyclization process of PI from precursor PAA involves simultaneous imidization, evaporation of residual solvent and crystallization, competitively. Therefore, the cyclization process will influence the final structure and properties of PI [2–5]. For example, the mechanical properties of PI such as the specimen modulus and the residual stress were changed by the selection of imidization processes [6]. When PI films are used as flexible printed circuitry boards and interlayer dielectrics, the residual stress between PI and adherend is a very essential factor preventing the improvement of product performance. In order to control the final properties of PI, it is essential to analyze the imidization process in detail.

Differential scanning calorimetry (DSC) is a general technique for thermal analysis of polymers. DSC gives us a variety of thermal information, for example, glass transition, melting behavior, thermal history and the degree of crystallinity. However, in a complicated curing reaction such as the imidization process, various overlapped phenomena would have occurred in the same temperature region, and they cannot be separated by conventional DSC because it gives only the heat flow change of the sample during linear heating.

Recently, a new thermal technique, temperature modulated DSC (T-MDSC), was developed by Reading et al [7]. In T-MDSC measurement, a linear change of temperature with small sine wave modulation, that is, periodic heating was given to the sample and the reference, and the oscillated heat flow curve is obtained. This oscillated heat flow curve can be separated into components of following the modulation (reversing heat flow) and non-following the modulation (non-reversing heat flow) by Fourier transform technique. Thus, the overlapped phenomenon in the same temperature region can be isolated by T-MDSC method.

In this study, the imidization process from precursor PAA to PI was analyzed using the T-MDSC method, and its effect on the glass transition temperature (T_g) of PAA was investigated.

2. Experimental

2.1. Sample preparation

PAA precursor was prepared by the conventional

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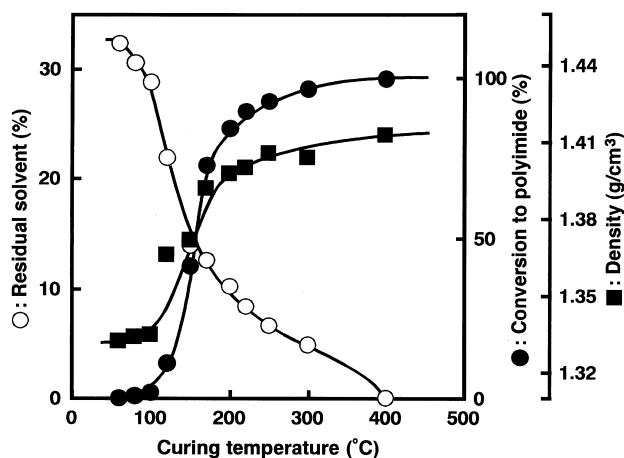


Fig. 1. Curing temperature dependence of the amount of residual solvent, the conversion to PI and the density of polyamic acid PMDA-ODA cast from NMP solution.

ring-opening polyaddition reaction [1]. Pyromellitic dianhydride (PMDA) was added dividedly several times to a three neck flask without precipitation to NMP in which oxidianiline (ODA) was previously dissolved. After the mixture was stirred for 1 h under dry nitrogen gas flow, PMDA-ODA PAA 13.8 wt% in NMP solution was synthesized. PMDA-ODA PAA was also synthesized in a tetrahydrofuran(THF)/methanol(MeOH) = 8/2 (by weight) mixed solvent system [8,9] using the same procedure as shown above. The boiling temperature of the THF/MeOH mixed solvent (66°C) is much lower than that of NMP (202°C) which is an aprotic polar solvent.

The PAA film was cast from PAA solution on polyethylene terephthalate (PET) film under reduced pressure at 60°C for 24 h. After the PAA film (thickness of 50 μm) was cut off from the PET substrate, small pieces of PAA in an aluminum pan were further dried at 100°C for 5 min in the DSC unit prior to the measurements.

2.2. Temperature modulated DSC measurement

The thermal behavior of the PAA cast film was measured by DSC (Seiko Instruments Inc. DSC220CU) from -30 to 300°C, equipped with a refrigerated cooling system. A heating rate of 5°C/min, an oscillation amplitude of $\pm 1.5^\circ\text{C}$ and an oscillation frequency of 0.02 Hz were employed. These conditions were chosen so as to include an oscillation period of at least 5–6 times within the transition temperature range [10,11]. About 10 mg of the PAA film sample was put in the aluminum pan, and nitrogen gas was purged (30ml/min) during the measurements. Temperature and the heat flow were calibrated by using indium, tin and lead as standards.

Conversion to PI from PAA was measured by a Fourier transform infrared spectrophotometer (FT-IR) (Shimadzu FT-IR4200) at a resolution of 2 cm^{-1} , 10 accumulations. The PAA film was thermally cured at 80, 100, 120, 150, 170, 200, 220, 250 and 300°C, and finally at 400°C successively for 1 h at each step. The conversion was measured after each curing step. The adsorption band at 1380 cm^{-1} (imide II: C-N stretching vibration) was monitored during curing from PAA to PI [12]. The adsorption band at 1500 cm^{-1} (C-C stretching of the *p*-substituted benzene) is selected as an internal standard. The conversion to PI was determined by the following equation,

Conversion to PI (%)

$$= (D_{1380 \text{ cm}^{-1}}/D_{1500 \text{ cm}^{-1}})/(D_{1380 \text{ cm}^{-1}}/D_{1500 \text{ cm}^{-1}})_{400^\circ\text{C}} \quad (1)$$

$$\times 100$$

where, D is the optical density.

The amount of residual solvent was measured by a thermogravimeter (SEIKO Instruments Inc. TG/DTA220U). Stepwise thermal imidization condition during thermogravimetry measurement was as same as the condition during FT-IR measurement. Total weight loss during heating process includes both the evaporation of solvent and a dehydration with cyclization. The amount of dehydration could

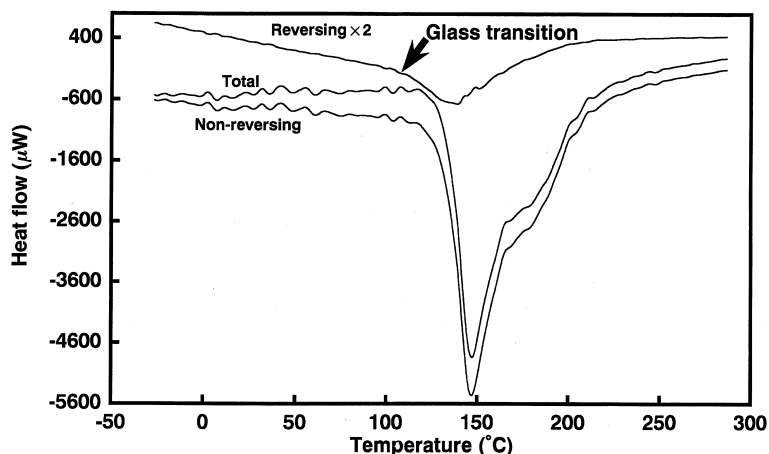


Fig. 2. Separated results of the modulated DSC thermogram of polyamic acid PMDA-ODA cast from NMP solution.

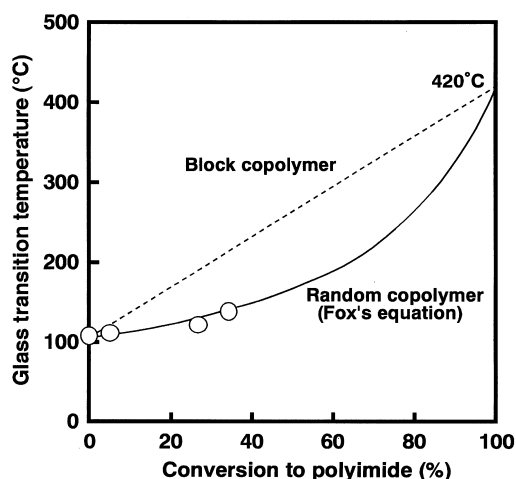


Fig. 3. Relationship between T_g of polyamic acid PMDA–ODA cast from NMP solution and the conversion to PI.

be calculated from the conversion to PI from FT-IR. Thus, by subtracting the amount of dehydration from the total weight loss, the amount of residual solvent during heating process was evaluated. The specimen density was measured by a floatation method (chlorobenzene–carbon tetrachloride system) at 30°C after each curing step.

3. Results and discussion

3.1. Glass transition of polyamic acid PMDA–ODA

Fig. 1 shows the changes (○) of the amount of residual solvent, the conversion (●) to PI and the specimen density (■) during the curing processes of PMDA–ODA PAA cast from the NMP solution. As the cast film contained 32.3 wt% of NMP, PAA has not converted into PI yet. With increasing curing temperature, the amount of residual solvent decreased, and both the conversion to PI and the density increased. The decrease in the amount of residual solvent means the successive evaporation of solvent during the curing process. The increase in the density indicates the increase of both the conversion to PI and the crystallinity of PI. Accordingly, processing of PI from precursor PAA involves imidization with dehydration, evaporation of residual solvent and crystallization around 150°C, simultaneously.

Fig. 2 shows the separated results of the T-MDSC thermogram of PMDA–ODA PAA cast from the NMP solution. Generally, the non-reversing heat flow should contain the information about enthalpy relaxation, crystallization, thermal decomposition, thermal curing, evaporation of the solvent, etc. In this case, it involved dehydration with cyclization and evaporation of the residual solvent. On the other hand, the change of the heat flow in the reversing heat flow is based on the glass transition of PAA, which appeared around 107°C. As shown above, by using T-MDSC method,

we could well separate the reversing and the non-reversing components of the heat flow, and the hidden glass transition of PMDA–ODA PAA could be manifested. Generally, glass transition appears as a stepwise change in the heat capacity, however in this study, it was observed as an endothermic broad peak. Several exothermic and endothermic events were considered to influence the heat flow during transition. The weight loss progressed during the DSC measurement is one of the factors for the exothermic shift of the heat flow. However, when the heat flow change of 0.53 mW during the transition from 132 to 190°C is assumed to be brought only by the sample weight loss, it could be calculated to correspond to be 11.2 wt% for the as-cast PAA film. This is about half of that of the observed weight loss of 22.6 wt% during the transition. For the imidized sample (200°C, 1 min), the weight loss of 2.2 wt% could be calculated, however, this is much less than the observed value (8.8 wt%). These indicate that the heat flow change was overestimated by only considering the weight loss. In fact, above the T_g of PAA, PAA is in a rubbery state, but it was successfully converted to PI in a glassy state. This revitrification should bring the change in heat capacity, which will appear as an exothermic shift of the heat flow during the transition [13,14]. However, the exothermic shift is restrained compared with that of calculated results because of the residual solvent which brings the high molecular mobility. Accordingly, the competitive effects of weight loss, revitrification and residual solvent are considered to bring the endothermic broad peak during the transition.

3.2. Effect of several factors on the glass transition

Fig. 3 shows the relationship between T_g of PMDA–ODA PAA by T-MDSC method and the conversion to PI. The imidization was performed by thermal curing at 200°C for a desired time. T_g of PAA increased with the conversion to PI by thermal curing. The skeletal structure of PI is much more rigid compared with that of PAA because of cyclization. Partially cured PAA is regarded as PAA–PI copolymer. T_g of copolymer can fall between two extreme states. One is for a block copolymer, the other is for a random copolymer. T_g of random copolymer can be expressed with the following so-called Fox's equation,

$$1/T_g = \{w_{\text{PAA}}/T_g(\text{PAA})\} + \{w_{\text{PI}}/T_g(\text{PI})\} \quad (2)$$

where, w_{PAA} is the weight fraction of PAA and w_{PI} is the weight fraction of PI. And also, T_g of block copolymer can be expressed simply as additivity of each component [15].

$T_g(\text{PI})$ at 420°C was obtained from dynamic mechanical analysis [16,17]. $T_g(\text{PAA})$ and $T_g(\text{PI})$ are linked with the broken line (for block copolymer) and the solid line (for random copolymer) in Fig. 3. Observed values corresponded to the predicted values from Fox's equation. This indicates that the cyclization reaction from PAA to PI progressed randomly on the polymer chain.

In order to investigate the effect of solvent on the T_g of

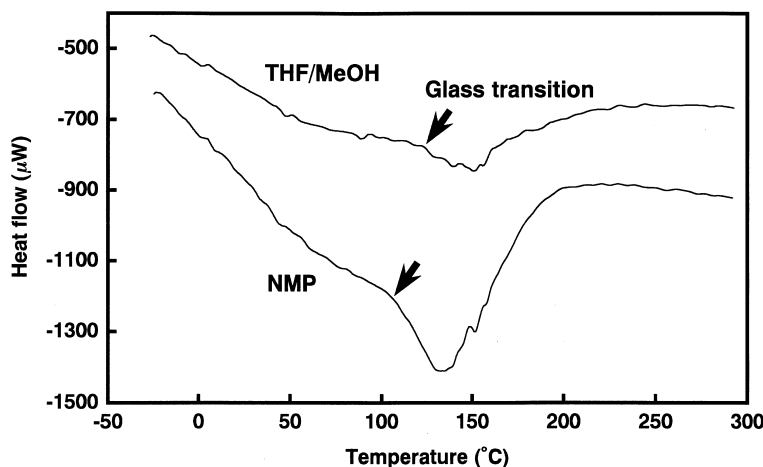


Fig. 4. Reversing heat flow of the modulated DSC thermograms of polyamic acid PMDA-ODA cast from different solvents.

PAA, two different kinds of solvent systems were used for dissolving and casting of PAA.

Fig. 4 shows the T-MDSC reversing heat flow curve of PMDA-ODA PAA cast from the NMP solution and that from the THF/MeOH mixed solution. In both cases, the glass transitions were clearly observed, as shown with the arrows. The T_g value of PAA cast from the THF/MeOH mixed solvent system was 15°C higher than that of the NMP system. In spite of the same chemical structure of PMDA-ODA PAA, these results indicate that the difference in solvents for dissolving and casting has influenced the molecular mobility of PAA. The amount of residual solvent in the PAA specimen before T-MDSC measurement are 32.3 wt% for the NMP system and 25.3 wt% for the THF/MeOH system. Thus the plasticization by solvent is apparently one reason for the depression of T_g for the NMP system [2]. However, solvent evaporation occurred simultaneously during the T-MDSC measurement. So next, the amount of residual solvent around the glass transition range was measured.

Fig. 5 shows the relationship between the conversion to PI from PAA cast from different solvents and the amount of residual solvent. The amount of residual NMP is much more than that of residual THF/MeOH before thermal curing, as described above. However, they are reversed with the progress of imidization, that is, residual NMP decreased abruptly at the initial stage of imidization. On the other hand, larger amount of solvent remained for the THF/MeOH system in spite of its lower boiling temperature. This implies THF/MeOH mixed solvent has high affinity to PAA or PI, and the difference in T_g for both the systems cannot be explained simply by the plasticization effect of solvent.

Fig. 6 shows the relationship between the curing temperature and the conversion to PI from PAA cast from different solvents. Imidization reaction started at around 100°C and almost finished at around 200°C where the conversion to PI is almost complete for both the solvent systems. However, the conversion of the THF/MeOH system was higher than that of the NMP system at any curing temperature. Thus,

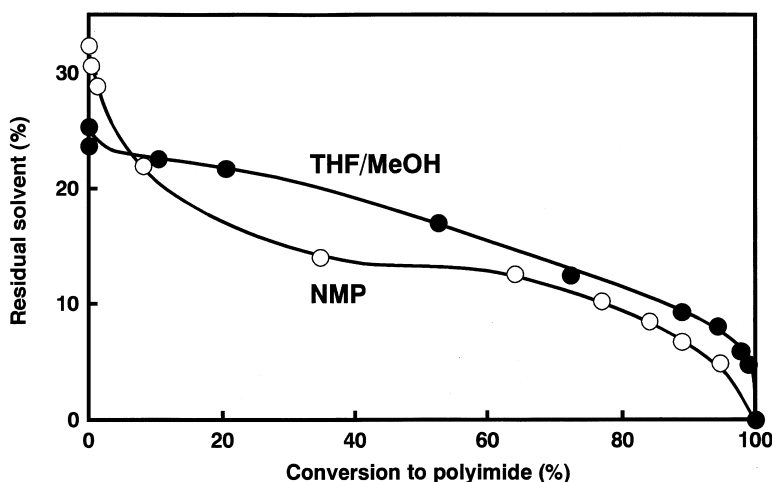


Fig. 5. Relationship between the amount of residual solvent and the conversion to PI from polyamic acid PMDA-ODA cast from different solvents.

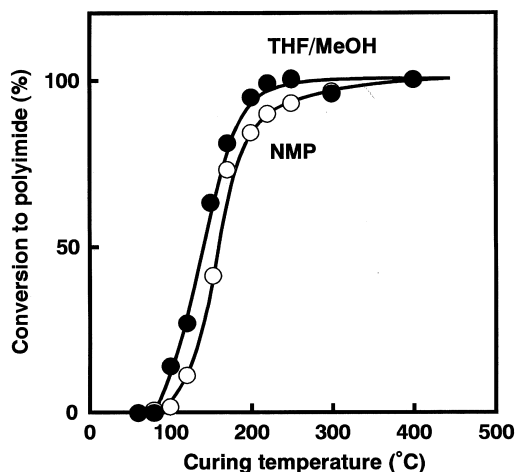


Fig. 6. Relationship between the curing temperature and the conversion to PI from polyamic acid PMDA–ODA cast from different solvents.

much more amount of residual solvent for the THF/MeOH system brings PAA molecules high mobility, which results in the higher conversion to PI. Accordingly, higher conversion to PI is the reason for higher T_g of PMDA–ODA PAA cast from THF/MeOH. That is cyclization reaction from PAA to PI occurred prior to glass transition for the THF/MeOH system, however, solvent evaporation rather than cyclization reaction occurred in advance of glass transition for the NMP system.

4. Conclusion

The glass transition temperature of precursor PMDA–ODA PAA cast from NMP solution was found to be 107°C by using T-MDSC method, a novel technique of thermal analysis. T_g of PAA raised as a function of conversion from PAA to PI by thermal curing, which is because the PAA chain is cyclized and converted into a

rigid structure. Imidization reaction was considered to progress randomly. Since the cyclization occurred simultaneously with the evaporation of solvent, the residual solvent affects the imidization reaction during thermal curing processes, which results in the change in T_g of PAA. In conclusion, T-MDSC method is a useful technique to analyze imidization processes including the various overlapping thermal phenomena.

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