Molecular relaxation processes in isomeric BPDA polyimide films

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Abstract

Dynamic mechanical analysis was performed on the isomeric s-,a -, and i-BPDA polyimides (PIs) combined with four kinds of ODA and APB diamines, respectively. In the α relaxation process the T_α corresponding to T_g moves towards high temperature in order of s-, a-, and i-BPDA for para diamine PI, while the T_α hardly moves for meta diamine PI regardless of BPDA isomer. In the other hand, the temperature of β relaxation process increases in order of i-, a-, and s-BPDA regardless of the kind of diamine. These behaviors may be interpreted in terms of steric effects due to the configuration of BPDA and diamine.

1. Introduction

It is well known that aromatic polyimides(PIs) with high linearity and symmetry possess high glass transition temperature(T_g), excellent dimensional stability, and outstanding thermal stability. On the other hand, for high-temperature asymmetric PIs were there few reports about the relation between structure and thermal, mechanical properties.

Recently, it has been reported that new polyimides from asymmetric 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA) or 2,2',3,3'- biphenyltetra -carboxylic dianhydride (i-BPDA) have higher T_gs than the corresponding symmetric BPDA(s-BPDA) based polyimides[1].

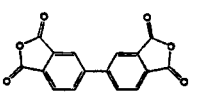
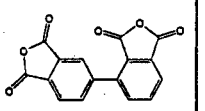
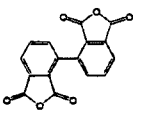
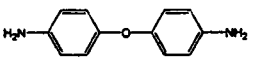
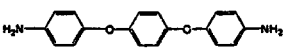
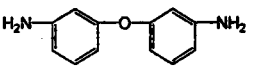
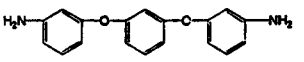
The aim of the present paper is to investigate the steric effect of these three BPDA isomers on the α and β molecular relaxation motions of the corresponding PI films from four kinds of aromatic diamines.

2. Experimental

The twelve BPDA-type polyimides are listed in Table 1. Samples shown here include four aromatic diamines: 4,4'-oxydianiline (4,4'-ODA), 3,3'-oxydianiline (3,3'-ODA), 1,4-bis (4-aminophenoxy) benzene (1,4,4-APB), and 1,3-bis (3-aminophenoxy) benzene (1,3,3-APB). Details of the procedures to prepare the PI films used here can be found elsewhere [2].

Dynamic mechanical analysis (DMA) data were obtained for thin film specimens with 23.7 mm length, 5 mm width and 0.05 mm thickness using a Rheometrics Solids Analyzer RSA II instrument at a heating rate of 5℃/min over the frequency range 10^{-3} to 10 Hz in an inert atmosphere of nitrogen gas.

Table 1.
Chemical structures of monomers used here and notation of corresponding polyimides

		s-BPDA	a-BPDA	i-BPDA
				
4,4'-ODA		s-BPDA/4,4'-ODA	a-BPDA/4,4'-ODA	i-BPDA/4,4'-ODA
1,4,4-APB		s-BPDA/1,4,4-APB	a-BPDA/1,4,4-APB	i-BPDA/1,4,4-APB
3,3'-ODA		s-BPDA/3,3'-ODA	a-BPDA/3,3'-ODA	i-BPDA/3,3'-ODA
1,3,3-APB		s-BPDA/1,3,3-APB	a-BPDA/1,3,3-APB	i-BPDA/1,3,3-APB

The T_gs of these polyimide films were determined via the corresponding inflection temperatures on the storage modulus (E') and the T_βs via the corresponding the β relaxation peak temperatures on the loss modulus (E").

3. Results and discussion

3.1 α relaxation process

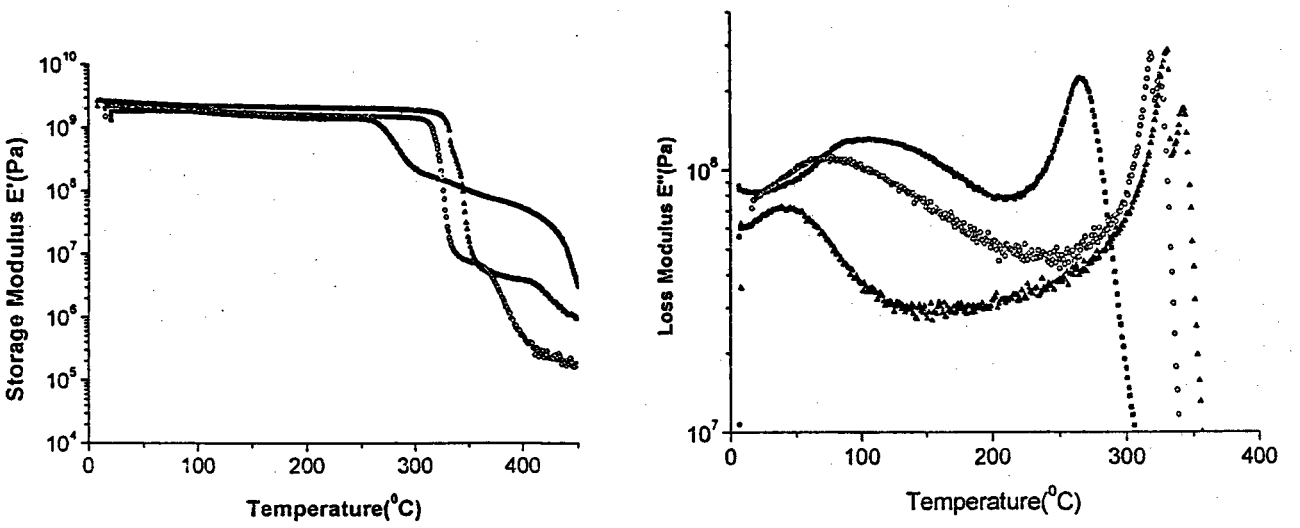


Fig. 1. DMA curves of PIs films from 4,4'-ODA : s-BPDA(■), a-BPDA (○), i-BPDA (▲)

Fig. 1 shows the temperature dependence of storage modulus E' and loss modulus E" of PI(s,a, i-BPDA/4,4'-ODA), respectively. It is of note to report that the α transition peak corresponding to T_g moves towards high temperature in order of s-, a-, and i-BPDA.

Fig. 2 illustrates the temperature dependence of E' and E" of PI (s,a,i-BPDA /3,3'-ODA), respectively. The temperatures of the α transition is hardly changed in contrast to 4,4'-ODA with isomeric BPDA.

For the temperature dependence of E' and E" of PI(s,a,i-BPDA /1,4,4-APB), the T_α shifts towards higher temperature in order of s, a, and i-BPDA. On the other hand, the T_α of PI(s,a,i-BPDA/1,3,3-APB) are almost the same for the three isomeric BPDA polyimides in a manner similar to 3,3'-ODA.

Among these three isomeric BPDA, i-BPDA may need the largest space for the segmental motion responsible for α relaxation process and s-BPDA needs the smallest one . Then, in the combination with rigid para diamines of 4,4'-ODA and 1,4,4-APB, the α relaxation temperature is the highest for i-BPDA and the lowest for s-BPDA. On the other hand, the T_α is hardly changed with BPDA isomers combined with flexible meta diamines of 3,3'-ODA and 1,3,3-APB, which can provide much larger space in comparison with the space characteristic of BPDA isomers.

3.2 β relaxation processes

As shown in Fig.1 and 2, a sub-Tg process, i.e. β relaxation process occurred above room temperature.

Table 2 lists both the β and α relaxation temperatures at 1 Hz for polyimide films. It is of noteworthy enough that the T_β, unlike T_α, increases in order of i-, a-, and s-BPDA for all diamines . The relaxation peaks due to the T_β of PI(i-BPDA/1,4,4- or 1,3,3-APB) will be located at the lower temperatures below room temperature

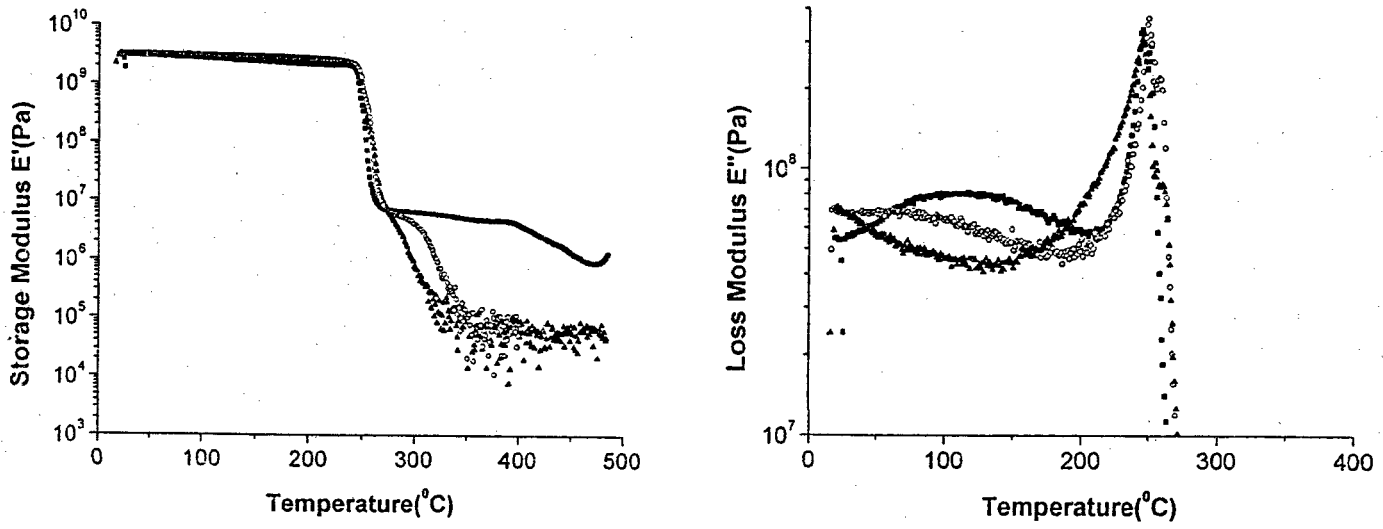


Fig.2. DMA curves of PIs films from3,3'-ODA : s-BPDA(■), a-BPDA (○) , i-BPDA (▲)

Although there have been many reports for the β relaxation process of aromatic polyimides, the most reasonable one may be the interpretation in terms of a cooperative motion [3,4]. It is considered that the β relaxation may be ascribed to the local rotation of the rigid segment composed of BPDA group and an adjacent diamine group. Taking into account steric interactions, the rigid segment of most bulky i-BPDA may only vibrate most slightly around its position among the three isomers, resulting in the lowest T_β.

References

[1] P. M. Hergenrother et al., Polymer 43, 5077 (2002).
[2] C. Chen et al.. In preparation.
[3] Z. Sun et al., Polymer, 33, 4728 (1992).
[4] F. Li et al., Polymer, 40, 4571 (1999).

Table 2.
The β and α relaxation temperatures as determined from DMA measurement for aromatic PIs derived from three isomeric BPDA

BPDA	Diamine	T_β(℃)	T_α(℃)
s-BPDA	4,4´ - ODA	105	262
a-BPDA	4,4´ - ODA	68	319
i-BPDA	4,4´ - ODA	39	330
s-BPDA	3,3´ - ODA	96	243
a-BPDA	3,3´ - ODA	51	245
i-BPDA	3,3´ - ODA	-	246
s-BPDA	1,4,4 - APB	93	257
a-BPDA	1,4,4 - APB	72	263
i-BPDA	1,4,4 - APB	-	293
s-BPDA	1,3,3 - APB	98	200
a-BPDA	1,3,3 - APB	43	205
i-BPDA	1,3,3 - APB	-	206