

RAPID COMMUNICATION

Dynamic tensile properties of a novel Kapton-type asymmetric polyimide derived from 2-phenyl-4,4'-diaminodiphenyl ether

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The excellent properties of aromatic polyimides (PIs) such as Kapton and Apical, which are derived from pyromellitic dianhydride (PMDA) and 4,4'-diaminodiphenyl ether (4,4'-ODA; DuPont Co. and Kaneka Co., respectively), are well known, including high dimensional stability and outstanding thermal and environmental stability.^{1–3} These properties are attributed not only to their rigid (planar and symmetric pyromellitimide) structures but also to the formation of highly ordered structures due to strong intermolecular interactions such as charge-transfer complexes. Accordingly, the aromatic PIs do not display high molecular mobility above the glass transition temperature (T_g), indicating that the processing conditions for molding were severe.

Yokota and co-workers^{4,5} previously reported that groundbreaking thermoplastic PIs derived from asymmetric and non-planar 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA) exhibited a large drop in the storage modulus (E') above the T_g at 319 °C, as observed in dynamic mechanical analysis (DMA) measurements. These observed phenomena were found to be quite different from those of symmetric PI derived from 3,3',4,4'-biphenyltetracarboxylic anhydride (s-BPDA), indicating that the irregular geometry of a-BPDA restricted-free rotation and caused a decrease in the intensity of the intermolecular interaction.⁶ Meanwhile, amorphous PIs derived from non-planar and asymmetrical diamines have also been reported. Yang *et al.*⁸ reported that the PIs derived from PMDA and 3-phenyl-1,4-bis(4-aminophenoxy) benzene (p-TPEQ) showed a higher T_g at 286 °C in comparison with bis(4-aminophenoxy)benzene-based PI ($T_g=272$ °C).⁸ Morikawa *et al.*^{9–11} also reported the preparation and thermal properties of aromatic

PIs derived from a series of phenyl group-substituted 4,4'-ODA derivatives. Particularly, bis(4-amino-2-biphenyl)ether-based PMDA PI showed significant improvements in solubility in polar aprotic solvents and a higher T_g at 303 °C than the aforementioned p-TPEQ-based PIs.

We found that the asymmetric and aromatic PI derived from PMDA and 2-phenyl-4,4'-diaminodiphenyl ether (p-ODA; Figure 1) showed a high T_g and a large drop in the E' above the T_g , which caused an amorphous structure to form, despite the PMDA/ODA-type backbone structure (Figure 2).

PI(PMDA/p-ODA) was prepared by conventional thermal imidization of the corresponding poly(amic acid), whose inherent viscosity is almost 0.8–1.0 (dl g⁻¹). The steric structure of p-ODA had no significant influence on the polymerization reactivity. PI(PMDA/p-ODA) showed good chemical resistance and no solubility in common polar aprotic solvents such as *N*-methylpyrrolidone.

Figure 3 shows the temperature dependency of the E' curves of the PI(PMDA/p-ODA) and PI(PMDA/4,4'-ODA) films that were obtained with DMA measurements in air.

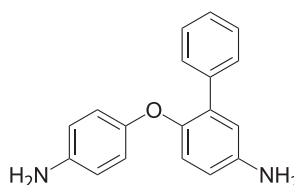


Figure 1 Structure of 2-phenyl-4,4'-diaminodiphenyl ether (p-ODA). p-ODA is an asymmetric diamine that is a 4,4'-diaminodiphenyl ether with a pendant phenyl group at the 2-position.

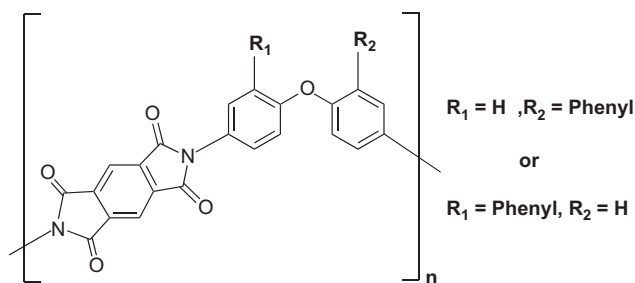


Figure 2 Structure of PI(PMDA/p-ODA). There are three possible types of repeated units in the PI(PMDA/p-ODA) chain: Head-to-head, head-to-tail and tail-to-tail. p-ODA, 2-phenyl-4,4'-diaminodiphenyl ether; PI, polyimide; PMDA, pyromellitic dianhydride.

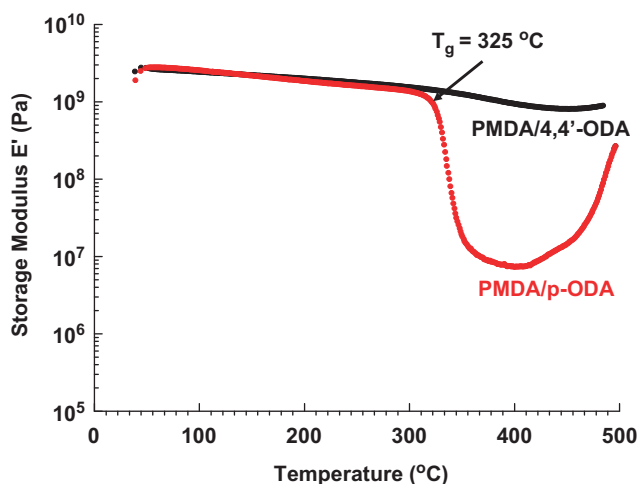


Figure 3 Dynamic mechanical analysis curves of PI(PMDA/4,4'-ODA) and PI(PMDA/p-ODA) films. The large drop in the E' of PI(PMDA/p-ODA) that was seen in the dynamic mechanical analysis measurements is thought to be due to the existence of a phenyl group; this randomized repeated unit in the polymer backbone is thought to restrict the intra/intermolecular interactions of the polymer chains (see main text). p-ODA, 2-phenyl-4,4'-diaminodiphenyl ether; PI, polyimide; PMDA, pyromellitic dianhydride.

Table 1 Thermal and mechanical properties of PI(PMDA/p-ODA) and PI(PMDA/4,4'-ODA) films

	T_g (°C)		T_{d5} (°C) ^b	E_{ave} (GPa) ^a	$\sigma_{b,ave}$ (MPa) ^b	$\varepsilon_{b,ave}$ (%) ^c
	DSC	DMA				
PI(PMDA/p-ODA)	333	325	549	3.3	158	38.5
PI(PMDA/4,4'-ODA)	— ^d	360 ^e	571	3.2	279	68.6

Abbreviations: p-ODA, 2-phenyl-4,4'-diaminodiphenyl ether; PI, polyimide; PMDA, pyromellitic dianhydride.

^aAverage values of modulus.

^bAverage values of tensile strength.

^cAverage values of elongation at break.

^dNot detected obviously.

^eDetermined by the intersection of two tangent of storage modulus curve.

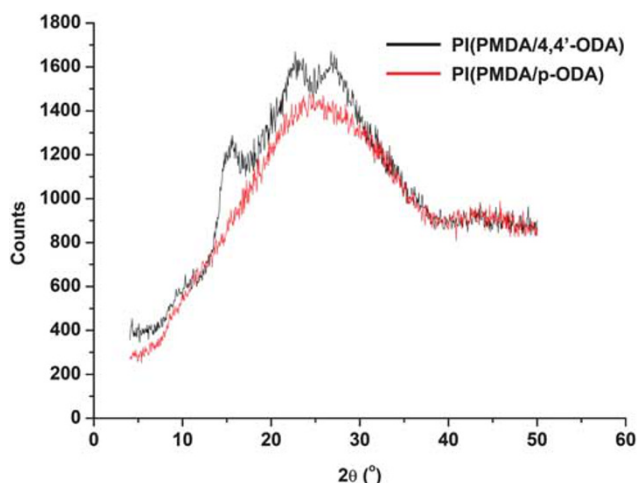


Figure 4 Reflection mode wide-angle X-ray diffraction patterns of PI(PMDA/4,4'-ODA; black line) and PI(PMDA/p-ODA; red line). PI(PMDA/4,4'-ODA) shows a typical crystallized pattern, as shown in references 1–3 and 12. PI(PMDA/p-ODA) showed a broad peak, indicating that PI(PMDA/p-ODA) formed an amorphous structure. p-ODA, 2-phenyl-4,4'-diaminodiphenyl ether; PI, polyimide; PMDA, pyromellitic dianhydride.

PI(PMDA/p-ODA) clearly showed a high T_g at 325 °C and a significant drop in the E' from 10^9 to 10^7 Pa (rubbery plateau region) above the T_g . These data are thought to be attributable to the rotational inflexibility of the ether linkage of p-ODA, which restricted the conformational change of the PMDA/4,4'-ODA backbone structure. The steric hindrance of the pendant phenyl groups of p-ODA also restricted the intra/intermolecular interactions of the PI chains.

The thermal and mechanical properties of PI(PMDA/p-ODA) that were determined by differential scanning calorimetry and tensile measurements are summarized in Table 1. PI(PMDA/p-ODA) showed high thermal stability, up to 400 °C in a nitrogen atmosphere, and a high T_{d5} value of 549 °C was recorded on the thermal gravimetry analysis curve. Moreover, PI(PMDA/p-ODA) was also found to be very tough based on the observed high tensile properties. These data were clearly attributed to the similarity in the chemical structure of PI(PMDA/p-ODA) compared with that of Kapton.

Figure 4 displays the reflection mode of the wide-angle X-ray diffraction patterns of PI(PMDA/4,4'-ODA) and PI(PMDA/p-ODA) films. A prominent annealing effect that results in molecular ordering is well known in conventional Kapton-type aromatic PI films.¹² However, a PI(PMDA/p-ODA) film annealed at 400 °C yielded a typical amorphous pattern, which did not depend on the annealing temperature. The data obtained from the DMA measurements strongly supported the hypothesis that the pendant phenyl groups of p-ODA restricted the intra/intermolecular interactions of PI chains to form amorphous structures.

In conclusion, the PI(PMDA/p-ODA) film exhibited good chemical resistance, a high T_g , excellent mechanical properties and the formation of amorphous structures. The pendant phenyl group of p-ODA was surprisingly effective in causing typical PMDA-based aromatic PIs to yield an amorphous structure. The detailed second-order structure, the thermal and mechanical properties and the application possibilities for molding are now under investigation. We believe the aromatic PIs derived from asymmetric p-ODA diamine will greatly enhance the possibility of developing new heat-resistant composite materials with good processability. Studies on the detailed thermal and mechanical properties of phenylethynyl-terminated imide oligomers derived from PMDA and p-ODA and their cured resin are also now in progress.^{13,14}

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Supplementary Information accompanies the paper on Polymer Journal website (<http://www.nature.com/pj>)