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Notes

Studies on Imidization Behaviors of Differently Processed Samples of Poly(imide-*alt*-amic ester) Prepared from MDPM and 6FDA

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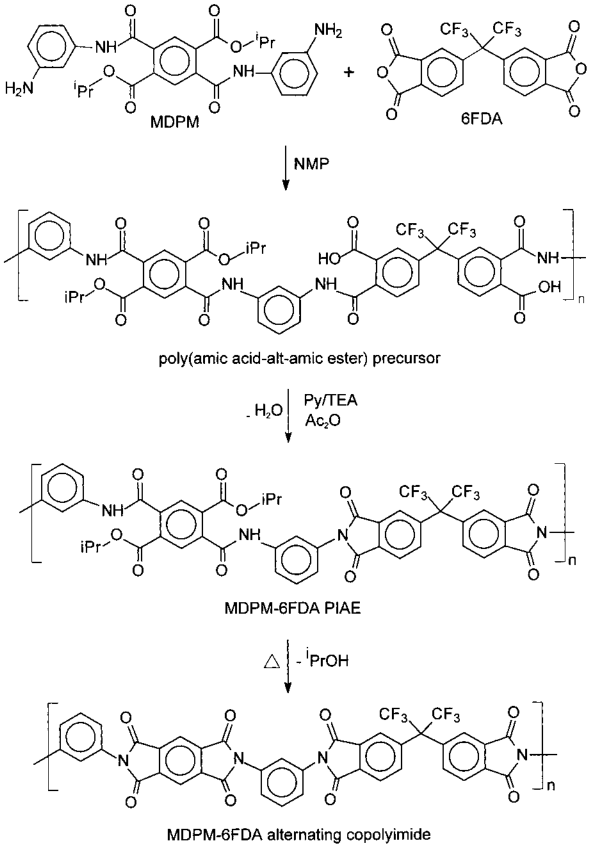
Introduction

In the past several decades, a great number of results have been reported about aromatic polyimides which are of interest for microelectronic applications due to their outstanding thermal, electrical, and mechanical properties.[1,2] Particularly concerned are formation of poly(amic acids), imidization kinetics, and physical or mechanical properties of resulting polyimides associated with their structure−property relationships.[3−7] Since polyimides are usually prepared by thermal or chemical imidization of precursors such as poly(amic acids), poly(amic esters), etc., the nature of precursors is also an important factor to affect the properties of the final polyimides. For example, Goeschel et al. have reported that the polyimide films prepared from poly(amic ester) exhibited a higher degree of molecular ordering than those from poly(amic acid), even if both precursors produced identical chemical structure of polyimide.[8] Miwa et al. have also observed significant differences in thermal expansion coefficients between the polyimides from poly(amic acids) and poly(amic esters) and discussed the importance of interactions between the precursors and solvent.[9]

However, little has been studied about the effect of the processing method or sample form of precursor on imidization. The precursor sample state, whether it is a powder, a film, or a fiber, is certainly important because it could result in polyimides of different physical and/or thermal properties even though the final polyimides have the same chemical structure. In general, it is very complicated to study the effect of a precursor sample state on the resulting polyimides because thermal and hydrolytic instability of poly(amic acids) hindered the characterization of them by X-ray diffraction (XRD), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA).

Scheme 1. Synthesis of MDPM-6FDA PIAE and Subsequent Imidization for the Alternating Copolyimide



Recently, we have reported a successful synthesis of novel precursors of alternating copolyimides, poly(imide-*alt*-amic ester) (PIAE), which exhibited excellent hydrolytic and thermal stability as compared to those of conventional precursor poly(amic acid)s.[10−14] Taking advantage of its thermal and hydrolytic stability, we were able to isolate the precursor in highly pure powder form and other forms. It is the object of the present study to investigate the effect of morphological differences in precursors on their thermal imidization behaviors and on the properties of the resulting polyimides.

Experimental Section

MDPM-6FDA PIAE used in this work was synthesized[14] by polymerization of *N*,*N*′-bis(3-aminophenyl)-2,5-bis[(isopropyloxy)carbonyl] benzene-1,4-dicarboxamide (MDPM)[9] and 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) in *N*-methylpyrrolidinone (NMP) followed by a selective chemical dehydration[15] as illustrated in Scheme 1. The reaction mixture was injected into methanol to obtain a yellowish powder of MDPM-6FDA PIAE which was purified further by reprecipitating tetrahydrofuran (THF) solution of PIAE from methanol/water (1:1 v/v) and by drying the collected powder in a vacuum oven at 60 °C. This procedure was repeated for several times to obtain light-yellow fibrous particles, which was abbreviated PPT.

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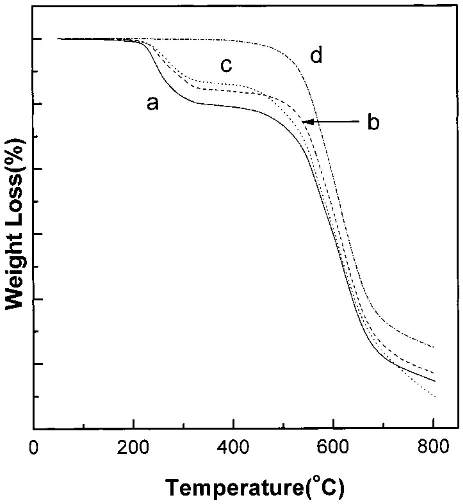

Figure 1. TGA diagram of MDPM-6FDA PIAE film (FLM) annealed at (a) 170 °C, (b) 190 °C, (c) 210 °C, and (d) 350 °C for 0.5 h.

A 16 μm thickness film was prepared by casting THF solution of MDPM-6FDA PIAE on a glass substrate and evaporating solvent in a vacuum oven at 60 °C for 5 h. This sample was abbreviated FLM. A strip of FLM (approximately 12.5 mm in width) was stretched with a vertically pending weight (200 g) at 170 °C for 0.5 h. The stretched film was abbreviated SFL. To prepare the most amorphous sample, THF was evaporated from the solution of MDPM-6FDA PIAE by using a vacuum pump at room temperature. Bulk powder (BLK) was obtained after grinding the resulting solid mass in a mortar. All the samples were annealed at 170 °C for 0.5 h prior to further experiments to give the equal thermal history as SFL.

The thermal imidization process was investigated by using a differential scanning calorimeter (Perkin-Elmer DSC-7) and a thermogravimetric analyzer (Dupont 2100). The crystallinity of MDPM-6FDA PIAEs and the corresponding polyimides after cure were examined by an X-ray diffraction analyzer (Rigaku D-MAX-3B). PIAE samples were heated at 350 °C for 2 h to convert the precursor to the corresponding polyimide samples.

Results and Discussion

Four different MDPM-6FDA PIAE samples were prepared to investigate the effect of precursor morphology on imidization behavior as described in the Experimental Section. To determine the stretching temperature at which no thermal imidization occurs, TGA analyses were performed for samples annealed at various temperatures (170, 190, 210, or 350 °C, respectively) for 0.5 h. As shown in Figure 1, all films started to lose weight at near 180 °C, which corresponded to the elimination of isopropyl alcohol during the course of imidization. If no imidization had occurred during annealing, the theoretical weight loss should be 12.9 wt %, the calculated weight of isopropyl alcohol in the precursor polymer. From TGA diagrams in Figure 1, it was confirmed that imidization did not take place for the sample annealed at 170 °C, and the weight loss (12.98 wt %) of that sample coincided well with the theoretical value. For samples annealed at 190 °C or higher, the weight loss was found to be less than 12%, indicating the occurrence of thermal imidization during annealing. Thus, the stretching was conducted at 170 °C.

XRD diagrams of BLK, FLM, SFL, and PPT were shown in Figure 2. All PIAE samples exhibited some degrees of crystallinity with two major broad peaks at $2\theta = 18°$ and $2\theta = 8.5°$. The peak at $2\theta = 18°$ is related to the intermolecular spacing (4.98 Å), and the peak at $2\theta = 8.5°$ is related to the intramolecular ordering of the repeating unit along the chain axis (13 Å). Comparison of the relative peak intensity at $2\theta = 18°$ and $2\theta = 8.5°$ indicated that the crystallinity of precursor increased in the order of BLK, FLM, SFL, and PPT. Although there may be a substantial discrepancy to directly compare the diffraction patterns of powder and film samples, it was obvious that the overall degree of intermolecular ordering in PPT sample was the highest. We assumed that, since MDPM-6FDA PIAE in THF solution exhibited a lyotropic liquid crystalline nature,[15] injection of MDPM-6FDA PIAE solution into vigorously stirred nonsolvent during precipitation process could result in a shear-induced molecular alignment, which produced fiberlike particles with higher crystallinity. In contrast, intermolecular ordering in FLM sample induced by a bar-coating process should be randomized with evaporation of solvent, which resulted in a lower degree of crystallinity.

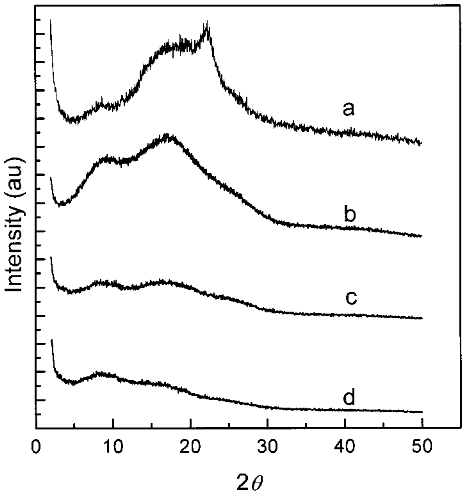

Figure 2. XRD diagram of (a) PPT, (b) SFL, (c) FLM, and (d) BLK samples of MDPM-6FDA PIAE.

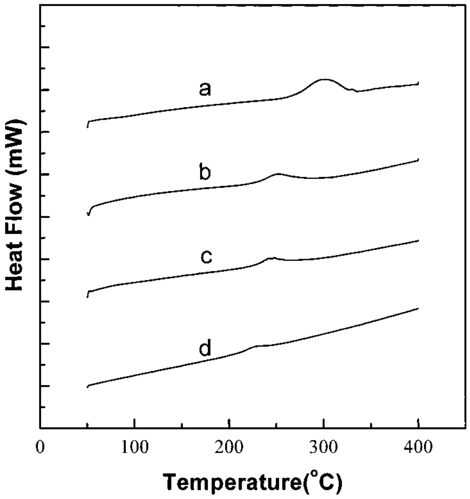

Figure 3. DSC diagram of (a) PPT, (b) SFL, (c) FLM, and (d) BLK samples of MDPM-6FDA PIAE.

Imidizations of four different precursor samples, BLK, FLM, SFL, and PPT, were examined by using DSC, and the results are shown in Figure 3. Endothermic peaks representing the temperature of maximum imidization rate increased gradually from 228 °C for BLK to 297

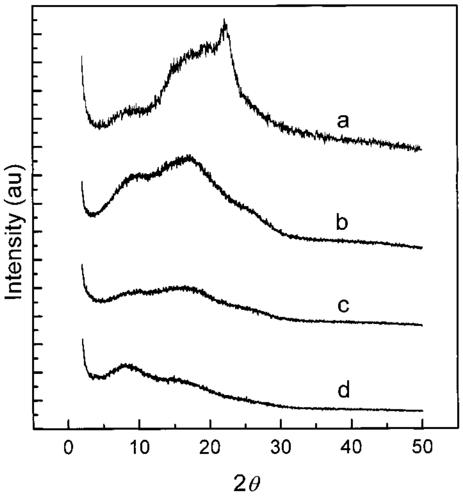

Figure 4. XRD diagram of MDPM-6FDA polyimides after heating of (a) PPT, (b) SFL, (c) FLM, and (d) BLK samples at 350 °C for 2 h.

°C for PPT. These endothermic peaks, which disappeared at the second heating cycle, corresponded to elimination of isopropyl alcohol during imidization reaction of amide acid ester group in the precursor polymer. Elimination of isopropyl alcohol was also evidenced in TGA experiments. It is notable that the onset of imidization temperature was near 180 °C, which was about 80 °C higher than that of poly(amic acid)s (~100 °C).[16] This enhanced thermal stability is attributed to the existence of a rigid imide ring in PIAE and the stabilization of carboxylic acid moiety by protection with the ester group. Reaction enthalpy measured by the area of the endothermic peak was also increased in the order of increasing imidization temperature. Initial imidization temperatures, peak imidization temperatures, and reaction enthalpies for the four samples are summarized in Table 1. The peak imidization temperature of BLK was observed at 228 °C, whereas that of PPT was observed at 297 °C. Considering both precursors have the same chemical structure, the difference of 69 °C in the peak imidization temperature was remarkable.

Combining the results of XRD and DSC studies, it was apparent that the crystallinity of precursor was altered by different processing methods, which consequently affected thermal imidization behavior. The increase in imidization temperature with respect to the increase in precursor crystallinity can be ascribed to the chain mobility caused by intermolecular ordering. For a precursor polymer to be cyclized to form an imide linkage, configurational rearrangement of polymer chains is necessary. Kreuz et al.[5] have reported that the reactivity in imide forming reaction was reduced due to diffusional limitations, chain stiffness effects, and inability to achieve reactive configurations, which are consistent with our results. In the case of a precursor sample with higher crystallinity, more energy is required to be cyclized to form an imide linkage, which resulted in a higher imidization temperature.

To investigate the effect of precursor crystallinity on the properties of resulting polyimides, above four samples were imidized at 350 °C for 2 h, and XRD diagrams of the resulting polyimides are shown in Figure 4. No appreciable changes in the diffraction pattern were found in all cases during the thermal imidization process. These results indicated that polymer morphology was preserved during the imidization process of MDPM-6FDA PIAE. The preservation of morphology after thermal imidization at 200 °C has been reported by Takahashi et al. for a semiflexible poly(amic acid) such as poly(4,4′-oxydiphenylenepyromellitamic acid).[16] According to them, the preservation of morphology is attributed to the fact that imidization can occur without requiring a substantial rearrangement of spatial configurations of poly(amic acid) chains at 200 °C, which is below the glass transition temperature of resulting polyimide. However, this explanation is not satisfactory in our case because precursor samples were heated to 350 °C. Instead, we assumed that the structural rigidity of precursor polymer influenced the preservation of morphology in the final polyimide. Since half of the amide units were already converted to the rigid imide linkages in MDPM-6FDA PIAE as compared to poly(amic acid), molecular freedom for the chain rearrangement would have been suppressed even in the precursor state.

Table 1. Imidization Characteristics of MDPM-6FDA PIAE Samples

sample	initial imidization temp (°C)	imidization peak temp (°C)	reaction enthalpy (J/g)
PPT	256	297	183
SFL	222	251	62
FLM	215	242	59
BLK	197	228	57

Table 2. Thermal Properties of MDPM-6FDA Copolyimides Prepared by Heating PPT, SFL, FLM and BLK Samples at 350 °C for 0.5 h

sample	T_{d5}[a] (°C)	residue[b] (%)	T_g[c] (°C)
PPT-PI	547	55.91	352
SFL-PI	541	52.43	350
FLM-PI	535	51.65	347
BLK−PI	531	50.74	341

[a] Temperature at 5% weight loss in TGA diagram. [b] Residue after 800 °C in TGA diagram. [c] Taken from DSC diagram.

The thermal stability of final polyimides prepared from precursors of different crystallinities was investigated by TGA and DSC, and the results are summarized in Table 2. As the crystallinity of precursor increased, the decomposition temperature at which 5% weight loss occurs (T_{d5}) and the residue after 800 °C increased. Laius et al.[17] have reported that polyimides with higher crystallinity had higher thermal stability because more energy is required in the polyimide with higher crystallinity to overcome the restriction of segmental motion of polyimide chain for degradation reaction, which is consistent with the present results. Since the crystallinities of polyimides were preserved from precursor samples, the polyimide from PPT showed the highest thermal stability. The T_g of polyimides also increased with increase of precursor crystallinity. Although the differences of T_g's between neighboring samples are within the boundary of experimental error, the difference of T_g between polyimides prepared from PPT and BLK was 11 °C, which was significant. All these results indicated that the difference in crystallinities of precursors originating from different sample processing methods could affect the crystallinity of resulting polyimide and consequently their final properties.

Conclusion

Imidization behaviors of differently processed polyimide precursors were investigated. The imidization temperature of polyimide precursors increased in the order BLK, FLM, SFL, and PPT, which was the increasing order of crystallinity of precursor samples. The crystallinity of precursor was preserved in the final polyimide after thermal imidization. Consequently, the morphology of precursors affected the properties of final polyimide such as thermal stability and T_g.

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