Investigation of Glass Transition Behaviors in Poly(amic acid) Precursors of Semiflexible Polyimides by Oscillating Differential Scanning Calorimetry

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ABSTRACT: Aromatic poly(amic acid) precursors always form complexes with dipolar aprotic solvents via strong acid/base interaction and are expected to have relatively high glass transition temperatures (T_g's) which are overlapped with or higher than the imidization temperatures, so that their T_g's could not be determined in spite of their wide usages. In the present study, the measurement of T_g was attempted for poly(amic acid) precursors of three different aromatic polyimides synthesized in *N*-methyl-2-pyrrolidone (NMP) from the respective dianhydrides and diamines: poly(4,4′-oxydiphenylene pyromellitamic acid) (PMDA−ODA), poly(*p*-phenylene 3,3′,4,4′-oxydiphthalamic acid) (ODPA−PDA), and poly(*p*-phenylene benzophenonetetracarboxamic acid) (BTDA−PDA). Phase transitions, as well as imidization reactions in the precursor/NMP mixtures, were measured with varying compositions by a newly developed oscillating diffferential scanning calorimetry. Compositions in the mixtures were determined by proton nuclear magnetic resonance spectroscopy. For solvent-rich mixtures, a melting point depression of the NMP solvent was observed, whereas for precursor rich mixtures, T_g depression was detected. In particular, T_g's measured for the precursor rich mixtures were best fitted by a modified Gordon−Taylor equation as a function of composition, in order to estimate T_g's of the poly(amic acid)s in solvent free, that is, true T_g's of the precursor polymers: 207.4 °C for PMDA−ODA, 166.3 °C for ODPA−PDA, and 213.2 °C for BTDA−PDA precursor. The Kuhn segment length, which is a measure of chain flexibility, was estimated to be 43.3 Å for PMDA−ODA, 34.6 Å for ODPA−PDA, and 34.6 Å for BTDA−PDA. In addition, a phase diagram was constructed for the PMDA−ODA precursor/NMP mixture. For the highly dried precursor samples, the chemical repeat unit was also determined to complex with 1.4−1.7 NMP molecules, depending on the precursors.

Introduction

A representative aromatic polyimide is poly(4,4′-oxydiphenylene pyromellitimide), which is well-known as Kapton film.[1] This polyimide has been widely used since being introduced commercially in the 1960s.[2,3] It is commonly prepared from its poly(amic acid) precursor solution. Its structure and properties have been characterized in detail by a number of research groups.[3−9] In addition, the thermal imidization of the poly(amic acid) has been investigated in detail,[4−16] despite its complexity.

However, in spite of the wide usage as well as the detailed characterization of the polyimide, the glass transition in the poly(amic acid) precursor has not yet been able to be measured. There are two main difficulties in measuring T_g in the poly(amic acid) under solvent free conditions. First, the poly(amic acid) forms complexes with dipolar aprotic solvents through a strong interaction between the orthoamic acid groups of the precursor polymer and the basic solvent molecules, so that it is very difficult to remove all solvent molecules from the cast poly(amic acid) specimen. Each orthoamic acid group of the poly(amic acid) in a dipolar aprotic solvent, for example *N*-methyl-2-pyrrolidone (NMP), is known to complex with one or two solvent molecules.[10,17] For this complex formation, the dried poly(amic acid) specimen still contains typically >20 wt % of NMP, depending on the drying conditions.[4,5,12] The residual solvent significantly reduces T_g of the poly(amic acid) and, furthermore, influences severely its imidization kinetic. Second, the poly(amic acid) is expected to exhibit a relatively high T_g due to its relatively high chain rigidity. Over the T_g range or below, it starts to imidize to the corresponding polyimide. In general, aromatic poly(amic acid)s, including the poly(amic acid), are known to start imidization about 130 °C, and the imidization reaction is accelerated with increasing temperature.[11−13,15,16] That is, the glass transitions of most aromatic poly(amic acid)s are overlapped with or higher than their imidization temperatures.

In the present study we have attempted to investigate glass transition behaviors of the poly(amic acid) precursor of poly(4,4′-oxydiphenylene pyromellitimide) and two other poly(amic acid)s [namely, poly(*p*-phenylene oxydiphthalamic acid) and poly(*p*-phenylene benzophenonetetracarboxamic acid)] using a new differential calorimetric technique, oscillating differential calorimetry (ODSC).[18] In addition, the amount of residual solvent in precursor polymer specimens were measured by proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy. For a given precursor, T_g was measured with varying the content of residual solvent. The T_g's of the poly(amic acid)s in solvent free were estimated by best fitting of the measured T_g's with a modified Gordon−Taylor equation.[19,20] The estimated true T_g's were interpreted with considering the chain rigidity and rotational freedoms along the chemical bonds. In addition, a phase diagram was constructed for the poly(4,4′-oxydiphenylene pyromellitamic acid)/NMP mixture system.

Experimental Section

Aromatic dianhydrides and diamines used in this study were supplied by Chriskev Company: pyromellitic dianhydride

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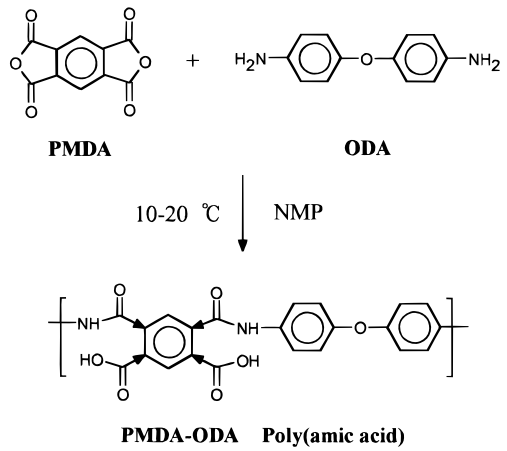

Figure 1. Synthetic scheme for the synthesis of poly(4,4′-oxydiphenylene pyromellitamic acid) (PMDA−ODA) from pyromellitic dianhydride and 4,4′-oxydiphenylenediamine in *N*-methyl-2-pyrrolidone (NMP) solvent.

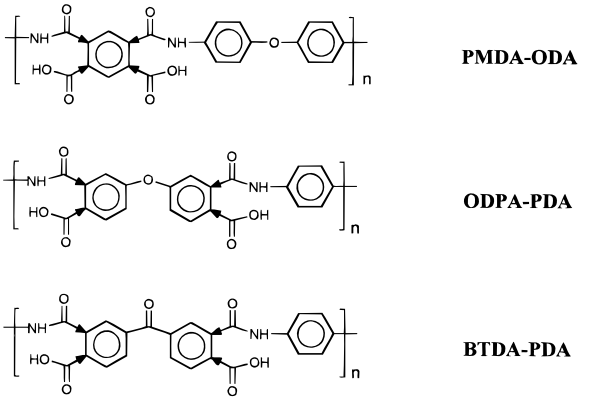

Figure 2. Chemical structures of aromatic poly(amic acid)s synthesized in this study.

(PMDA), 3,3′,4,4′-oxydiphthalic anhydride (ODPA), benzophenonetetracarboxylic dianhydride (BTDA), *p*-phenylenediamine (PDA), and 4,4′-oxydiphenylenediamine (ODA). All monomers were purified by sublimation under reduced pressure or recrystallized using proper solvents and then used for polymerization.

Poly(4,4′-oxydiphenylene pyromellitamic acid) (PMDA−ODA) was prepared in a glovebox filled with dry nitrogen gas by slowly adding the sublimed PMDA to the purified ODA in dry *N*-methyl-2-pyrrolidone (NMP) (see Figure 1). Once the dianhydride addition was completed, the reaction flask was capped tightly and stirring was continued for 2 days to make the polymerization mixture completely homogeneous. The other two poly(amic acid)s were prepared in the same manner as PMDA−ODA was synthesized: ODPA−PDA and BTDA−PDA precursors (see Figure 2). The solid contents of the precursor solutions were 10−15 wt %. The precursor solutions were filtered with silver metal membranes of 1.0 μm pore size, tightly sealed, and stored in a refrigerator before use.

In the synthesis of poly(amic acid)s, an attempt to control molecular weights was made by creating a stoichiometric imbalance of the monomers by using the diamine in small excess. For the synthesized poly(amic acid)s, intrinsic viscosity [η] measurements were carried out in NMP at 25.0 °C using an Ubbelohde suspended level capillary viscometer as found in a method described in the literature.[21,22] Here, in order to minimize the polyelectrolyte effect in the viscosity measurement, 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.[21,22] All the solutions were filtered through 0.5 μm Fluoropore filters of the Millipore Co. before measurement. For a given poly(amic acid), the relative and specific viscosities were measured at four different concentrations over the range of 0.10−0.60 g/dL, and the [η] value was determined by extrapolation of the reduced and inherent viscosities to infinite dilution. The [η] was determined to be 0.601 dL/g for the PMDA−ODA precursor, 0.613 dL/g for the ODPA−PDA precursor, and 0.589 dL/g for the BTDA−PDA precursor.

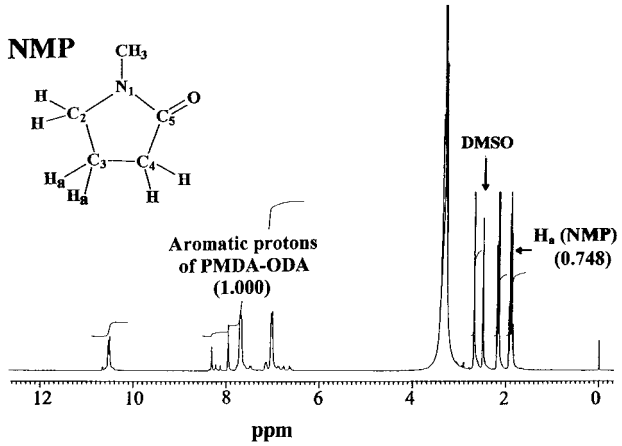

Figure 3. ^{1}H-NMR spectrum of a PMDA−ODA precursor sample soft-baked at 80 °C for 1 h, which was dissolved in dimethyl-d_6 sulfoxide (DMSO-d_6).

Poly(amic acid) solutions were cast on precleaned glass slides and soft-baked on a hotplate at 80 °C for 10−60 min. Some of the films soft-baked for 1 h were additionally dried in a vacuum oven at 50 °C for various times: 2 days, 4 days, and 7 days. The contents of residual NMP in these precursor films were determined by proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy as described in the following: Small pieces of a dried precursor film were dissolved in dimethyl-d_6 sulfoxide (DMSO-d_6), and the residual NMP and precursor polymer in the solution were characterized using a Bruker NMR spectrometer (Model: Aspect 300 MHz) with a proton probe. Then, the amount of NMP in weight percent was calculated from the measured NMR spectra as described previously elsewhere.[17]

Thermograms including glass transition and imidization in the dried precursor samples were measured from −60 to +400 °C using a Seiko oscillating differential scanning calorimeter (Model: ODSC-220CU) as described previously elsewhere.[17] During the measurements, dry nitrogen gas was purged with a flow rate of 80 cm^3/min. Calibrations of temperature and enthalpy were carried out using indium and tin, respectively. In scanning runs, samples of ca. 2 mg were used. A heating rate of 10.0 K/min was employed. An oscillating amplitude of 10.0 °C and an oscillating frequency of 0.02 Hz were used, respectively.

Results and Discussion

Residual NMP Measurements. Tiny pieces of a PMDA−ODA precursor sample soft-baked at 80 °C for 1 h were dissolved in DMSO-d_6 and characterized by ^{1}H-NMR spectroscopy. The measured NMR spectrum is shown in Figure 3. The two protons (2Ha) of the C_3 on the five-membered ring of NMP appeared at δ 1.75−2.05 ppm, whereas the ten aromatic protons in the repeat unit of the precursor polymer were revealed at δ 6.5−8.4 ppm as multiple peaks. The amount of NMP solvent in weight fraction was estimated from the integrations of these peaks as described previously elsewhere.[17] The content of residual NMP in the dried film was determined to be 47.0 wt %. Thus, the content of the precursor polymer was 53.0 wt %. For precursor samples dried under the other conditions, NMP and polymer contents were determined in the same manner. The results are summarized in Table 1. This characterization was extended to both ODPA−PDA and

Table 1. Compositions and T_g's of PMDA−ODA Precursor Samples Dried under Various Conditions

precursor sample no.	drying condition	composition[a] NMP (wt %)	composition[a] precursor (wt %)	T_g (or T_m)[b] (°C)	T_i[c] (°C)
1	(NMP itself)	100	0	−23.6[d]	
2	(precursor solution itself)	89.1	10.9	−27.9[d]	
3	80 °C/10 min	78.2	21.8	−32.1[d]	
4	80 °C/20 min	62.3	37.7	−29.8[d]	
5	80 °C/1 h	47.0	53.0	−6.0[e]	118.4
6	80 °C/1h + 50 °C/2 days (in vacuum)	42.7	57.3	43.4[e]	129.0
7	80 °C/1h + 50 °C/4 days (in vacuum)	31.5	68.5	94.8[e]	133.7
8	80 °C/1h + 50 °C/7 days (in vacuum)	28.5	71.5	119.5[e]	139.1

[a] Measured by proton NMR spectroscopy. [b] Measured by oscillating differential scanning calorimetry (ODSC). [c] Onset temperature of imidization measured by ODSC. [d] T_m measured from the peak maximum of NMP melting in ODSC run. [e] T_g measured from the onset of glass transition in ODSC run.

Table 2. Compositions and T_g's of ODPA−PDA Precursor Samples Dried under Various Conditions

precursor sample no.	drying condition	composition[a] NMP (wt %)	composition[a] precursor (wt %)	T_g[b] (°C)	T_i[c] (°C)
1	80 °C/1 h	38.9	61.1	29.1	125.0
2	80 °C/1 h + 50 °C/2 days (in vacuum)	32.7	67.3	78.8	138.2
3	80 °C/1 h + 50 °C/4 days (in vacuum)	26.8	73.2	89.0	145.2
4	80 °C/1 h + 50 °C/7 days (in vacuum)	25.0	75.0	109.4	147.3

[a] Measured by proton NMR spectroscopy. [b] T_g measured from the onset of glass transition in oscillating differential scanning calorimetry (ODSC). [c] Onset temperature of imidization measured by ODSC.

Table 3. Compositions and T_g's of BTDA−PDA Precursor Samples Dried under Various Conditions

precursor sample no.	drying condition	composition[a] NMP (wt %)	composition[a] precursor (wt %)	T_g[b] (°C)	T_i[c] (°C)
1	80 °C/1 h	39.5	60.5	36.2	137.5
2	80 °C/1 h + 50 °C/2 days (in vacuum)	33.9	66.1	81.6	143.8
3	80 °C/1 h + 50 °C/4 days (in vacuum)	26.0	74.0	111.7	145.5
4	80 °C/1 h + 50 °C/7 days (in vacuum)	25.0	75.0	136.1	152.5

[a] Measured by proton NMR spectroscopy. [b] T_g measured from the onset of glass transition in oscillating differential scanning calorimetry (ODSC). [c] Onset temperature of imidization measured by ODSC.

BTDA−PDA precursor samples dried at various conditions. The results are listed in Tables 2 and 3, respectively.

For these highly dried precursor samples, all the residual NMP molecules are assumed to participate in forming complexes with the orthoamic acid groups of the precursors, so that the number of NMP molecules bound to the repeat units of the precursors can be estimated from the contents of residual solvent measured by NMR spectroscopy. The number of the NMP molecules bound per the chemical repeat unit of precursor is calculated to be 1.7 for the PMDA−ODA, 1.4 for the ODPA−PDA, and 1.5 for the BTDA−PDA precursor. These are in good agreement with the results published previously in the literature.[10,17]

ODSC Measurements and Phase Diagram. A PMDA−ODA precursor sample with a residual NMP of 28.5 wt % was characterized by conventional DSC and by oscillating DSC. As shown in Figure 4, the heat flow curve of glass transition could not be recognized on the conventional DSC thermogram, because the endothermic heat flow due to the imidization is predominant over the temperature range 120−230 °C. Thus, only the imidization behavior of the precursor sample can be observed from the conventional DSC thermogram.

In contrast, Figure 5 shows the oscillating input temperature signals as well as the oscillating DSC output signals as a function of time. The ODSC thermogram can be nicely separated into two parts, the specific heat flow and the kinetic heat flow as described previously.[17] The separated specific and kinetic heat flows are plotted in Figure 6 as a function of temperature. The specific heat flow curve reveals clearly a glass

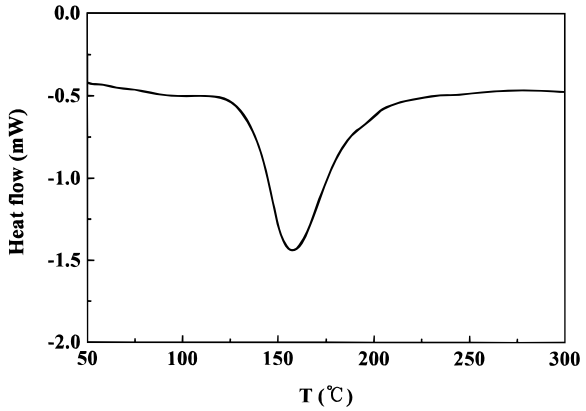

Figure 4. Conventional DSC thermogram of a PMDA−ODA precursor sample containing 28.5 wt % residual NMP solvent. A heating rate of 10.0 K/min was employed.

transition over 100−160 °C. From this thermogram, T_g was determined to be 119.5 °C for the dried precursor sample: Here, T_g is defined as the onset temperature of glass transition in the specific heat flow. 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 removals of the reaction byproduct (i.e., water) and residual solvent. The onset temperature of imidization (T_i) in the dried film was estimated to be 139.1 °C.

The ODSC measurement was extended to the other PMDA−ODA precursor samples dried at various conditions. For the precursor samples with a residual NMP of <50 wt %, the separated specific and kinetic heat flow curves are illustrated in Figures 7 and 8, respectively,

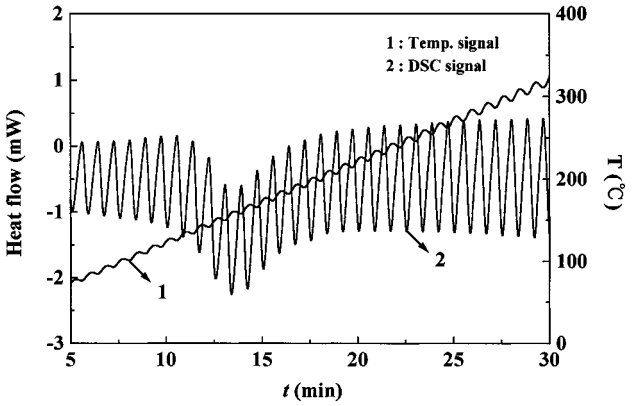

Figure 5. Input temperature signal and output ODSC signal of a PMDA−ODA precursor sample containing 28.5 wt % residual NMP solvent. A heating rate of 10.0 K/min was employed. The temperature amplitude and frequency used in the oscillation were 10.0 °C and 0.02 Hz, respectively.

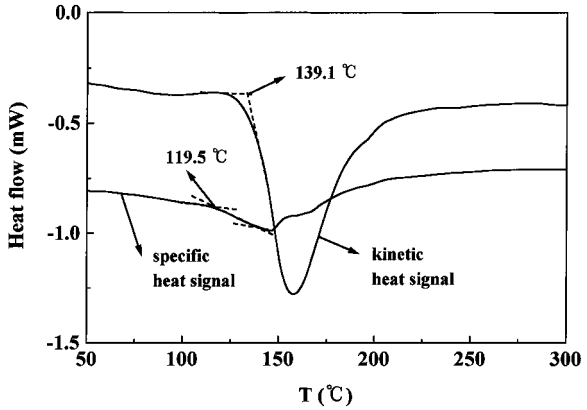

Figure 6. Signals of specific and kinetic heat flow component separated from the ODSC thermogram in Figure 5, which was obtained for a PMDA−ODA precursor sample containing 28.5 wt % residual NMP solvent.

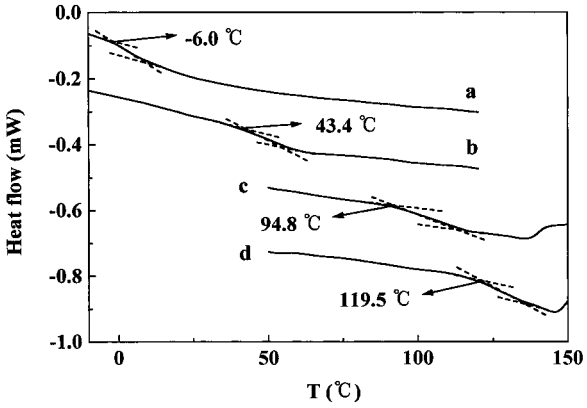

Figure 7. Signals of specific heat flow component separated from ODSC thermograms obtained for PMDA−ODA precursor samples containing various amounts of residual NMP: (a) 47.0 wt % NMP; (b) 42.7 wt %; (c) 31.5 wt %; (d) 28.5 wt %. A heating rate of 10.0 K/min was employed. The temperature amplitude and frequency used in the oscillation were 10.0 °C and 0.02 Hz, respectively.

and compared with those of the sample described above, respectively. Both T_g and T_i of each sample were estimated from the heat flow curves and listed in Table 1. As the content of residual NMP in the precursor sample reduced to 28.5 wt % from 47.0 wt %, T_g increased to 119.5 °C from −6.0 °C and T_i also increased to 139.1 °C from 118.4 °C. Overall, the residual NMP in the precursor sample caused significant reductions

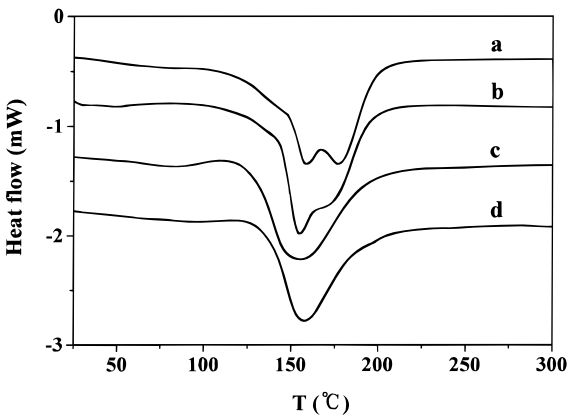

Figure 8. Signals of kinetic heat flow component separated from ODSC thermograms obtained for PMDA−ODA precursor samples containing various amounts of residual NMP: (a) 47.0 wt % NMP; (b) 42.7 wt %; (c) 31.5 wt %; (d) 28.5 wt %. A heating rate of 10.0 K/min was employed. The temperature amplitude and frequency used in the oscillation were 10.0 °C and 0.02 Hz, respectively.

in both glass transition and imidization temperatures. However, the effect of residual NMP is relatively more significant in the T_g than the T_i.

The ODSC investigation was also carried out for the PMDA−ODA precursor samples contained >50 wt % NMP, including NMP itself as well as the precursor solution with a concentration of 10.9 wt %. These samples exhibited a melting transition or a glass transition at a temperature region much lower than the imidization temperature. For this fact, measurements were carried out in the conventional mode. The results are listed in Table 1. The melting point (T_m) of the pure NMP was −23.6 °C: Here, T_m is defined as the temperature of the peak maximum of NMP melting in the conventional DSC signal. For these NMP-rich mixtures, T_m of the NMP component was depressed, depending on the content of precursor polymer. T_m was depressed to −27.9 °C for the precursor solution itself with 10.9 wt % precursor, −32.1 °C for the sample with 21.8 wt % precursor, and −29.8 °C for the sample with 37.7 wt % precursor.

In addition, from these T_g and T_m data with varying compositions, a phase diagram was constructed for the PMDA−ODA precursor/NMP mixture. The result is illustrated in Figure 9. For the NMP-rich mixture, the T_m of the NMP component was almost linearly depressed with an increase in the precursor content, whereas for the precursor-rich mixture the T_g of the precursor component was convexly depressed with an increase in the solvent content. They are extrapolated to meet together at the composition of 51.7 wt % NMP and 48.3 wt % precursor. Here, in the NMP rich region, *regime* I, the dashed line was generated from the linear fitting of the measured T_m's, whereas in the precursor rich region, *regime* II, the solid curve was made by best fitting of the measured T_g's with a modified Gordon−Taylor equation. The phase behavior in the *regime* II is described further in the latter part.

Both ODPA−PDA and BTDA−PDA precursors in the dried sample were characterized by ODSC in the same manner as the PMDA−ODA precursor samples were investigated. For all the ODSC thermograms, the specific heat flow parts were separated from the kinetic heat flow parts. Both T_g's and T_i's, which were estimated from the separated specific and kinetic heat flow curves, respectively, are summarized in Tables 2 and 3.

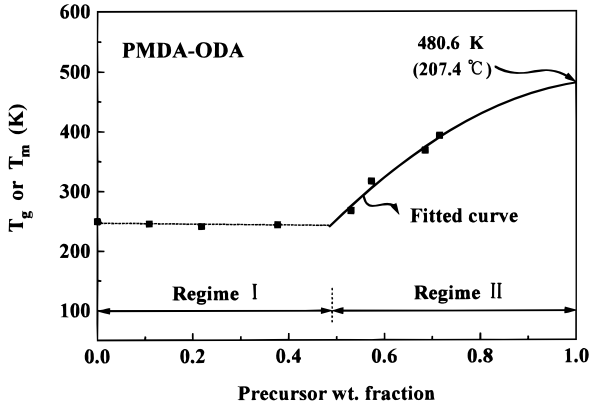

Figure 9. Variation of glass transition temperature (T_g) or melting point (T_m) of the PMDA−ODA precursor/NMP solvent mixture as a function of precursor weight fraction. The "■" symbols denote the measured phase transition temperatures. The solid curve is the curve fitted by a modified Gorden−Taylor equation, eq 6, from the T_g data measured in *regime* II.

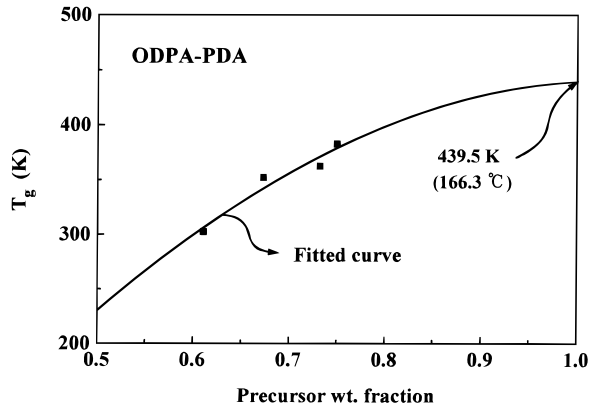

Figure 10. Variation of glass transition temperature (T_g) or melting point (T_m) of the ODPA−PDA precursor/NMP solvent mixture as a function of precursor weight fraction. The "■" symbols denote the measured phase transition temperatures. The solid curve is the curve fitted by a modified Gorden−Taylor equation, eq 6, from the measured T_g data.

Determination of T_g's of Poly(amic acid) Precursors under Solvent Free Conditions. Here, it was attempted to estimate true T_g's of the poly(amic acid) precursors, namely, T_g's of the precursors in solvent free from the T_g's measured for the precursor/NMP mixtures. As shown in Figures 9−11, for all the precursor/NMP mixtures, T_g variations with composition are convex particularly in the precursor rich region, *regime* II.

In fact, the type of T_g−composition profile in a miscible mixture is known to depend strongly upon the interaction nature between the components: linear,[23] concave,[24] and convex[19,20,25,26] types. Both the linear and concave relationships indicate that the blend components interact together via mainly van der Waals attraction, leading to the miscible blends. The convex relationship is known to result from strong intermolecular interactions, such as hydrogen bonding, acid−base interaction, and charge complexation, between the blend components.

The T_g variations with composition were attempted to be described by several theoretical and empirical expressions.[19,20,23−31] In particular, convex T_g behaviors with composition in miscible polymer−polymer blend systems have been successfully described by a modified Gordon−Taylor equation.[19,20,26] Therefore, in the present

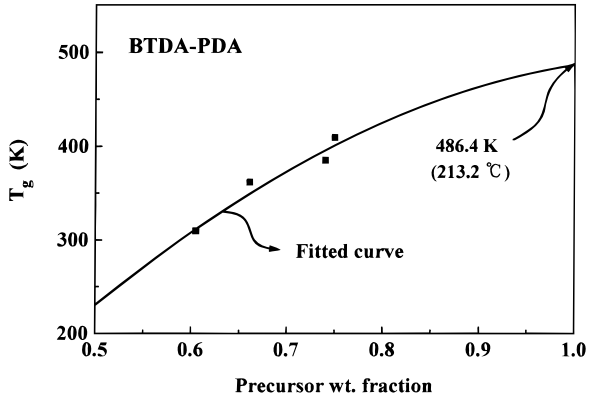

Figure 11. Variation of glass transition temperature (T_g) or melting point (T_m) of the BTDA−PDA precursor/NMP solvent mixture as a function of precursor weight fraction. The "■" symbols denote the measured phase transition temperatures. The solid curve is the curve fitted by a modified Gorden−Taylor equation, eq 6, from the measured T_g data.

study the modified Gordon−Taylor expression was adapted in order to illustrate convex T_g variations with composition observed for all the three poly(amic acid)s contained residual NMP solvent via strong acid−base complexation between the orthoamic acid group of the polymers and the secondary amino group of the NMP molecules and, furthermore, to estimate their true T_g's under solvent free conditions.

The modified Gordon−Taylor equation can be expressed as follows[19,20,26]

$$T_g = \frac{\Delta\alpha_s T_{g,s} W_s + \Delta\alpha_p T_{g,p} W_p}{\Delta\alpha_s W_s + \Delta\alpha_p W_p} + \frac{\Delta k W_s W_p}{\Delta\alpha_s W_s + \Delta\alpha_p W_p} \quad (1)$$

where

$$\Delta\alpha_i = \alpha_{r,i} - \alpha_{g,i} \quad (2)$$

$$\Delta k = k_g - k_r \quad (3)$$

Here, T_g is the glass transition temperature of a mixture containing the weight fractions, W_s and W_p, of two components (i.e., NMP solvent, s, and precursor polymer, p) in which glass transition temperatures are $T_{g,s}$ [that is, the melting point (T_m) of NMP] and $T_{g,p}$, respectively. $\Delta\alpha_i$ is the difference between the volume expansion coefficients, $\alpha_{r,i}$ and $\alpha_{g,i}$, of the component i in the rubbery (or liquid) and glassy states. k_g and k_r are the parameters representing the volume changes on mixing of two components in a mixture expressed as follows

$$V_g = V_{g,s} W_s + V_{g,p} W_p + k_g W_s W_p \quad (4)$$

$$V_r = V_{r,s} W_s + V_{r,p} W_p + k_r W_s W_p \quad (5)$$

where V_g and V_r are the specific volumes of a mixture in the glassy and rubbery (or liquid) states, respectively. $V_{g,i}$ and $V_{r,i}$ are the specific volumes of the component i in the glassy and rubbery (or liquid) states, respectively. The changes in the specific volumes with the temperature are assumed to be linear.

Equation 1 was originally developed to describe T_g variations over the entire compositions in a mixture, so that it can not be directly applicable for the precursor/NMP mixtures which exhibited convex T_g variations only in the precursor rich region. Thus, eq 1 was further modified. That is, the $\Delta\alpha_s$ and $T_{g,s}$ terms of the pure

Table 4. Constants Used to Estimate T_g's of Poly(amic acid)s under Solvent Free Conditions[a]

precursor	V_W (cm^3/g)	$\Delta\alpha_p$ ($cm^3/g\cdot K$)	Δk	W_c	T_g (°C)
PMDA−ODA	0.484	2.66×10^{-4}	$0.106(1 - W_c)$	0.497	207.4
ODPA−PDA	0.484	2.66×10^{-4}	$0.106(1 - W_c)$	0.527	166.3
BTDA−PDA	0.482	2.65×10^{-4}	$0.106(1 - W_c)$	0.524	213.2

[a] The V_W and $\Delta\alpha_s$ of the pure NMP solvent were calculated to be 0.595 cm^3/g and 3.27×10^{-4} $cm^3/g\cdot K$, respectively.

solvent are replaced by the $\Delta\alpha_c$ and $T_{g,c}$ terms of the mixture with the critical concentration W_c. In addition, the weight fractions of solvent and precursor, W_s and W_p, in a mixture are again fractionated by the $(1 - W_c)$ term rather than 1.0, which covers the entire concentration range, respectively. With these modifications, eq 1 can be rewritten as follows[17]

$$T_g = \frac{\Delta\alpha_c T_{g,c}\left(\frac{1 - W_p}{1 - W_c}\right) + \Delta\alpha_p T_{g,p}\left(\frac{W_p - W_c}{1 - W_c}\right)}{\Delta\alpha_c\left(\frac{1 - W_p}{1 - W_c}\right) + \Delta\alpha_p\left(\frac{W_p - W_c}{1 - W_c}\right)} + \frac{\Delta k\left(\frac{1 - W_p}{1 - W_c}\right)\left(\frac{W_p - W_c}{1 - W_c}\right)}{\Delta\alpha_c\left(\frac{1 - W_p}{1 - W_c}\right) + \Delta\alpha_p\left(\frac{W_p - W_c}{1 - W_c}\right)} \quad (6)$$

where

$$W_c \le W_p \le 1.0 \quad (7)$$

$$\Delta\alpha_c = \Delta\alpha_s(1 - W_c) + \Delta\alpha_p W_c \quad (8)$$

Here, $\Delta\alpha_s$ and $\Delta\alpha_p$ were calculated from the van der Waals volumes (V_W's)[32] of the repeating unit of a precursor and the NMP solvent molecule, respectively, as reported in the literature.[33] For the NMP solvent and the precursor polymers, both V_W's and $\Delta\alpha$'s were calculated, respectively. For the precursor/NMP mixtures, Δk ($=k_g - k_r$) in eq 6 cannot be obtained in a convenient manner. However, it was previously estimated for poly(*p*-phenylene biphenyltetracarboxamic acid) (BPDA−PDA) in NMP:[17]

$$\Delta k = 0.106(1 - W_c) \quad (9)$$

In the present study, eq 9 was adapted to calculate Δk's of the poly(amic acid)s under the assumption that the constant value, 0.106, in the equation is not sensitive to the type of aromatic poly(amic acid) precursor. The results are listed in Table 4.

For the PMDA−ODA precursor/NMP mixture in *regime* II, the measured T_g's were best fit by eq 6 with varying W_c. As shown in Figure 9, the best fit result was obtained with $W_c = 0.497$, resulting in $T_g = 207.4$ °C for the PMDA−ODA precursor under the solvent free condition. This analysis was extended for the ODPA−PDA and BTDA−PDA precursors in only the *regime* II regions. The best fit curves are presented in Figures 10 and 11, and the results are listed in Table 4. The estimated true T_g was 166.3 °C for the ODPA−PDA and 213.2 °C for the BTDA−PDA precursor. In comparison, the true T_g increases in the order ODPA−PDA < PMDA−ODA < BTDA−PDA precursor. Overall, all the precursors exhibit T_g's higher than the onset temperatures in their imidizations.

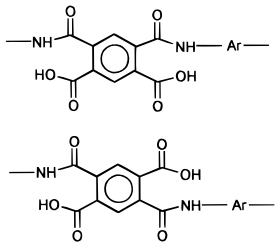

Figure 12. Possible isomeric repeat units in the PMDA−ODA precursor: Ar denotes the ODA unit.

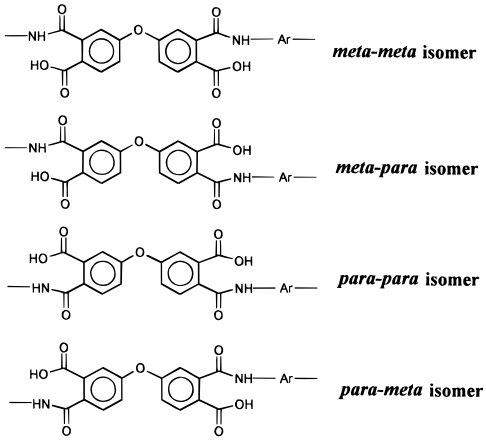

Figure 13. Possible isomeric repeat units in the ODPA−PDA precursor: Ar denotes the PDA unit.

Chain Rigidities and Their Relationships to T_g's. In general, the T_g of a polymer is strongly dependent upon the chain rigidity. Thus, we attempted to estimate chain rigidities of the poly(amic acid) precursors here. The Kuhn statistical segment length (L_K)[34] is known to be a measure of chain rigidity. Although the Kuhn statistical segment length does not provide everything concerning the chain rigidity, it can give some information about the chain rigidity. For this reason, Kuhn statistical segment lengths of the precursor polymers were estimated in accordance with a calculation procedure reported previously.[17,35] The calculation was carried out with the three assumptions in that follow. First, the amide linkage in the repeat unit of a poly(amic acid) possesses a planar *trans*-structure.[36] Second, in the poly(amic acid)s all the backbone skeletal valence angles, such as $\angle C_{ar}-C-N$, $\angle C-N-C_{ar}$, $\angle C_{ar}-O-C_{ar}$, and $\angle C_{ar}-C-C_{ar}$ (see Figure 2), are equal to 120°.[17,37] Finally, the precursors are alternatively linked by their possible isomeric repeat units. For the PMDA−ODA pecursor, the chemical repeat units have two different isomeric structures as shown in Figure 12: *meta* and *para* isomeric units. For both ODPA−PDA and BTDA−PDA precursors, the chemical repeat units have four different isomeric structures as shown in Figures 13 and 14: *meta−para*, *meta−meta*, *para−para*, and *para−meta* isomeric units. The calculated results are listed in Table 5.

The calculated L_K was 43.3 Å for the PMDA−ODA precursor and 34.6 Å for both the ODPA−PDA and the BTDA−PDA precursors. That is, chain rigidity is in the decreasing order PMDA−ODA > ODPA−PDA ≈ BTDA−PDA. These chain rigidities may be directly related to the T_g's: In general, a higher chain rigidity produces a higher T_g. Therefore, from the estimated L_K, T_g is expected to be in the decreasing order PMDA−ODA > ODPA−PDA ≈ BTDA−PDA. This expection is in good agreement with the experimental results for PMDA−

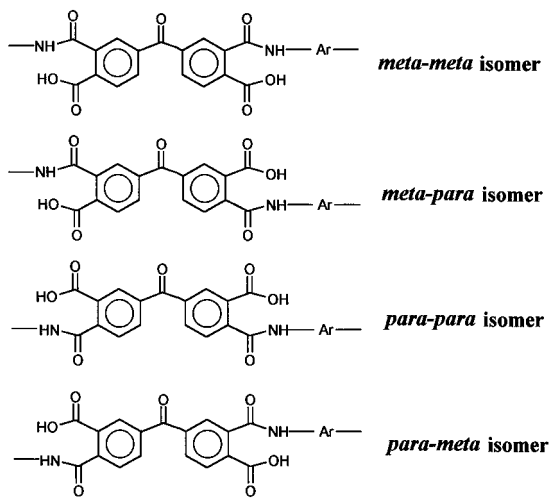

Figure 14. Possible isomeric repeat units in the BTDA−PDA precursor: Ar denotes the PDA unit.

Table 5. Kuhn Statistical Segment Lengths (L_K's) with Their Parameters and Glass Transition Temperatures (T_g's) for Several Poly(amic acid)s[a]

poly-(amic acid)	ν	$\langle h^2\rangle/n$ (Å^2)	λ (Å)	L_K (Å)	L_K^{-1} ($\times 10^2$) (Å^{-1})	T_g (K)
PMDA−ODA	6	2756.9	63.9	43.3	2.31	480.6
ODPA−PDA	8	2204.8	63.9	34.6	2.89	439.5
BTDA−PDA	8	2204.8	63.9	34.6	2.89	486.4

[a] ν, the number of linear bonds per structural repeat unit; $\langle h^2\rangle$, the mean square of end-to-end distance of a precursor polymer; n, the number of structural repeat units in a precursor polymer; λ, the contour length (that is, the length of a fully extended chain) divided by the number of structural repeat units, n; T_g, the glass transition temperature of a precursor polymer in solvent free.

ODA and ODPA−PDA precursors. However, BTDA−PDA exhibited a higher T_g than that of ODPA−PDA although its L_K was estimated to be same as that of ODPA−PDA. Furthermore, its T_g is higher than that of the PMDA−ODA precursor even though its L_K is smaller than that of PMDA−ODA. This is evidence that the L_K in the BTDA−PDA was underestimated. This may result from two reasons as follows. First, for the BTDA−PDA precursor, the rotational freedom along the $C_{ar}-C-C_{ar}$ linkage seems to be resticted by the oxygen atom of the carbonyl linkage which makes π-conjugations with the linked aromatic carbons, forming a coplanar structure with the linked phenyl rings. The limited rotational freedom in the BTDA−PDA repeat unit causes a reduction in the overall chain flexibility, consequently leading to an increase in its T_g. Second, the conjugation with carbonyl may affect the proportions of isomeric units, increasing the chain rigidity.

Conclusions

Three poly(amic acid) precursors were synthesized in dipolar aprotic NMP solvent from the respective aromatic dianhydrides and diamines: PMDA−ODA, ODPA−PDA, and BTDA−PDA precursors. The precursor solutions were cast and then dried at various conditions. The amounts of residual NMP solvent in the dried precursor samples were determined by proton NMR spectroscopy to be 25.0−89.1 wt %, depending on the drying conditions. From the NMR spectroscopic results for the highly dried precursor samples, it has been estimated that the chemical repeat unit in a poly(amic acid) complexes with 1.4−1.7 NMP molecules, depending on the precursors.

For samples of the poly(amic acid)s dried at various conditions, T_g's were successfully measured as a function of residual NMP content by the new oscillating DSC technique, which was recently developed. In particular, for the PMDA−ODA precursor/NMP mixture, its phase diagram was constructed from the T_g's measured with varying compositions. In addition, T_g's of the precursors in solvent free (namely, true T_g's of the precursors) were estimated by best fitting the measured T_g's with a modified Gordon−Taylor equation: 207.4 °C for PMDA−ODA, 166.3 °C for ODPA−PDA, and 213.2 °C for BTDA−PDA precursor.

In addition, the Kuhn statistical segment length, which is a measure of chain rigidity, was calculated for the precursor polymers: 43.3 Å for the PMDA−ODA precursor and 34.6 Å for both the ODPA−PDA and the BTDA−PDA precursors. In general, higher chain rigidity gives a higher T_g. BTDA−PDA revealed a relatively high T_g in spite of its relatively small Kuhn statistical segment length. This may be attributed to the underestimation in the chain rigidity calculation.

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(1) Kapton film is the trade mark of Du Pont Chemical Company.

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