ELSEVIER

Polymer 40 (1999) 2263–2270

polymer

Glass transition behaviours in aromatic poly(amic dialkyl ester) precursors with various chain rigidities

S.I. Kim, T.J. Shin, M. Ree*

Department of Chemistry and Polymer Research Institute, Pohang University of Science and Technology, San 31, Hyoja-dong, Pohang 790-784, South Korea

Received 12 March 1998; accepted 2 June 1998

Abstract

Five different poly(amic dialkyl ester) precursors with various chain rigidities were synthesized and their powder and film samples were prepared in residual solvent free: poly(4,4′-oxydiphenylene biphenyltetracarboxamic diethyl ester); poly(*p*-phenylene biphenyltetracarboxamic diethyl ester); poly(*p*-phenylene biphenyltetracarboxamic dimethyl ester); poly(4,4′-oxydiphenylene pyromellitamic diethyl ester); and poly(*p*-phenylene pyromellitamic diethyl ester). Glass transition temperatures (T_gs) of these precursors, which have never been reported so far, were successfully determined in the present study by the new oscillating differential scanning calorimetry (o.d.s.c.). In addition, their imidization behaviours and morphological structures were investigated by o.d.s.c. and X-ray diffraction, respectively. The measured T_gs are in the range 179.2–235.4°C, depending upon the precursor backbone structure as well as the history of sample preparation: these T_gs are very close to the imidization temperatures (T_is), causing difficulties in the T_g measurements. The measured T_is are in the range 198.1–235.4°C, depending upon the precursor backbone structure as well as the history of sample preparation. The T_gs are dependent on the chain rigidity and the morphological structure, whereas the T_is are influenced by the chemical nature in addition to the chain rigidity and the morphological structure.

Keywords: Poly(amic dialkyl ester); Glass transition; Imidization

1. Introduction

Most aromatic polyimides are not processable, due to their insolubility and high glass transition temperature (T_g) [1–3]. Thus, they are always processed in their soluble precursor forms and then imidized chemically or thermally [1–4]. One soluble polyimide precursor is poly(amic acid), which is widely used in the fabrication of devices because of its easy synthesis [1,2,5]. However, poly(amic acid) is in equilibration with the constituent anhydride and amine monomer in solution, so that it is very sensitive to any temperature variation and moisture contact, causing a number of problems in quality control and the fabrication process [1,2,6]. Another soluble polyimide precursor is poly(amic dialkyl ester) [4,7–13]. This precursor has a high hydrolytic stability, due to the absence of monomer–precursor polymer equilibration, providing a processability more adequate for device fabrication. For this reason, poly(amic dialkyl ester) has recently gained great attention from the industry [4,9,10,13].

However, in comparison with poly(amic acid)s, the imidization of poly(amic dialkyl ester)s has been rarely studied. Recently, the thermal imidization of several poly(amic dialkyl ester)s was investigated in our laboratory by thermogravimetric analysis (t.g.a.), and their imidization kinetics could be understood to be affected by their backbone structures, their alkyl leaving groups, and their glass transition temperatures [13,14]. However, the T_gs of most aromatic poly(amic dialkyl ester)s could not yet be determined. In general, aromatic poly(amic dialkyl ester)s are expected to exhibit high T_g due to their relatively high chain rigidities. Near or above their T_g ranges, they are converted to the polyimides. Because of this particular circumstance, the T_gs of aromatic poly(amic dialkyl ester) precursors could not so far be measured.

However, we have recently investigated the glass transition behaviours in several aromatic poly(amic acid)s using a new differential calorimetric technique, oscillating differential calorimetry (o.d.s.c.) [15,16]. The major advantage of o.d.s.c. is to separate effectively the specific heat flow, that appears in thermally reversible phenomena such as glass and melting transition, from the kinetic heat flow that appears in thermally irreversible phenomena such as

---

* Corresponding author. Tel.: +82-562-279-2120; Fax: +82-562-279-3399; E-Mail: ree@vision.postech.ac.kr

0032-3861/99/$ - see front matter © 1999 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(98)00440-6

chemical reaction, evaporation and decomposition [17–21]. In this study, we have attempted to utilize the advantageous o.d.s.c. for investigating the glass transition behaviours of poly(amic dialkyl ester)s. Several poly(amic dialkyl ester)s have been synthesized. For precursor polymers, we have tried to prepare samples in both powders and films which are free from residual solvent. For the samples, T_gs and T_is were measured by o.d.s.c., whereas the content of residual solvent was determined by proton nuclear magnetic resonance (^{1}H n.m.r.) spectroscopy.

2. Experimental

2.1. Synthesis and sample preparation

Pyromellitic dianhydride (PMDA), biphenyltetracarboxylic dianhydride (BPDA), *p*-phenylene diamine (PDA) and 4,4′-oxydiphenylene diamine (ODA) were supplied from Chriskev Company in Kansas, USA. All the other chemicals used in this study were purchased from Aldrich Company. PMDA was purified by drying at 120°C for 1 day in vacuum, and BPDA was purified by recrystallization with acetic anhydride. PDA and ODA were purified by sublimation under reduced pressure, respectively. *N*-methyl-2-pyrrolidone (NMP) was distilled over calcium hydride under reduced pressure.

Poly(4,4′-oxydiphenylene biphenyltetracarboxamic diethyl ester) (BPDA-ODA ES) was prepared in a glove box filled with dry nitrogen gas by adding the equivalent number of moles of biphenyltetracarboxylic diethyl ester diacyl chloride (BPDA diethyl ester diacyl chloride) in dried ethyl acetate to the purified ODA in dry NMP (see Fig. 1). The polymerization was carried out at 0–5°C with vigorous stirring, followed by continuous stirring for an additional 20 h. The precursor polymer solution was precipitated in deionized water under vigorous stirring in a mixer equipped with a knife blade and filtered, followed by washing with methanol several times in order to remove the HCl byproduct. Then the precursor product in powder was dried for 7 days at 80°C in a vacuum oven with 2×10^{-6} torr in order to remove all the residual solvents. Here, the used BPDA diethyl ester diacyl chloride was prepared via the reaction of BPDA diethyl ester dicarboxylic acid with oxalyl chloride in an excess under dry nitrogen gas. The BPDA diethyl ester dicarboxylic acid was prepared by the reaction of BPDA with ethanol. That is, the sublimed BPDA was added to ethanol and refluxed for 5–8 h, followed by distillation of excess ethanol under a reduced pressure (see Fig. 1).

Other poly(amic dialkyl ester)s were synthesized in the same manner as BPDA-ODA ES prepared: poly(*p*-phenylene biphenyltetracarboxamic diethyl ester) (BPDA-PDA ES), poly(*p*-phenylene biphenyltetracarboxamic dimethyl ester) (BPDA-PDA MS), poly(4,4′-oxydiphenylene pyromellitamic diethyl ester) (PMDA-ODA ES), and poly(*p*-phenylene pyromellitamic diethyl ester) (PMDA-PDA ES) (see Fig. 2). In order to synthesize BPDA-PDA MS, methanol was used instead of ethanol.

For the synthesized precursors, intrinsic viscosity [η] measurements were conducted in NMP at 25.0°C using an Ubbelohde suspended level capillary viscometer as a method described in the literature [22,23]. NMP was purified by distillation over phosphorus pentoxide (P_2O_5) under reduced pressure and further treated with 0.02 M P_2O_5, followed by filtration before use, in order to minimize polyelectrolyte effect in the viscosity measurement. All the solutions were filtered through 0.5 μm Fluoropore filters of the Millipore Company. The [η] value was determined by the extrapolations of the measured reduced and inherent viscosities with varying concentrations to the infinite dilution: the [η] was 0.454 dl g^{-1} for the BPDA-ODA ES, 0.850 dl g^{-1} for the BPDA-PDA ES, 0.677 dl g^{-1} for the BPDA-PDA MS, 0.503 dl g^{-1} for the PMDA-ODA ES, and 0.474 dl g^{-1} for the PMDA-PDA ES.

To prepare precursor films, the precursor polymers in

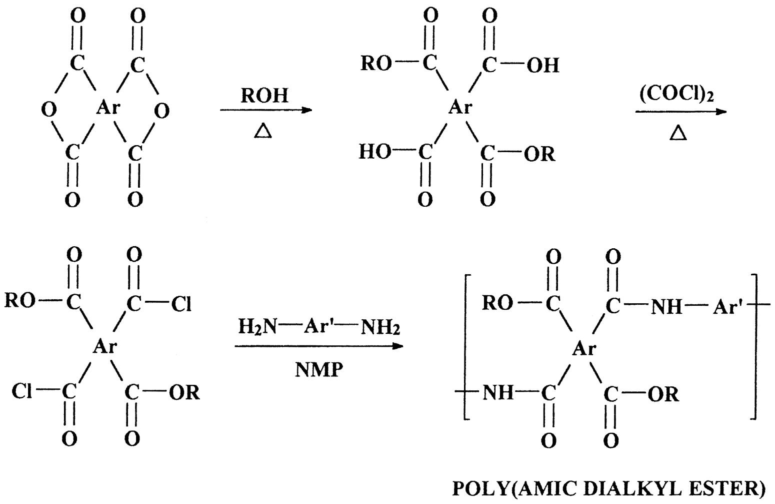

Fig. 1. Synthetic scheme of poly(amic dialkyl ester)s from dianhydride and diamine.

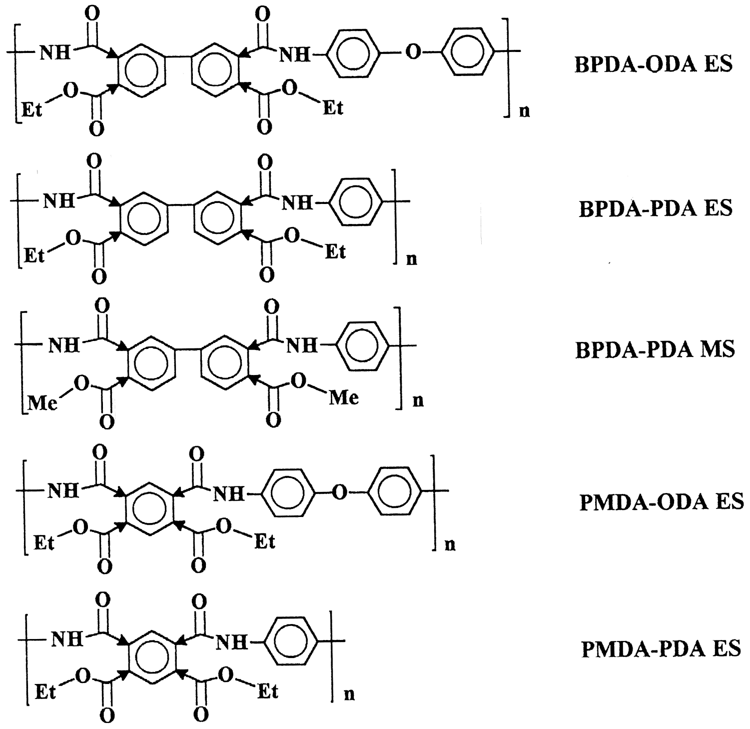

Fig. 2. Chemical structures of aromatic poly(amic dialkyl ester)s synthesized in this study.

powder form were dissolved in NMP with a concentration of 5 wt%. The precursor solutions were filtered with silver metal membranes of 1.0 μm pore size before use. The precursor solutions were spin-cast on precleaned glass slides, followed by softbaking on a hot plate of 80°C for 1 h, giving precursor films of ca 10 μm thick. Then, the cast films were immersed into methanol in excess for 10 days in order to extract out residual NMP and, thereafter, dried in a high vacuum of 2×10^{-6} torr at 80°C for 3–7 days.

2.2. Measurements

For dried precursor powders and films, the content of residual NMP was determined by ^{1}H n.m.r. spectroscopy. That is, a small amount of a dried precursor powder or film was dissolved in dimethyl-d_6 sulfoxide (DMSO-d_6) and then characterized using a Bruker n.m.r. spectrometer (model Aspect 300 MHz) with a proton probe.

For wide angle X-ray diffraction (WAXD) measurements, poly(amic dialkyl ester)s in powder form were palletized in a thickness of 1 mm. WAXD measurements performed at room temperature using a Rigaku vertical diffractometer (Model RINT-2500) with a rotating anode X-ray generator. The CuK$_\alpha$ radiation source was operated at 40 kV and 60 mA. A divergence slit of 1° was employed, together with two receiving slits of 0.5°. All the measurements were carried in $\theta/2\theta$ mode. The 2θ scan data were collected at an interval of 0.01° over the range of 4–70°, and the scan speed was 0.1°(2θ)/min.

Thermograms including glass transition and imidization in precursor samples in powders and films were measured over −60°C to 400°C using a Seiko o.d.s.c. (model ODSC-220CU), as described previously elsewhere [15,16]. During the measurement, dry nitrogen gas was purged with a flow rate of 80 cm^3 min^{-1}. Calibrations of temperature and enthalpy were carried out using indium and tin as standards, respectively. Samples of ca 2 mg were used. A heating rate of 10 K min^{-1} was employed. The employed oscillating amplitude and frequency were 10.0°C and 0.02 Hz, respectively.

3. Results and discussion

3.1. Poly(amic dialkyl ester)s in powder

A small amount of a BPDA-ODA ES in powder, which was dried in a vacuum oven at 80°C for 7 days, was dissolved in DMSO-d_6 and characterized by ^{1}H n.m.r. spectroscopy. The n.m.r. spectrum is shown in Fig. 3. Chemical shifts for the protons of NMP did not appear, indicating that the dried BPDA-ODA ES in powder did not contain residual NMP. Similar characterizations were conducted for the other precursors in powders: BPDA-PDA ES; BPDA-PDA MS; PMDA-ODA ES; PMDA-PDA ES. The n.m.r. spectra indicate that no residual NMP remained in any of the precursor powders.

Fig. 4 shows X-ray diffraction patterns measured for the precursors in powders. For BPDA-ODA ES, the first diffraction peak is centered at 12.1° (2θ), giving a d-spacing of 7.3 Å. This periodicity arises from the repeat distance along the polymer chain. Thus, the repeat distance of

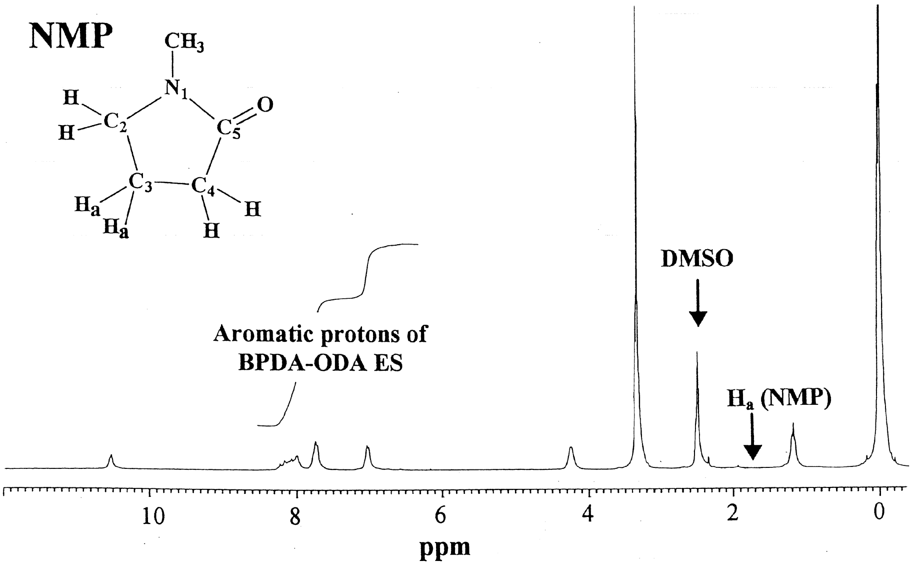

Fig. 3. ^{1}H n.m.r. spectrum of a BPDA-ODA ES powder sample dried in a high vacuum at 80°C for 7 days, which was dissolved in DMSO-d_6.

7.3 Å corresponds to the mean length of the chemical repeat unit projected along the axis of the fully extended polymer chain. The coherence length is calculated from the full-width at half maximum of the diffraction peak separation and an instrumental broadening of 0.15° (2θ) using the Scherrer equation [24]. The estimated coherence length is 12 Å. The value of this coherence length means that the molecular ordering along the chain axis consists of approximately 1.6 (= 12 Å/7.3 Å) chemical repeat units. In addition, two amorphous halos appeared in the high angle region: one is at 20.7° and the other at 43.3°. From the peak maximum of the first-order amorphous halo, the mean interchain distance is estimated to be 4.3 Å. Its coherence length is estimated to be 8 Å, which corresponds to the approximately 1.9 polymer chains. Overall, the WAXD results suggest that for the BPDA-ODA ES in powder its ordered phase consists of approximately 1.6 chemical repeat units along the chain axis and 1.9 chains along the lateral direction without any regular packing.

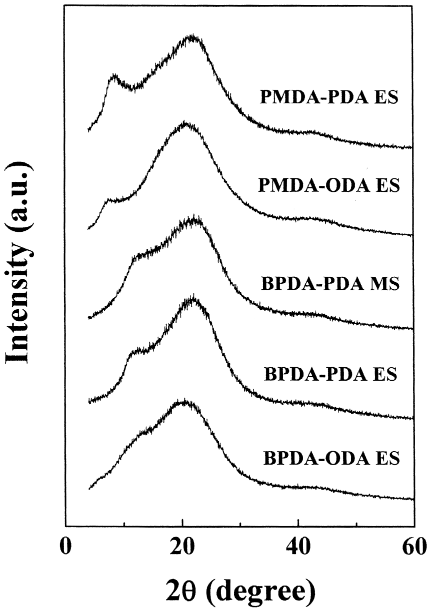

Fig. 4. WAXD patterns of the palletized powder samples of poly(amic dialkyl ester)s. The CuK$_\alpha$ radiation source was employed.

Similar diffraction patterns were observed for the other precursors. However, the diffraction peak in the low angle region, which arises from the repeat distance along the molecular chain, is significantly enhanced in intensity and its *d*-spacing is varied, depending on the sort of precursors. For the diffraction peak at the low angle region, the *d*-spacing and coherence length are estimated to be 7.6 Å (11.6°) and 20 Å for BPDA-PDA ES, 7.3 Å (12.2°) and 18 Å for BPDA-PDA MS, 11.8 Å (7.5°) and 19 Å for PMDA-ODA ES, and 10.5 Å (8.4°) and 21 Å for PMDA-PDA ES, respectively. For the first-order amorphous halo peak, the mean interchain distance and coherence length are calculated to be 4.1 Å (21.9°) and 9 Å for BPDA-PDA ES, 4.1 Å (21.9°) and 8 Å for BPDA-PDA MS, 4.3 Å (20.9°) and 7 Å for PMDA-ODA ES, and 4.1 Å (21.8°) and 7 Å for PMDA-PDA ES, respectively. In conclusion, for the BPDA-PDA ES, the ordered phase includes 2.6 chemical repeat units along the chain axis and 2.2 polymer chains in the lateral direction, whereas for the BPDA-PDA MS, the ordered phase consists of 2.5 chemical repeat units along the chain axis and 2.0 polymer chains along the lateral direction. For the PMDA-ODA ES, the ordered phase is built with 1.6 chemical repeat units along the chain axis and 1.6 polymer chains in the lateral direction, whereas for the PMDA-PDA ES, the ordered phase is constructed by 2.0 chemical repeat units along the chain axis and 1.7 polymer chains in the lateral direction.

In comparison, the degree of molecular ordering in the precursor powder is in the decreasing order BPDA-PDA ES $>$ BPDA-PDA MS $>$ PMDA-PDA ES $>$ BPDA-ODA ES $>$ PMDA-ODA ES.

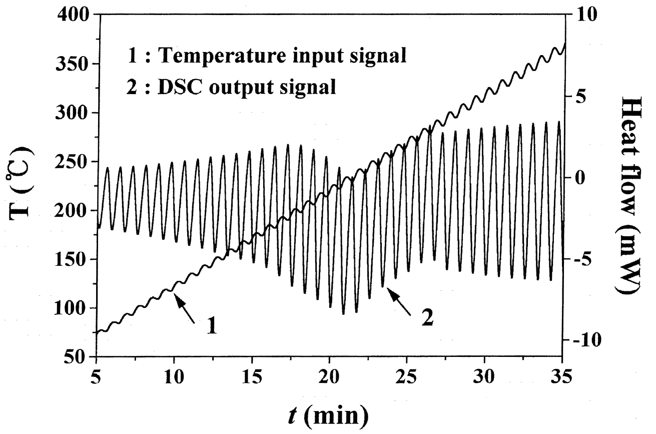

Fig. 5. The input temperature signal and output o.d.s.c. signal of a BPDA-ODA ES powder sample in residual NMP solvent free. A heating rate of 10.0 K min^{-1} was employed. The temperature amplitude and frequency used in the oscillation were 10.0°C and 0.02 Hz, respectively.

With these structural data, both the glass transition and imidization behaviours of the precursor polymers in powders were investigated by d.s.c. For the precursors we have first tried to measure glass transitions by conventional d.s.c. However, glass transitions could not be recognizable for all the precursors because the endothermic heat flow due to the imidization is predominant over the temperature range of 175–280°C. For this reason, all the precursor powders were characterized by o.d.s.c.

Fig. 5 shows an o.d.s.c. thermogram obtained from the BPDA-ODA ES as a typical example of an o.d.s.c. thermogram. This figure shows the oscillating input temperature as well as the o.d.s.c. output signals as a function of time. The o.d.s.c. output signals can be nicely separated into two parts, the specific heat flow and the kinetic heat flow, as described previously [15,16]. The separated specific and kinetic heat flows are plotted in Fig. 6 as a function of temperature. The specific heat flow curve reveals clearly a glass transition over 170–200°C. From this thermogram, the T_g was determined to be 179.2°C: here, T_g is defined as the onset temperature of glass transition. On the other hand, the kinetic heat signal curve shows a broad, big endothermic heat flow peak, which results from the imidization reaction and the removal of the reaction byproduct (i.e. ethanol). The onset T_i was estimated to be 203.5°C.

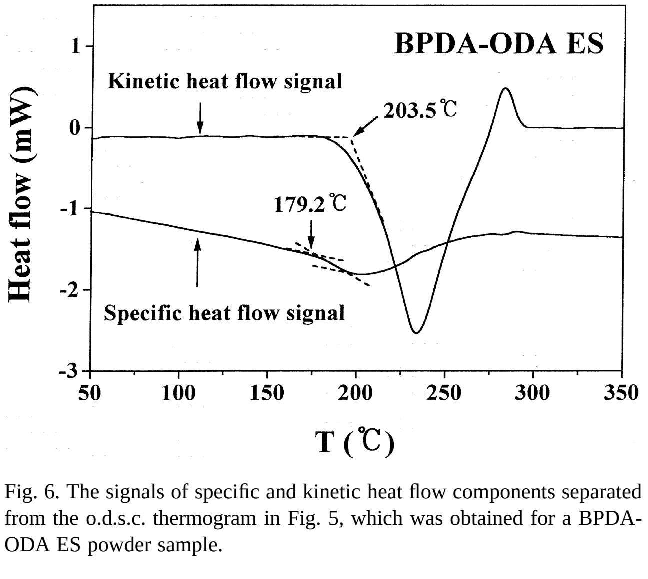

Fig. 6. The signals of specific and kinetic heat flow components separated from the o.d.s.c. thermogram in Fig. 5, which was obtained for a BPDA-ODA ES powder sample.

Table 1
Compositions, T_gs and T_is of poly(amic dialkyl ester)s in powders

Precursor sample[a]	Composition[b]		T_g^c (°C)	T_i^d (°C)
	NMP (wt%)	Precursor (wt%)		
BPDA-ODA ES	0	100	179.2	203.5
BPDA-PDA ES	0	100	–	201.2
BPDA-PDA MS	0	100	–	198.1
PMDA-ODA ES	0	100	189.8	206.3
PMDA-PDA ES	0	100	–	225.2

[a] Dried in a high vacuum at 80°C for 7 days
[b] Measured by proton n.m.r. spectroscopy
[c] T_g measured from the onset of glass transition in o.d.s.c. run
[d] T_i measured from the onset of imidization in o.d.s.c. run

The other precursors were characterized by o.d.s.c. in the same manner as the BPDA-ODA ES was examined. All the o.d.s.c. thermograms measured were separated into the specific heat flow and kinetic heat flow parts, respectively, as shown in Fig. 7. The measured T_gs and T_is are summarized in Table 1. T_i was measured for all the precursors. The T_is are in the range 198.1–225.2°C, depending on the precursor backbone structures. In comparison, T_i decreases in the order PMDA-PDA ES > PMDA-ODA ES > BPDA-ODA ES > BPDA-PDA ES > BPDA-PDA MS. However, T_g was measured for only PMDA-ODA ES. For the rest of the precursors, T_gs could not be determined from their specific heat flow curves. This result may be caused by one or both of two reasons in the following. One is that the heat capacity changes through their glass transitions are very small, so that the calorimeter could not detect them within its resolution limit. The other is that their T_gs are higher than the T_is, so that the T_gs could not be detected. If the former is the clue for no detection of the T_gs, there is still a possibility to measure them, because the heat capacity change of glass transition is dependent upon the morphological structure in the precursor sample. Thus, we have prepared the precursors in films rather than powders. O.d.s.c. measurements for the precursor films and results are discussed in Section 3.2.

3.2. Poly(amic dialkyl ester)s in films

BPDA-ODA ES films softbaked at 80°C for 1 h were immersed into methanol in large excess for 10 days and then followed by drying in a vacuum oven at 80°C for 3–7 days. A tiny piece of the soft baked film was dissolved in DMSO-d_6 and characterized by ^{1}H n.m.r. spectroscopy. The chemical shifts of the protons of NMP were not detected in

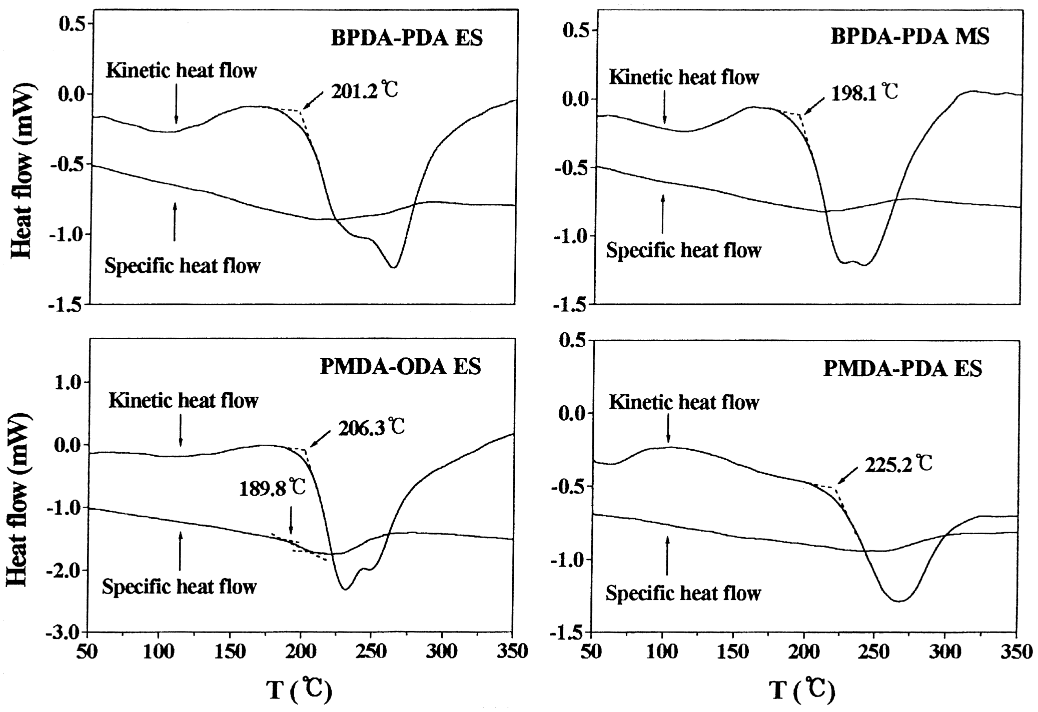

Fig. 7. The signals of specific and kinetic heat flow diagrams of various poly(amic dialkyl ester) precursors in powders which were free from residual solvent.

the n.m.r. spectrum, indicating that no residual NMP remained in the dried BPDA-ODA ES film. For the other precursors in films, the same n.m.r. characterization was conducted, however no residual NMP was detected.

All film samples of the precursors in solvent free were investigated by o.d.s.c. in the same manner as their powder samples were examined. The measured specific and kinetic heat flow diagrams are shown in Fig. 8. Both T_gs and T_is which were estimated from the separated specific and kinetic heat flow curves, respectively. Even for BPDA-PDA ES, BPDA-PDA MS and PMDA-PDA ES in which their T_gs could not be measured in powders, T_gs were able to be determined from the specific heat flow curves. The results are summarized in Table 2.

The measured T_gs are in the range of 201.1–234.2°C, depending on the precursor backbone chemistry. T_g is in the decreasing order BPDA-PDA MS > BPDA-PDA ES > PMDA-ODA ES > PMDA-PDA ES > BPDA-ODA ES. In general, T_g of a polymer is related directly to its chain rigidity: higher chain rigidity gives higher T_g. The Kuhn statistical segment length (L_K) [25] is a measure of chain rigidity although it does not provide everything concerning the chain rigidity. We have previously calculated L_Ks of various poly(amic acid)s, which are another type of polyimide precursors [15,16]. The L_Ks can be adapted for the corresponding poly(amic dialkyl ester)s because a poly(amic acid) and its dialkyl ester have the same polymer backbone, only different side groups, carboxylic acid versus carboxylic alkyl ester. The L_K decreases in the order PMDA-PDA ES (88.7 Å) > BPDA-PDA MS = BPDA-PDA ES (62.2 Å) > PMDA-ODA ES (43.3 Å) > BPDA-ODA ES (41.2 Å). Therefore, the T_gs of the poly(amic dialkyl ester)s except PMDA-PDA ES are in good agreement with the prediction based on the Kuhn segment lengths calculated. The relatively low T_g of PMDA-PDA ES is not fully understood at this moment. The difference in the T_gs of BPDA-PDA MS and BPDA-PDA ES might result from the different side groups (carboxylic methyl ester versus carboxylic ethyl ester) and the morphological difference due to the different sizes of the side groups.

In comparison, both BPDA-ODA ES and PMDA-ODA ES films exhibited relatively higher T_gs and T_is than did their powder samples, respectively. These differences in the T_gs might also be due to their morphological differences driven by the different sample preparations.

Table 2
Compositions, T_gs and T_is of poly(amic dialkyl ester)s in films

Precursor sample[a]	Composition		T_g^c (°C)	T_i^d (°C)
	NMP (wt%)	Precursors (wt%)		
BPDA-ODA ES	0	100	201.1	213.7
BPDA-PDA ES	0	100	231.7	230.0
BPDA-PDA MS	0	100	234.2	235.4
PMDA-ODA ES	0	100	226.3	230.3
PMDA-PDA ES	0	100	221.6	222.2

[a] Dried in a high vacuum at 80°C for 3–7 days
[b] Measured by proton n.m.r. spectroscopy
[c] T_g measured from the onset of glass transition in o.d.s.c. run
[d] T_i measured from the onset of imidization in o.d.s.c. run

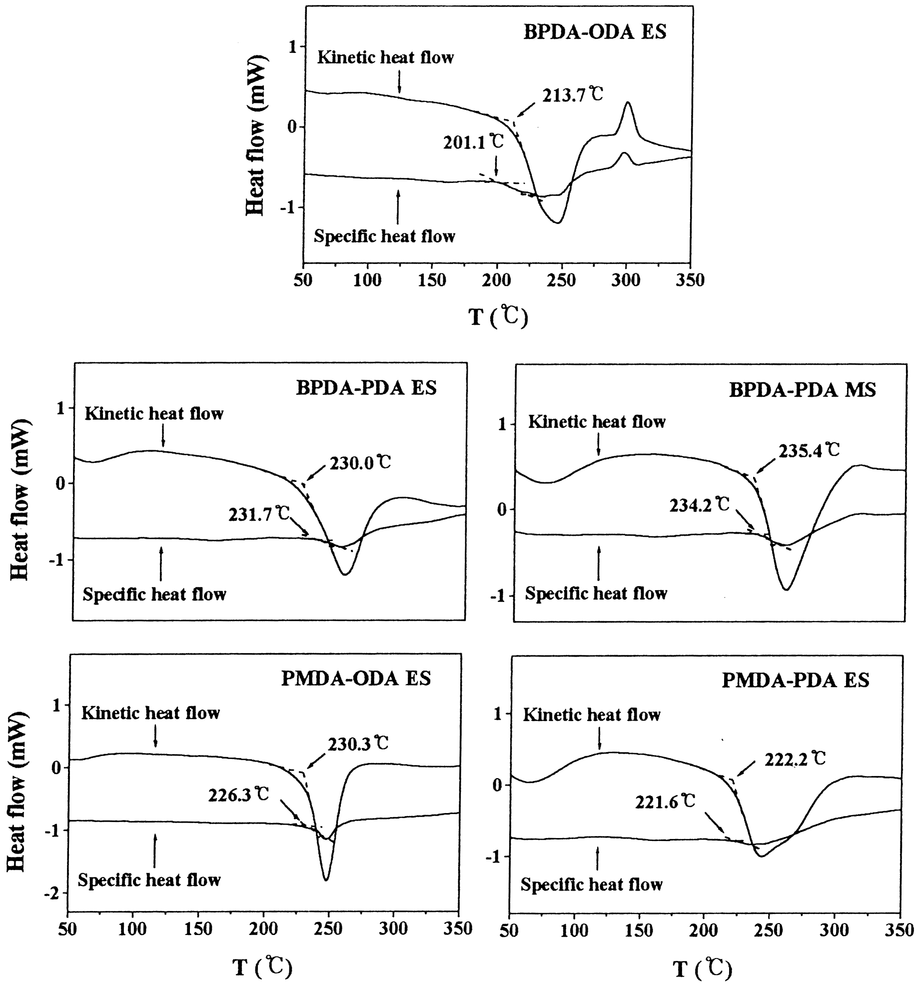

Fig. 8. The signals of specific and kinetic heat flow diagrams of various poly(amic dialkyl ester) precursors in films which were free from residual solvent. A heating rate of 10.0 K min^{-1} was employed. The temperature amplitude and frequency used in the oscillation were 10.0°C and 0.02 Hz, respectively.

Overall, for all the precursors in films the T_gs are very close to their T_is, causing difficulties in the T_g measurements: ΔT ($= T_i - T_g$) is in the range -1.7 to 12.6°C, depending upon the precursor backbone chemistry.

For the precursor films, T_is are in the range 213.7–235.4°C, depending on the sort of precursor. In comparison, T_i decreases in the order BPDA-PDA MS $>$ BPDA-PDA ES $>$ PMDA-ODA ES $>$ PMDA-PDA ES $>$ BPDA-ODA ES. This order is the same as the order of T_gs. This may be evidence that the imidization temperature of a poly(amic dialkyl ester) is related to its chain rigidity: for the precursors except PMDA-PDA ES, higher chain rigidity requires a higher T_i.

The T_is in the precursor films are always higher than those in the corresponding power samples by 3.0–37.3°C, depending on the sort of precursor. In addition, the order of the T_is of the powder samples is quite different from that of the T_is of the film samples. These differences in the T_is may also result from the morphological differences caused by the different sample preparations. The results indicate that the imidization of a poly(amic dialkyl ester) is influenced by its morphological structure in addition to the chain rigidity. In fact, besides these factors the imidization of a poly(amic dialkyl ester) should be dependent upon its chemical nature, including the nucleophilicity of the nitrogen atom of the amide linkage and the electrophilicity of the carbonyl carbon atom of the carboxylic alkyl ester group on the chemical repeat unit.

4. Conclusions

Five different poly(amic dialkyl ester) precursors were synthesized: BPDA-ODA ES, BPDA-PDA ES, BPDA-PDA MS, PMDA-ODA ES, and PMDA-PDA ES. These precursor samples in powders and films were successfully prepared without residual solvent, and then their T_gs and T_is were first determined successfully by o.d.s.c. In addition, the morphological structures of the precursors in powders were examined by X-ray diffraction.

For the precursors in powders, both BPDA-ODA ES and PMDA-ODA ES revealed T_gs, but the others did not show T_gs. However, T_gs were detectable for all the precursors in films. This result might come from the morphological differences caused by the sample preparation processes. The glassy state might be highly disturbed in the powder samples, resulting in a relatively very small heat capacity change through the glass transition. In contrast, the glassy state might be relatively well developed in the film samples, and its heat capacity change through the glass transition is reasonably large, allowing the detection of its T_g. The measured T_gs are in the range 179.2–235.4°C, depending upon the precursor backbone structure as well as on the history of sample preparation. These T_gs are very close to their T_is, causing difficulties in the T_g measurements: ΔT ($= T_i - T_g$) is in the range of -1.7°C to 24.3°C, depending upon the precursor backbone chemistry and the history of sample preparation. The measured T_is are in the range of 198.1–225.2°C for the powder samples and 213.7–235.4°C for the film samples, depending upon the sort of precursors.

For the precursors except PMDA-PDA ES, higher chain rigidity reveals higher T_g and higher T_i. The T_gs are shown to be further influenced by the morphological variation caused by sample preparation processes, whereas the T_is are observed to be further affected by both the chemical nature of precursor and the morphological variation caused by sample preparation processes.

Acknowledgements

This study was supported in part by the Korean Science and Engineering Foundation (Contract Nos. 941-0300-001-2 and 95-0501-08-01-3) and by the Ministry of Education via the New Materials Program in 1997.

References

[1] Sroog CE Prog Polym Sci 1991;16:561.
[2] Ghosh KL, Mittal KL, editors. Polyimides: fundamentals and applications. New York: Dekker, 1996.
[3] Feger C, Khojasteh MM, Molis SE, editors. Polyimides: trends in materials and applications, Proc. 5nd Intern. Conf. Polyimide, Mid-Hudson Section of Soc. Plastic Eng., Ellenville, NY, 1994. Hopewell Junction, NY: Mid-Hudson Section of Soc. Plastic Eng., 1996.
[4] Czornyj G, Chen KJ, Prada-Silva G, Arnold A, Souleotis HA, Kim S, Ree M, Volksen W, Dawson D, DiPietro R Proc Elect Comp Tech (IEEE) 1992;42:682.
[5] Ree M, Kim K, Woo SH, Chang H J Appl Phys 1996;81:698.
[6] Ree M, Yoon DY, Volksen WJ. Polym Sci, Part B: Polym Phys 1991;29:1203; Polym Mat Sci Eng (ACS) 1989;60: 179.
[7] Ree M, Rojstaczer S, Yoon DY, Volksen WJ Polym Sci, Part B: Polym Phys 1992;30:133.
[8] Bell VL, Jewell RA. J Polym Sci, Part A-1 1967;5:3043.
[9] Arnold AF, Cheng YY, Cotts PM, Diller RD, Hofer DC, Khojasteh MM, Macy EH, Shah PR, Volksen W (Intern. Business Machines Co.), US Patent No. 4849501, 1989.
[10] Houlihan FM, Bachman BJ, Wilkins CW, Pryde CA. Macromolecules 1989;22:4477; Polym Mat Sci Eng (ACS) 1988;59:225.
[11] Kim Y, Ree M, Chang T, Ha CS, Nunes TL, Lin JSJ Polym Sci, Part B: Polym Phys 1995;33:2075.
[12] Dawson DJ, DiPietro RA (Intern. Business Machines Co.), US Patent No. 5420232, 1995.
[13] Kim K, Ryou JH, Kim Y, Ree M, Chang T Polym Bulletin 1995;34:219.
[14] Kim K, Ree M, to be published.
[15] Kim SI, Pyo SM, Ree M Macromolecules 1997;30:7890.
[16] Kim SI, Pyo SM, Ree M. Polymer, in press.
[17] Seiko Instrument Inc., TA Application Brief No.64, 1993.
[18] Reading M Trends in Polymer Sci 1993;8:248.
[19] Jung DH, Kwon TW, Bae DJ, Moon IK, Jeong YH Meas Sci Technol 1992;3:475.
[20] Boller A, Jin Y, Wunderlich B J Therm Anal 1994;42:307.
[21] Hatta I Jpn J Appl Phys 1994;33:686.
[22] Swanson SA, Cotts PM, Siemens R, Kim SH Macromolecules 1991;24:1352.
[23] Cotts PMJ Polym Sci, Part B: Polym Phys Ed 1986;24:923.
[24] Scherrer P Nachr Gottinger Gessell 1918;2:98.
[25] Kuhn W Kolloid-Z 1936;76:258.