Thermal Expansion Behavior of Various Aromatic Polyimides

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Synopsis

The thermal expansion behavior for various aromatic polyimides was investigated. Usually polymers, including polyimides, have high thermal expansion coefficients ($3-6 \times 10^{-5}$ K^{-1}), compared with metals and ceramics. However, there are some polyimides which have very low thermal expansion coefficients below 1×10^{-5} K^{-1}. This property was observed for the polyimides obtained from pyromellitic dianhydride or 3,3', 4,4'-biphenyltetracarboxylic dianhydride and aromatic diamines which were constituted of only benzene rings fused at para positions. It was proposed that their low thermal expansion coefficient related to the linearity in their polymer molecular skeltons.

INTRODUCTION

Polyimides have been recognized as very high performance plastics due to their excellent heat resistance and toughness.[1] Therefore, they have been used as insulation films for electrical and electronics applications, including the substrate for flexible printed circuits,[2] and the insulation layer for semiconductor devices.[3] Various kinds of polyimides have been synthesized,[1,4-6] and many reports have appeared on their properties.[7-12] In particular, much attention has been directed towards their most remarkable feature, i.e., high heat resistance, and a number of papers have included chemical and physical thermal stability investigations.

The authors have studied the relationships between the chemical structure of polyimides and various properties, such as imidization reactivity,[13] absorbed water content,[14] thermal decomposition rate,[15] etc. The thermal expansion behavior of polyimides, however, has received very little attention. In fact, it has long been believed that polymers, including polyimides, have high thermal expansion coefficients compared with metals and ceramics. In the present study, the authors show that certain kinds of aromatic polyimides have very low thermal expansion coefficients.

EXPERIMENTAL

Samples

A polyamic acid varnish was prepared by reacting an aromatic diamine with an aromatic dianhydride (Table I) in *N*-methyl-2-pyrrolidone at room temperature. The varnish was coated on a glass plate and dried at 100°C

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$-\!\left(R_1-N\!\begin{smallmatrix}CO\\CO\end{smallmatrix}\!R_2\!\begin{smallmatrix}CO\\CO\end{smallmatrix}\!N\right)\!-$

	$-R_1-$			$>R_2<$	
(A)		(p-PDA)	(1)		(PMDA)
(B)		(m-PDA)	(2)		(BPDA)
(C)	CH_3 CH_3	(o-TLD)	(3)	C=O	(BTDA)
(D)		(DATP)			
(E)	-O-	(DDE)			
(F)	-S-	(DDS)			
(G)	$-CH_2-$	(DDM)			
(H)	CH_3	(2,4-DATO)			
(I)	-O- -O-	(BAPB)			
(J)	-O- $C(CH_3)_2$ -O-	(DAPP)			
(K)	-O- $C(CF_3)_2$ -O-	(DAPFP)			

Table I
Materials

for 1 h. Then, the resulting film was stripped off and cured at 200°C for 1 h and at 400°C for 1 h in nitrogen gas. This gave a polyimide film. It was found that behavior changed regarding thermal expansion depending on whether curing shrinkage was unhindered (free cure), or shrinkage was prevented by fixing the film on an iron frame in one direction (unifix cure), or in two directions which were at right angles (bifix cure).

The sample number of the polyimide is expressed by a letter for diamine and a number for dianhydride in Table I. For example, no. A1 indicates a polyimide from *p*-PDA and PMDA.

Coefficient of Thermal Expansion

A film 5 mm wide, 65 mm long (between chucks), and 20–100 μm thick was used as sample. The sample was applied to a thermal mechanical analyzer (TMA 1500, Shinku Riko K.K.) and the change of the length was measured under the condition 5°C/min in air. Since the thermal expansion coefficient had a temperature dependency, the average value between 50 and 250°C was used as a representative value.

Wide Angle X-Ray Diffraction

A sample 30 mm wide, 40 mm long, and about 40 μm thick was measured by using a Geiger-Flex Rad (Rigaku Denki Co., Ltd.).

RESULTS AND DISCUSSION

Dependency of Temperature and Curing Conditions on Thermal Expansion Behavior

Figures 1 and 2 show the thermal expansion behavior of two polyimides when different curing conditions were used. Figure 1 shows the behavior for polyimide no. A3 obtained from *p*-PDA and BTDA. There were dimen-

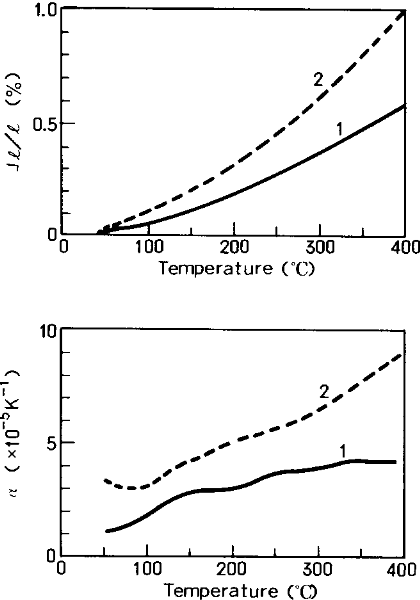

Fig. 1. Thermal expansion behavior for no. A3: (1) bifix cure; (2) free cure.

sional changes of 0.9% for free-cured film and 0.5% for bifix-cured film when the temperature was raised from 50 to 250°C. Thus, the thermal expansion coefficients of no. A3 were about 5×10^{-5} K^{-1} for free-cured film and about 3×10^{-5} K^{-1} for bifix-cured film. Figure 2 shows behavior for polyimide no. F3 obtained from DDS and BTDA. In this case, the films obtained by free and bifix cures had the same thermal expansion coefficient, 6×10^{-5} K^{-1}. Thus, the thermal expansion coefficient of polyimide was

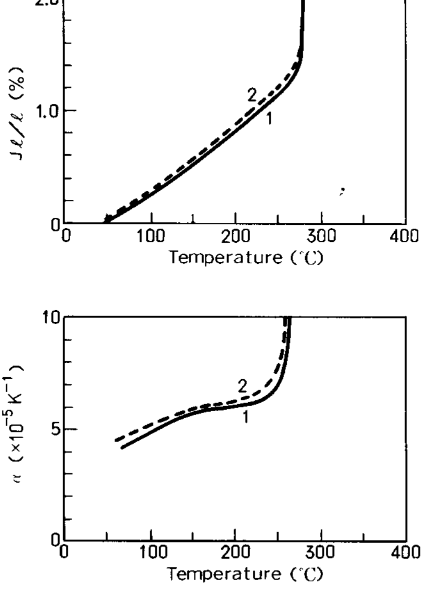

Fig. 2. Thermal expansion behavior for no. F3: (1) bifix cure; (2) free cure.

usually from 3 to 6 $\times$ 10^{-5} K^{-1}; it changed depending on the curing shrinkage conditions.

Figure 3 shows the thermal expansion behavior for polyimide no. D1 obtained from DATP and PMDA. It had a dimensional change of about 0.2% (free cure) or about 0.1% (bifix cure) in the temperature range of 50–250°C. The thermal expansion coefficient of the films were about 1 $\times$ 10^{-5} K^{-1} (free cure) and about 0.6 $\times$ 10^{-5} K^{-1} (bifix cure).

Figure 4 also represents the thermal expansion behavior. For the polyimide no. A2, the dimensional change by the bifix cure is 0.1% or less, while that by free cure was as large as about 0.4% in the range of 50–250°C. Using this polyimide, prevention of curing shrinkage at only one axis was also studied. As a result, it was found that in the prevented direction (UFX-X), the thermal expansion coefficient became smaller and the dimensional change was almost 0% up to about 250°C. But, perpendicular to the prevented direction (UFX-Y), the behavior was almost the same as for a free cure. The shrinkage of free-cured film at the time of imidization was about 10%. But the resulting effect was the same as that obtained by stretching a conventional polymer film several to several tens times.[16]

Relationship between Chemical Structure and Thermal Expansion Coefficient

The thermal expansion coefficients of free-cured and bifix-cured films for various polyimides were measured by a similar method as mentioned above. Figure 5 shows a relationship between the chemical structures and thermal expansion coefficients. Most thermal expansion coefficients were included in the range of 3–6.5 $\times$ 10^{-5} K^{-1}. However, the polyimides obtained from

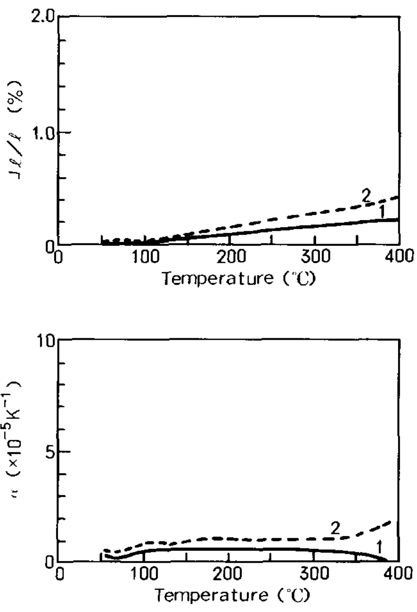

Fig. 3. Thermal expansion behavior for no. D1: (1) bifix cure; (2) free cure.

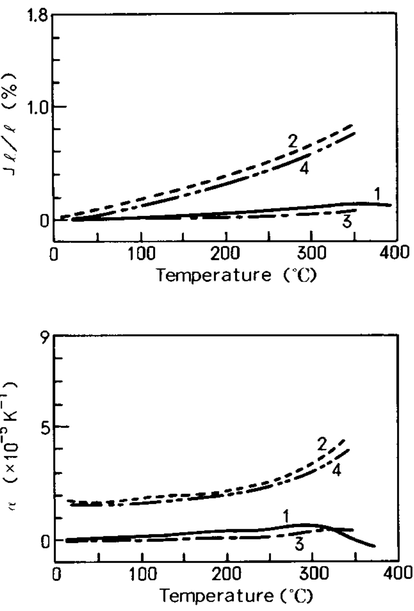

Fig. 4. Thermal expansion behavior for no. A2: (1) bifix cure; (2) free cure; (3) UFX-X; (4) UFX-Y.

the specific aromatic diamines, *p*-PDA, *o*-TLD, and DATP, had very low values. The aromatic diamines had common characteristics in their chemical structure. Their skeltons were composed of only benzene rings fused at the para position. Benzene rings which had a side group were also included. But the polyimides obtained from the diamines which had a flexible linkage, such as methylene, ether, ketone, thioether, isopropylidene, and hexafluoroisopropylidene, had high thermal expansion coefficients.

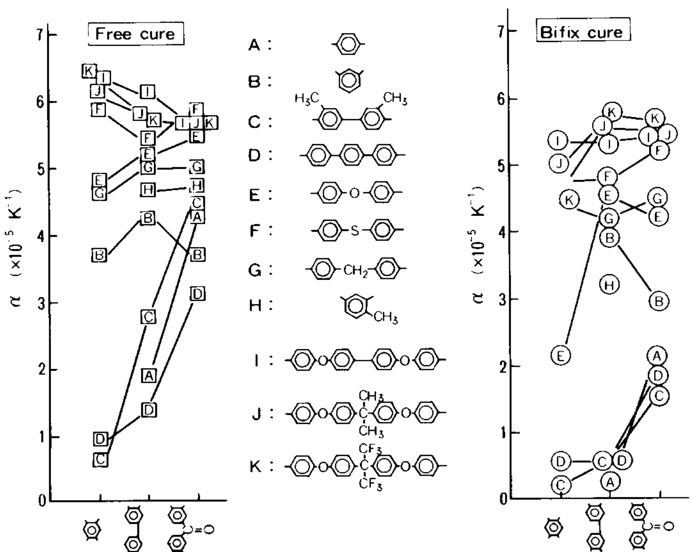

Fig. 5. Coefficients of thermal expansion for polyimides.

Similarly, polyimides obtained from 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) which had a ketone group had high thermal expansion coefficients. In contrast to them, in the case of polyimides obtained from pyromellitic dianhydride (PMDA) or 3,3′,4,4′-biphenyl tetracarboxylic dianhydride (BPDA) which had no flexible linkage, their thermal expansion coefficients were very low.

Figure 6 shows a relationship between thermal expansion coefficients for free-cured and bifix-cured films. From this result, the kinds of polyimides could roughly be divided into the following four groups.

1. Polyimides having low thermal expansion coefficients both in free cure and bifix cure. This group included those obtained from a combination of *o*-TLD or DATP, and PMDA.
2. Polyimides having low thermal expansion coefficients for bifix-cured films, but slightly large values for free-cured films. This group included those obtained from a combination of *p*-PDA, *o*-TLD, or DATP, and BPDA.
3. Polyimides having considerably large thermal expansion coefficients in the case of free cure but having about half those values in the case of bifix cure. This group included those obtained from a combination of *p*-PDA, *o*-TLD, or DATP, and BTDA, and a combination of DDE and PMDA.
4. Polyimides having large thermal expansion coefficient both in free and bifix cures. Almost all polyimides other than those mentioned above belong to this group.

Crystallizability of Polyimides

On the other hand, it is well known that thermal expansion coefficients of polymers become smaller on crystallization caused by stretching. Crystallizability of polyimides was studied by using wide angle *X*-ray diffraction. Measured results are shown in Figures 7 and 8. In Figure 7, the low thermal expansion polyimides were no. D1, no. C1, and no. A2. From this figure, no. D1 belonging to the group 1 had a sharp reflection and thus, crystal-

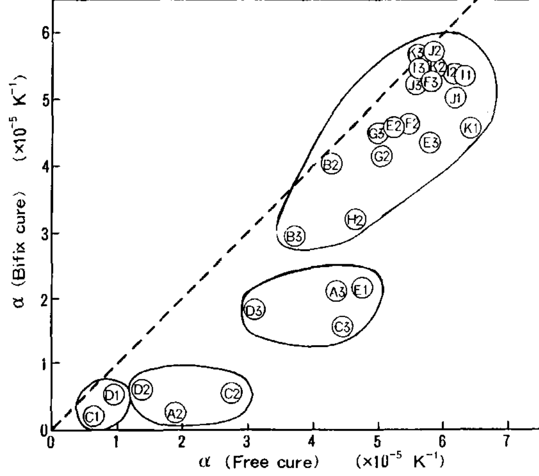

Fig. 6. Coefficients of thermal expansion for free-cured and bifix-cured polyimide films.

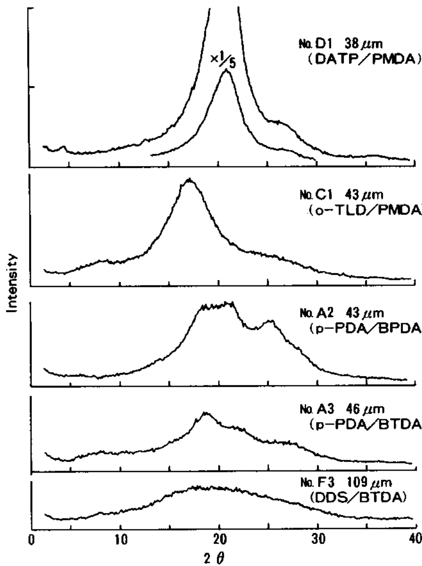

Fig. 7. Diffractograms for bifix-cured polyimide films.

lizability. Similarly, no. C1 seemed to have crystallizability to some extent. By contrast to them, no. A2 of group 2 seemed to have no crystallizability. It had no clear peak in its diffractogram similar to no. A3 and no. F3, which had high thermal expansion coefficients.

In Figure 8, the differences due to free cure, bifix cure, and unifix cure (UFX-X and UFX-Y) were studied for no. A2. The results showed almost no difference in wide angle X-ray diffraction data. If evaluated in detail, there was a tendency for the height of the broad peak to be lower for free-cured film than for fix-cured films. These results showed that there was no

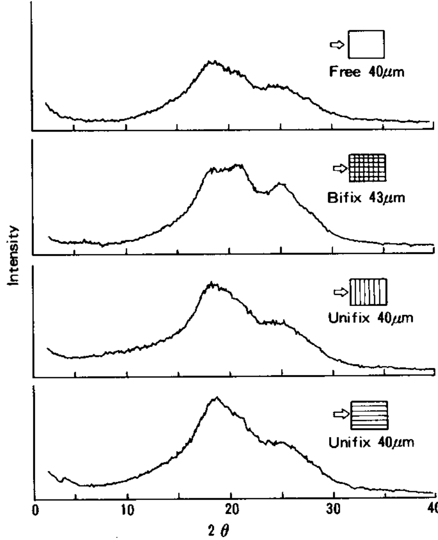

Fig. 8. Diffractograms for no. A2 films cured under various conditions.

relationship between lowering the thermal expansion coefficient of polyimide and crystallizability.

Conformation of Polyimides

Next, conformations of polyimides belonging to the individual groups 1–4 were studied, with comparison to several papers.[17,18] This result is shown in Figure 9. The polyimides belonging to the group 1 could only take a conformation wherein both the diamine and tetracarboxilic acid components were linearly arranged as shown in Figure 9(I). Therefore, they were rodlike in the direction of the molecular axis and rigid, as well as liable to be crystallized.

The polyimides belonging to group 2 had a reasonably linear conformation, although there was a somewhat zigzag structure due to the biphenyl skelton of BPDA as shown in Figure 9 (II).

The polyimides belonging to group 3 could be further divided into two groups; one which was synthesized from *p*-PDA, *o*-TLD, or DATP and BTDA and was on almost the same plane as shown in Figure 9(III) but was not very straight because of the benzophenone skelton, and the second which turned at the ether bond as shown in Figure 9(IV) and did not lie on the same plane, but had its skelton between the two ether bonds in a linear arrangement.

Almost all the other polyimides lost linearity in the conformation of the molecular chain due to ether, thioether, methylene, or ketone groups etc. as shown in Figure 9(V). That is, it seemed that the low thermal expansion coefficients appeared when the skeltal arrangement became linear. This

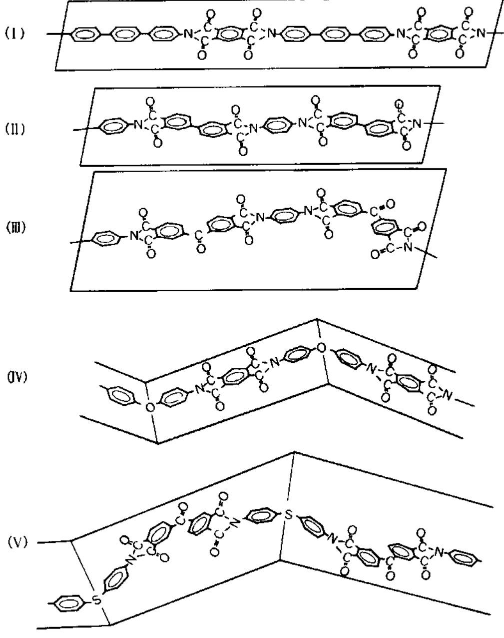

Fig. 9. Conformations of polyimides.

was because the polymer which had a linear conformation could expand very little in the direction of the molecular chain and so depressed the thermal expansion perpendicular to the molecular chain direction when the temperature was raised.

It also appeared that the effect of fixing the film during imidization on lowering and anisotropy in the thermal expansion coefficient was due to ordering of these rodlike polymer molecules. In the case of the free cure, the rodlike polymer molecules were directed randomly. In contrast to this, in the case of the fix cure, they were oriented in the direction in which curing shrinkage was prevented. Thus, the thermal expansion coefficient in the prevented direction for unifix-cured film (UFX-X) was lowered by depressing the thermal expansion, but it was not lowered perpendicular to the prevented direction (UFX-Y).

It was considered that the rodlike polymer molecules in bifix-cured film were ordered in the plane of the film. Thus, the thermal expansion coefficient in the direction of the plane was lowered. Then, the thermal expansion coefficient in the direction vertical to the film should be as large as UFX-Y.

CONCLUSIONS

1. Some polyimides which have very low thermal expansion coefficients were observed.
2. The polyimides obtained from PMDA or BPDA and diamines which were composed of only benzene rings fused at the para position had low thermal expansion coefficients.
3. It seemed that there was no relationship between the crystallinity and low thermal expansion coefficient; there were crystalline and noncrystalline polyimides having low thermal expansion coefficients.
4. It was proposed that the low thermal expansion coefficient appeared when the conformation of the molecular chain became linear.

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