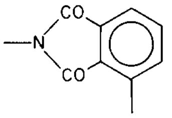
Beta relaxation in polyimides

Zhenhua Sun*, Lisong Dong, Yugang Zhuang, Linying Cao, Mengxian Ding and Zhiliu Feng†
Polymer Physics Laboratory, Changchun Institute of Applied Chemistry, Academia Sinica, Changchun 130022, People's Republic of China

(Received 26 March 1991; revised 23 January 1992; accepted 24 February 1992)

A series of polyimides with different structures have been synthesized and studied by dynamic mechanical analysis. The results obtained indicate that the β relaxation in polyimides is related to the rotation of rigid segment(s) of p-phenylene and imide groups around 'hinges' such as $-O-$, $-CH_2-$ and so on in diamines. It is noticed that two kinds of polyimides both with



imide groups have very weak β relaxation below the glass transition temperature. This phenomenon is due to the fact that the configuration of chains with the above imide groups hinders the rotation of the rigid segments in the chains.

(Keywords: beta relaxation; polyimides; dynamic mechanical analysis; synthesis)

INTRODUCTION

Polyimides have been recognized as high-performance plastics owing to their exceptional mechanical and thermal properties, and they are often used for functional and structural applications, e.g. aerospace, automotive, domestic and electronics[1–3]. Unfortunately, the use of some of these polymers has been limited by the fact that they are not readily melt processible or not soluble in any solvent. In order to overcome this shortcoming, some polyimides with 'hinges' in the dianhydride and diamine have been synthesized[4]. As a result, they have good melt processibility and solubility in some solvents, but at the expense of poorer mechanical properties and thermal stability. Hence in the study of the structure–property relationships of such polyimides, investigation of their relaxation properties is considered to be important.

The dynamic mechanical or relaxation properties of polyimides have been studied by many authors[4–15]. Three relaxation transitions, i.e. high-temperature (α), moderate-temperature (β) and low-temperature (γ), have been detected. However, the mechanism of the β relaxation is not clear. It was tentatively related to loss of water[5] or to interplane slippage of crystalline regions[6], but these conclusions are in conflict with other results. For instance, many investigators have ascribed the β relaxation to oscillations of p-phenylene groups by comparing the dynamic mechanical properties of polyimides with those of poly(2,6-disubstituted-1,4-phenylene oxides)[7–11]. Others have related the β process to the vibrational mobility of aromatic and benzimide rings[4,12]. In order to understand the mechanism of β relaxation in polyimides, a series of polyimides with different structures should be synthesized and studied systematically. This is the purpose of our work.

EXPERIMENTAL

Sample preparation

The polyimides used in this work were synthesized by a two-step technique[4]. The synthesis and characterization of the samples were described in refs 16 and 17. The molecular structures of the polyimides used in this study are given in *Table 1*. Besides these polyimides, random copolymers with various compositions of PTI-E/PTI(3,3)-E were also synthesized.

Dynamic mechanical analysis

D.m.a. was carried out with a Du Pont 982 DMA at a heating rate of 5°C min^{-1} from room temperature to 350°C. The specimens used were about 2 mm thick, compression moulded at 370°C and then quenched in water. The activation energy of the β relaxation of some polyimides was determined by a direct-reading viscoelastometer (Rheovibron DDV-II-EA) with frequencies of 110, 35, 11 and 3.5 Hz, at a heating rate of 1°C min^{-1} from room temperature to 250°C.

RESULTS AND DISCUSSION

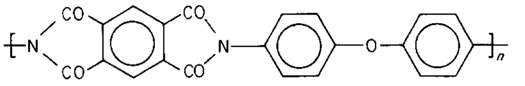
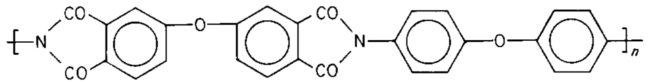
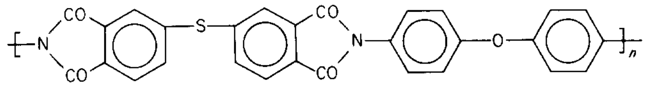
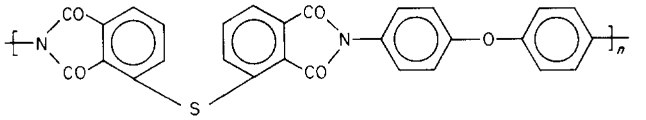
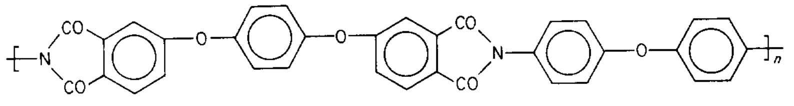
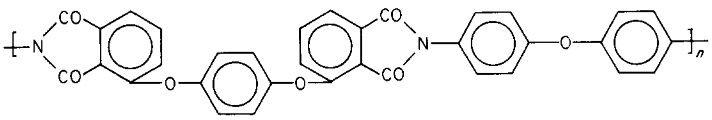
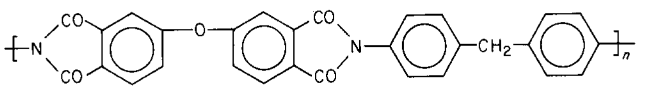
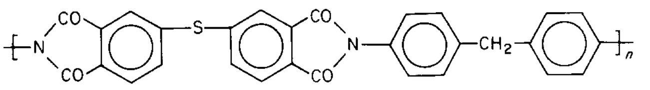
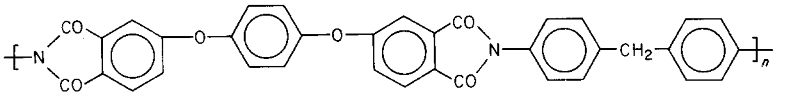
It is clearly seen in *Figure 1* that both PEI-E and PTI-E exhibit two relaxation peaks above room temperature denoted as α and β respectively. The α relaxation is accompanied by a sharp decrease in the storage modulus, and the β relaxation is very broad. Since no crystalline

---

*To whom correspondence should be addressed
†Formerly E. T. L. Voong and Voong Tse-Lieu

0032-3861/92/224728-04

Table 1 Chemical structures of polyimides used in this work

Polymer designation	Chemical structure
PM[a]	
POI-E	
PTI-E	
PTI(3,3)-E	
PEI-E	
PEI(3,3)-E	
POI-M	
PTI-M	
PEI-M	

[a] PM is listed only for comparison

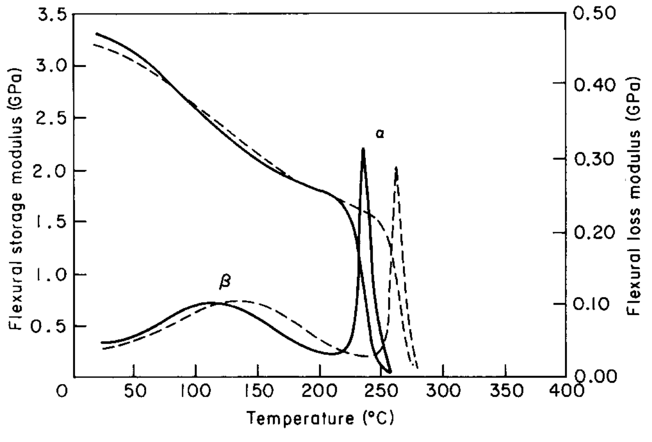
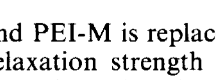


Figure 1 D.m.a. curves of PEI-E (——) and PTI-E (- - - -)

structure was detected in any of our samples, the origin of the β relaxation cannot be interpreted as the interplane slippage of crystalline regions. Our repeated experiments showed that the β relaxation is not affected by cyclic thermal treatment, which means that the β relaxation is not due to the loss of water or other solvent. It seems more reasonable to consider that the β relaxation arises from oscillations of *p*-phenylene groups, because a similar relaxation was found in poly(2,6-disubstituted-1,4-phenylene oxide), aromatic polyimides and other related symmetrically substituted polymers[18–23]. If the β relaxation is due only to the oscillations of *p*-phenylenes, the following speculations may be reasonable:

(1) With the same *p*-phenylene content, the β relaxation strengths of PEI-E and PEI(3,3)-E on the one hand, and those of PTI-E and PTI(3,3)-E on the other, should be comparable.

(2) If the



group of PEI-E and PEI-M is replaced by –S– or –O– linkages, the β relaxation strength should be reduced owing to the decrease in *p*-phenylene content.

However, although PEI(3,3)-E and PTI(3,3)-E have the same *p*-phenylene content as PEI-E and PTI-E respectively, their β relaxation strengths are much weaker (*Figure 2*).

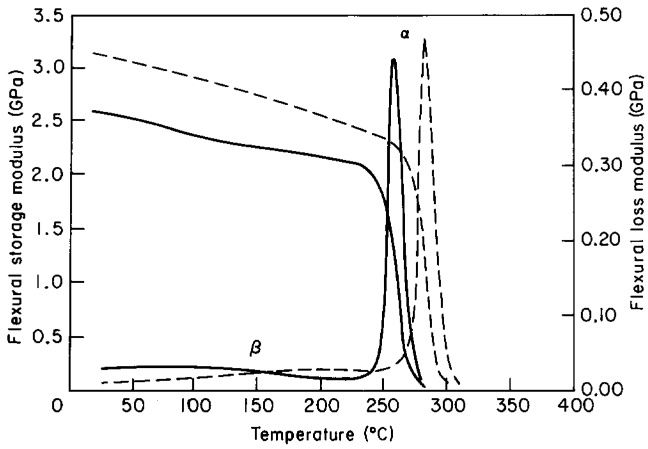


Figure 2 D.m.a. curves of PEI(3,3)-E (——) and PTI(3,3)-E (- - - -)

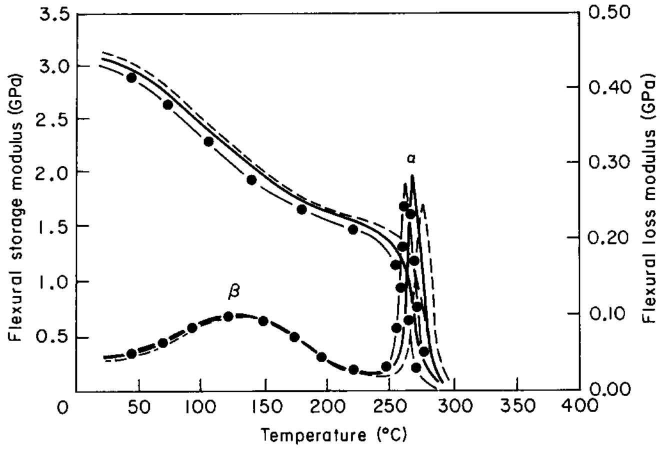
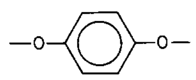


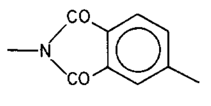
Figure 3 D.m.a. curves of PEI-M (——●——), PTI-M (———) and POI-M (- - - -)

Furthermore, the influence of replacing the



groups in PEI-E and PEI-M with –S– or –O– groups on the dynamic mechanical properties of the specimens is shown in *Figures 1* and *3*. The results indicate that a decrease of *p*-phenylene content does not weaken the β relaxation, but only makes the position of the β relaxation maximum shift to the higher-temperature region.

From the above results, it may be considered that the β relaxation is not only related to the oscillation of *p*-phenylene. It is clearly seen in *Figure 4* that the β relaxation strength in PTI-E/PTI(3,3)-E random copolymers is strongly dependent on the content of PTI-E, which increases with the increase in PTI-E content. Thus, the motions of other groups in the segments of the macromolecules, such as

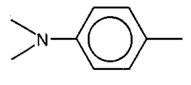


groups in PEI-E and PTI-E, might contribute to the damping observed in the β region.

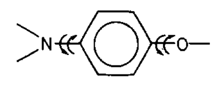
From the data in *Table 2*, it can be seen that the β transition temperatures (T_β) increase slightly with the glass transition temperatures (T_g). However, the overall activation energy of β relaxation (U_β) does not increase with T_β. Although PM has the highest T_g and T_β in all specimens, its U_β is the lowest, and this result can hardly be explained by the mechanism of the oscillation of *p*-phenylene groups.

Why do PEI(3,3)-E and PTI(3,3)-E have very weak β relaxation? Why does PM have the lowest U_β? In order to explain the above phenomena, the following mechanism is proposed.

Owing to the fact that conjugation exists at the



bond, the *p*-phenylene groups cannot rotate freely around the 'hinges', such as the type



So, it is considered that the β relaxation may be due to rotation of rigid segments around the 'hinges' in diamines, and the rigid segment is composed of a *p*-phenylene group and an adjacent imide group. This model is shown in *Figure 5*.

From *Figure 5*, it can be seen that, for all polyimides studied, the rotation of the rigid segment of PM is the easiest, because the rotation of one rigid segment does not influence the conformation of the other segments, and only needs a small free volume. So its activation energy is the lowest, 100 kJ mol^{-1}, as shown in *Table 2*. For POI-E, there are two rigid segments between two

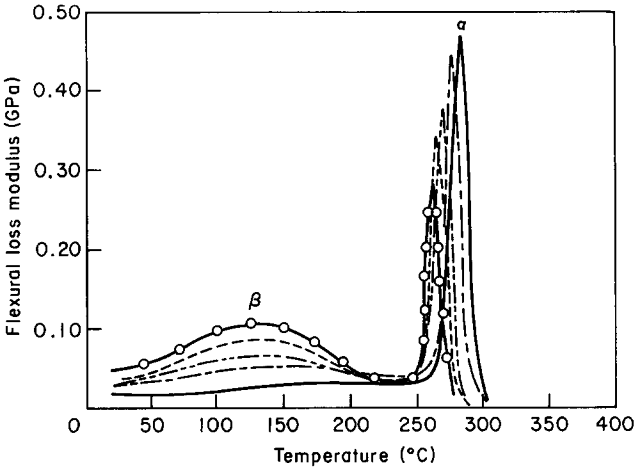


Figure 4 D.m.a. curves of random copolymers of PTI-E/PTI(3,3)-E: PTI-E (—○—○—); PTI(3,3)-E (———); PTI-E/PTI(3,3)-E, 3/1 (- - - -); PTI-E/PTI(3,3)-E, 1/1 (— — — —); PTI-E/PTI(3,3)-E, 1/2 (— - — - —) ●

Table 2 T_g, T_β and U_β of some polyimides

Polymer	PM[a]	POI-E	PTI-E	PEI-E
T_g (K)	750	535	544	514
T_β (K)	410	400	400	391
U_β (kJ mol^{-1})	100	115	126	147

[a] Data for PM obtained from ref. 4

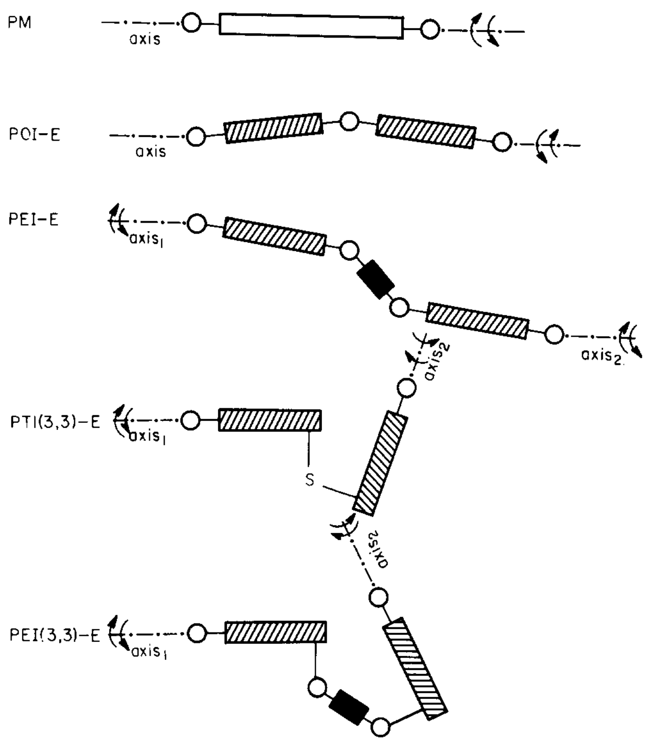
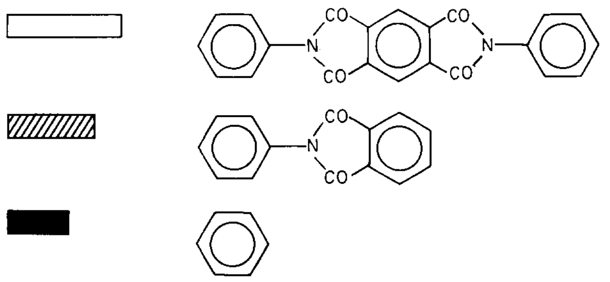


Figure 5 A new model for β relaxation in some polyimides. (The conformational diagrams of PM, POI-E and PEI-E are obtained from ref. 24)



nearby hinges in diamines contributes to the β relaxation. Although the rotation axes of the two rigid segments are collinear, their rotations need more free volume than that in PM, so the U_β of POI-E is larger than that of PM. For PEI-E, the rotation axes of the two rigid segments are only parallel (as shown in *Figure 5*). The rotation of the two rigid segments needs more free volume and can influence other segments nearby, so its activation energy is higher than those of POI-E and PM. Finally, for PTI(3,3)-E and PEI(3,3)-E, the rotation axes of the two rigid segments are nearly perpendicular, so the rotations of the two rigid segments are heavily resisted, and the rigid segments may only vibrate slightly around their positions, so their β relaxations are very weak.

From the above discussion, the proposed mechanism seems reasonable and suitable to explain all the above experimental results.

ACKNOWLEDGEMENTS

The authors are grateful for the financial support of the National Science Foundation of China and the National Science Foundation of Jilin Province of China.

REFERENCES

1 Sroog, C. E. *J. Polym. Sci., Macromol. Rev.* 1976, **11**, 161
2 Johnson, R. O. and Burlhis, H. S. *J. Polym. Sci., Polym. Symp.* 1983, **70**, 129
3 Hergenrother, P. M. *Angew. Makromol. Chem.* 1986, **145/146**, 323
4 Bessonov, M. I., Koton, M., Kudryavtsev, V. V. and Laius, L. A. 'Polyimides: Thermal Stable Polymers', Consultants Bureau, New York, 1987, p. 245
5 Wrasidlo, W. *J. Macromol. Sci., Phys. (B)* 1972, **6**, 559
6 Ikeda, R. M. *J. Polym. Sci., Polym. Lett. Edn* 1966, **4**, 353
7 Bernier, G. A. and Kline, D. E. *J. Appl. Polym. Sci.* 1968, **12**, 593
8 Butta, E., Petris, S. D. and Pasquini, M. *J. Appl. Polym. Sci.* 1969, **13**, 1073
9 Lim, T., Frosini, V., Zaleckas, V., Morrow, D. and Sauer, J. A. *Polym. Eng. Sci.* 1973, **13**, 51
10 Kochi, M., Shimada, H. and Kambe, H. *J. Polym. Sci., Polym. Phys. Edn* 1984, **22**, 1979
11 Kochi, M., Isoda, S., Yokota, R. and Kambe, H. *J. Polym. Sci., Polym. Phys. Edn* 1986, **24**, 1621
12 Harris, J. E. and Robeson, L. M. *J. Appl. Polym. Sci.* 1988, **35**, 1877
13 Pater, R. H. *Polym. Eng. Sci.* 1991, **12**, 13
14 Gillham, J. K. and Gillham, H. C. *Polym. Eng. Sci.* 1973, **13**, 447
15 Chartoff, R. P. and Chiu, T. W. *Polym. Eng. Sci.* 1980, **20**, 244
16 Ding, M., Dong, L., Zhang, J., Wang, X., Yang, Z., Li, H. and Cao, L., C-MRS International '90, 18–22 June 1990, Beijing, Elsevier, Amsterdam, in press
17 Ding, M., Li, H., Dong, L., Zhang, J., Yang, Z., Wang, X. and Cao, L. Symposium on Polymers, Chengdu, China, 1989, Preprints, pp. 331–2
18 Petris, S. de, Frosini, V., Butta, E. and Baccaredda, M. *Makromol. Chem.* 1967, **109**, 54
19 Eisenberg, A. and Cayrol, B. *J. Polym. Sci. (C)* 1971, **35**, 129
20 Cayrol, B., Eisenberg, A., Harrod, J. F. and Rocaniere, P. *Macromolecules* 1972, **5**, 676
21 Wrasidlo, W. *J. Polym. Sci., Polym. Phys. Edn* 1971, **9**, 1603
22 Frosini, V. and Butta, E. *J. Polym. Sci., Polym. Lett. Edn* 1971, **9**, 253
23 Ochi, M., Yoshizumi, M. and Shimbo, M. *J. Polym. Sci., Polym. Phys. Edn* 1987, **25**, 1817
24 Ref. 4, p. 179