Thermal expansion coefficients and moduli of uniaxially stretched polyimide films with rigid and flexible molecular chains

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The effects of linearity and rigidity of molecular chains and their cohesive energy density on the thermal expansion coefficient (*TEC*) and modulus of polyimide films were investigated, using various uniaxially stretched films. Rod-like polyimide film has a low *TEC* even in the case of unstretched film, and only more than 5% stretching gave a negative *TEC*. The larger the draw ratio, the larger the modulus in the machine direction became. By contrast, in the transverse direction, with an increase in draw ratio, the *TEC* became larger, and the modulus became smaller. These data suggest that this polyimide has a negative *TEC* and a very high modulus in the molecular chain direction, and a high *TEC* and a low modulus in the direction perpendicular to the molecular chain. In the cases of polyimides that had somewhat bent and rigid molecular chains, and flexible molecular chains, respectively, similar behaviour appeared. In the case of polyimide with a bent and flexible molecular chain, this behaviour hardly appeared. From these data, it was confirmed that the low *TEC* values of unstretched and biaxially fix-cured films were closely related not to the intermolecular cohesive energy and rigidity, but to the linearity of the molecular chain.

(Keywords: polyimide; low thermal expansion; thermal expansion coefficient; modulus; stretch; anisotropy; linearity; rigidity; cohesive energy density)

INTRODUCTION

Low-thermal-expansion polyimides are very useful insulating films in many kinds of electronics applications, because they can solve the problems of thermal stress due to thermal expansion coefficient (*TEC*) mismatch between two or more materials[1-3]. Their usefulness has been confirmed as interlayer dielectrics in very-large-scale integrated devices[4], substrates for flexible printed circuits[5], etc. Previous mechanistic studies suggested that all of the low-thermal-expansion polyimides had rod-like structures and very high Young's modulus, and that the molecular in-plane orientation caused by preventing shrinkage due to imidization and evaporation of solvent made the *TEC* lower. However, crystallizability and dense molecular packing were not the main factors for lowering *TEC*[2,4,6] as polyimides with somewhat bent and flexible linkages also had lowered *TEC*s because of the in-plane orientation effect[2,7].

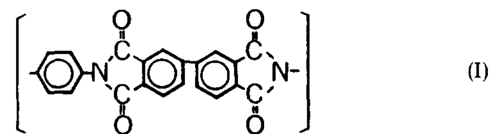
Several studies on the modulus of stretched polyimide films and fibres have revealed that the modulus of a uniaxially stretched (I) film is about[8] 60 GPa, and the modulus of the fibre of a polyimide obtained from benzidine and biphenyl tetracarboxylic dianhydride is[9] 80 GPa. Kaneda *et al.*[10] obtained very-high-modulus polyimide fibre from pyromellitic dianhydride, biphenyl tetracarboxylic dianhydride and *o*-tolidine. However, little was done regarding their *TEC*s.

In the present paper, the effects of linearity and rigidity of molecular chains and their cohesive energy density on the thermal expansion coefficient and modulus of polyimide films was investigated, using various uniaxially stretched films.

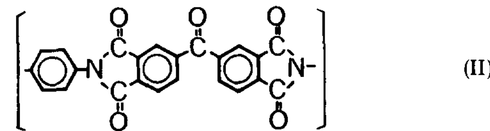
EXPERIMENTAL

Samples

Poly(amic acid) varnishes were obtained by reacting *p*-phenylenediamine (*p*-PDA) and 3,3′,4,4′-biphenyltetracarboxylic dianhydride (*s*-BPDA) (I), *p*-PDA and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) (II), 4,4′-diaminodiphenyl ether (DDE) and pyromellitic dianhydride (PMDA) (III), and DDE and *s*-BPDA (IV) in *N*-methylpyrrolidone (NMP) at ambient temperature.


(I)

Poly(*p*-PDA/*s*-BPDA)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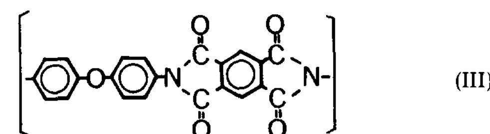
Poly(*p*-PDA/BTDA)


(III)

Poly(DDE/PMDA)

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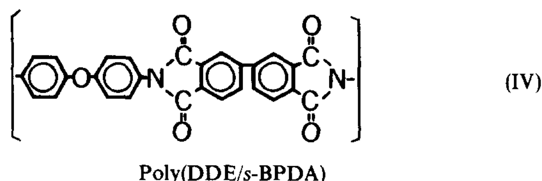

(IV)

Poly(DDE/*s*-BPDA)

The films were prepared by coating corresponding varnishes onto glass plates and drying at 100°C for 3 h. Uniaxially stretched films were prepared by stretching during the imidization reaction under load.

Bond angles of diamine and dianhydride components, cohesive energy density (*CED*) by Fedors' method[11], and crystal modulus[9] of the molecular chain are shown in *Table 1*.

Table 1 Materials

Polyimide	Bond angle (deg) diamine	Bond angle (deg) dianhydride	*CED* ($MJ\,m^{-3}$)	Crystal modulus (GPa)
(I) Poly(*p*-PDA/*s*-BPDA)	~0	~30	930	~180
(II) Poly(*p*-PDA/BTDA)	~0	~60	955	150
(III) Poly(DDE/PMDA)	~60	~0	918	18
(IV) Poly(DDE/*s*-BPDA)	~60	~30	834	<18

Linear thermal expansion coefficient

A film 5 mm wide, 15 mm long (between chucks) and 50–80 μm thick was used as sample. The sample was placed in the thermo-mechanical analyser (TMA 1500, Shinku-Riko Co. Ltd). It was heated to the maximum temperature heated previously in order to remove absorbed water, and any residual stress. After cooling to ambient temperature, changes in length of the polyimide film were measured at a heating rate of 5°C min^{-1} in air. Since the thermal expansion coefficient was temperature-dependent, the average value between 50 and 250°C was used as a representative value.

Modulus

A film 30 mm wide, 25 mm long (between chucks) and 50–80 μm thick in the case of measurement of modulus changes during imidization, and a film 5 mm wide, 25 mm long and 50–80 μm thick in the case of fully cured polyimide films, were used as samples. After the film was dried at 100°C for 10 min in the measurement oven, Young's modulus was measured using a Rheopexy Analyzer RPX-706 (Iwamoto Co. Ltd). A dynamic measurement was carried out at 10 Hz, under 15 μm displacement.

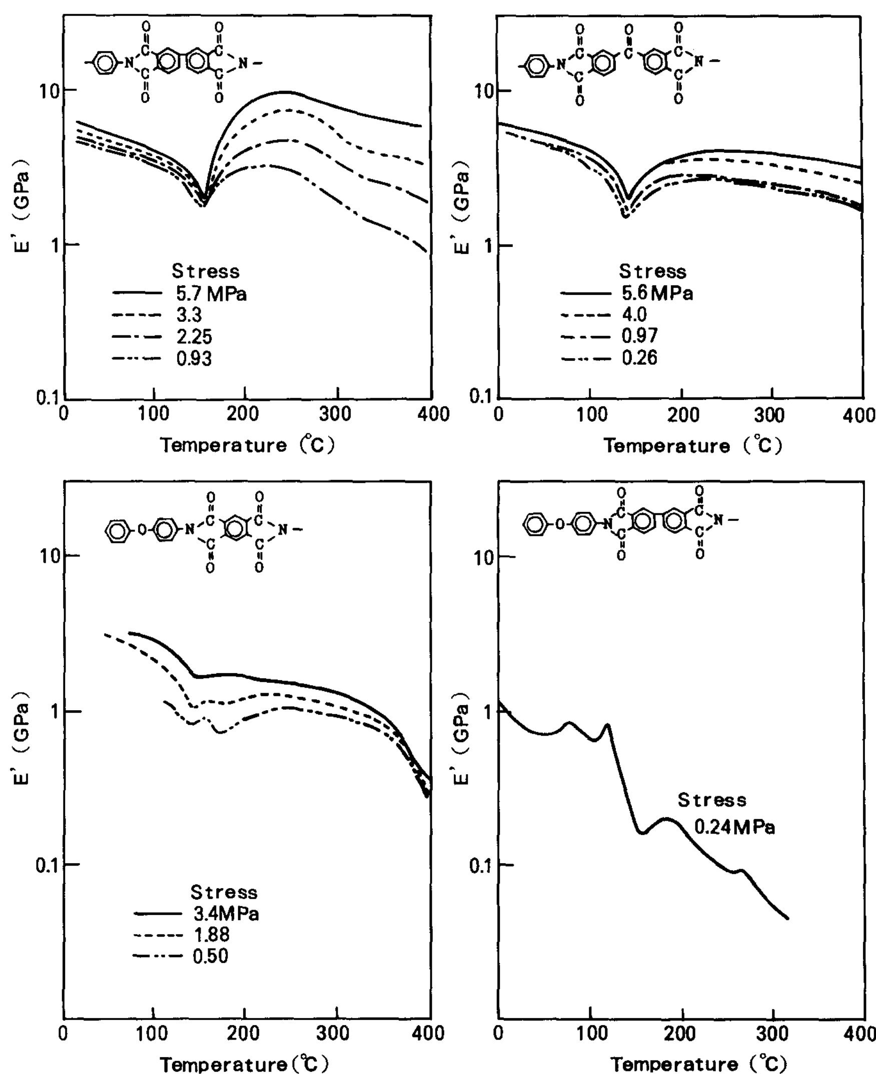

Figure 1 Changes in modulus of poly(amic acid) films during the imidization reaction under load

RESULTS AND DISCUSSION

Stretching behaviour during weight-loaded imidization

First of all, uniaxial stretching of fully imidized film was tried at temperatures higher than T_g. However, it was impossible to stretch the film in the case of the low-thermal-expansion polyimide (I). Then, stretching during the imidization reaction was tried, because the poly(amic acid) film is amorphous, although the resulting polyimide is partially crystalline. Therefore, it was considered that stretching during imidization would be easier than that after imidization. Our previous study[12] on the thermal imidization reaction in the solid state revealed that most of the reaction proceeded in the temperature range 150–250°C, with the condition that T_g of the corresponding polymer film almost equals reaction temperature. Therefore, a temperature higher than T_g is needed to complete the imidization reaction.

Changes in modulus and length of the film during the weight-loaded imidization reaction at a heating rate of 1.5°C min^{-1} are shown in *Figures 1* and *2*, respectively. All of the poly(amic acid) films had infinitesimal values of the modulus at about 150°C, which seemed to be the T_g values of poly(amic acids). An increase in modulus appeared at more than 150°C because the molecular chains were oriented and became more rigid due to the formation of imide rings on the polymer molecules. The extent of the increase in modulus became larger with increase in linearity of the molecular chains.

From the data shown in *Figure 2*, stretching of poly(amic acid) films took place in the temperature range 150–250°C, which is almost the same as the range of imidization. When the load was small in the cases of (II) and (III), shrinkage of the films, which seemed to be due to evaporation of residual solvent and to the imidization reaction, occurred.

Figure 3 shows the relationship between loading weight for stretching and draw ratio. Polyimides (I), (II) and (III) were stretched similarly, but (IV) was stretched to a much greater extent. Because (IV) had a low T_g and low crystallinity, stretching took place even after the imidization reaction.

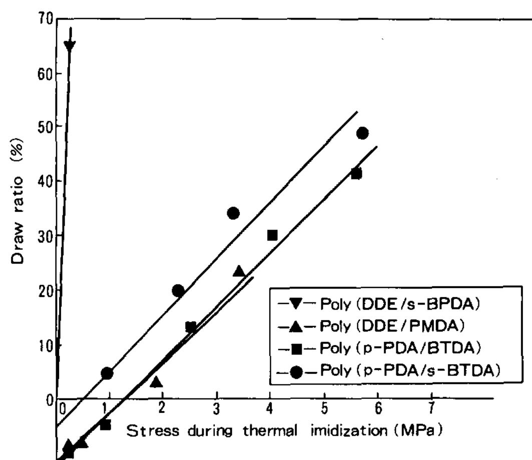

Figure 3 Draw ratio vs. stress during thermal imidization

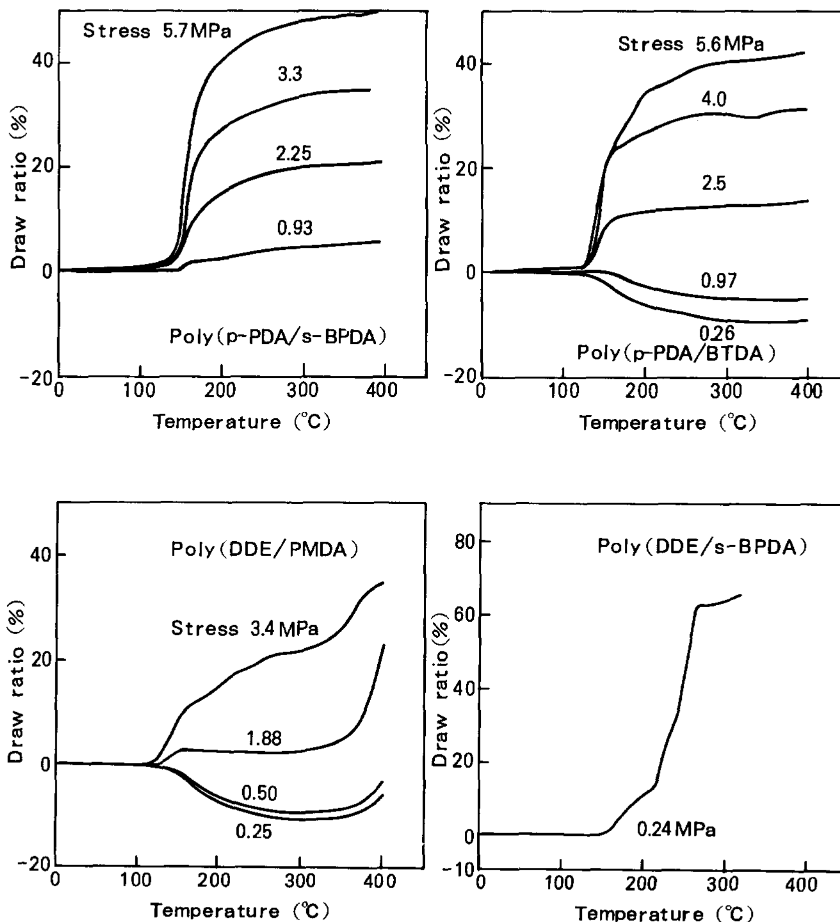

Figure 2 Drawing behaviour of poly(amic acid) films during the imidization reaction under load

Linear thermal expansion coefficients and moluli of the uniaxially stretched films

Figures 4 and *5* show the effects of draw ratio on *TEC*s and moduli of stretched films, respectively, in the machine (MD) and transverse directions (TD). In the case of (I), even unstretched, the film had a low *TEC*; when stretched only 5%, it had a very low negative *TEC* in the MD, but it did not decrease below -1×10^{-5} K^{-1} even if the draw ratio became larger than 20%, By contrast, with larger draw ratios, the larger the *TEC* in the TD became. *Figure 5* reveals that the modulus of (I) became higher in the MD and smaller in the TD with an increase in draw ratio. These data suggested that (I) had a negative *TEC* and very high modulus in the molecular chain direction, and comparatively high *TEC* and low modulus in the direction perpendicular to the molecular chain. The data showed that the cohesive energy density of (I) was not large enough to restrict thermal expansion between molecular chains.

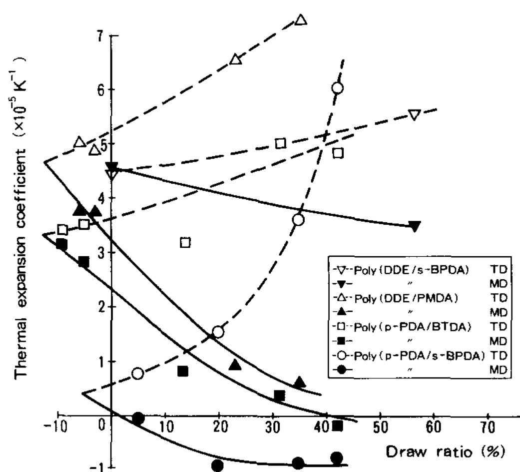

Figure 4 Thermal expansion coefficient vs. draw ratio

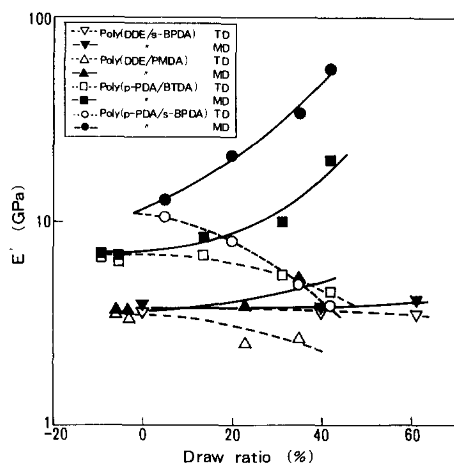

Figure 5 Modulus vs. draw ratio

In the cases of (II) and (III), whose molecular chains were somewhat bent and rigid, and somewhat bent and flexible, respectively, similar behaviour appeared. However, the *TEC*s of the unstretched films were comparatively large, and more than 40% drawing was needed to obtain almost zero *TEC*s. Also, the extent of the change in the modulus was smaller.

In the case of (IV), which had a bent and flexible molecular chain, this behaviour hardly appeared.

Figure 6 shows the relationship between *TEC* and modulus of the films both in the MD and TD. These results were similar to the data for oriented polyoxymethylene[13], liquid-crystal polymer[14], etc. However, the values differed a little from each other, i.e. there were some polymers with a relatively high *TEC* despite higher modulus, and some with lower *TEC* despite lower modulus. These seemed to appear because of the different linearity and rigidity of the polymer molecules.

Mechanism of lowering TEC in unstretched and biaxially fixed films

*TEC*s and moduli of the unstretched, biaxially fix-cured and 40% uniaxially stretched films are summarized in *Table 2*. From the data, *TEC* and modulus in the MD seemed to be closely related to the linearity and the rigidity of the polymer molecules, respectively. *TEC* and modulus in the TD were almost the same, since their cohesive energy densities were almost the same. Therefore, the polyimide with almost linear molecular

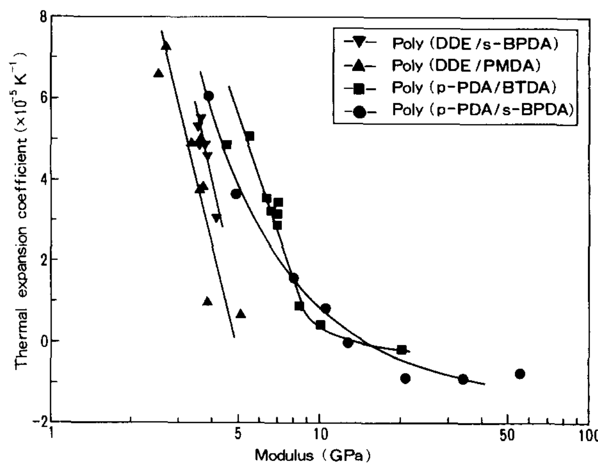

Figure 6 Thermal expansion coefficient vs. modulus

Table 2 Linear thermal expansion coefficients and moduli of the various polyimide films

	40% Uniaxially stretched film				Unstretched film		Biaxially fix-cured film	
	MD		TD					
Polyimide	*TEC* (10^{-5} K^{-1})	Modulus (GPa)	*TEC* (10^{-5} K^{-1})	Modulus (GPa)	*TEC* (10^{-5} K^{-1})	Modulus (GPa)	*TEC* (10^{-5} K^{-1})	Modulus (GPa)
(I) Poly(*p*-PDA/*s*-BPDA)	−1	55	6	4	0.4	11	0.3	11
(II) Poly(*p*-PDA/BTDA)	0	20	5	4.6	3.3	7	2.1	7
(III) Poly(DDE/PMDA)	0.5	5	8	2.7	4.7	3.5	2.2	3.2
(IV) Poly(DDE/*s*-BPDA)	3.5	3.5	5	3.5	4.5	3.6	4.6	3.5

structure had a lower *TEC*, even in the case of an unstretched film. Then, it was considered that the increase in linearity due to in-plane orientation by a biaxial fixcure made *TEC* lower. In the case of polyimides with somewhat bent molecular structures, although the *TEC* of the unstretched film was not low, that of the biaxially fixed film became lower because of the in-plane orientation. However, in the case of the polyimide with bent structure, since the in-plane orientation hardly increased with linearity of the molecular chain, its *TEC* did not become lower.

In the cases of polyimides which had somewhat bent and rigid chains, and flexible molecular chains, similar behaviour appeared. In the cases of polyimide which had a bent and flexible molecular chain, this behaviour was hardly apparent.

From these data, it was confirmed that the low thermal expansion coefficients of unstretched and biaxially fixcured films were closely related not to the rigidity and intermolecular cohesive energy, but to the linearity.

CONCLUSIONS

The effects of linearity and rigidity of molecular chains and their cohesive energy density on the thermal expansion coefficient (*TEC*) and modulus of polyimide film were investigated, using various uniaxially stretched films, in order to define a mechanism that describes the lowering of their low thermal expansion coefficient.

When the poly(amic acid) films were heated under load, most of the stretching took place in the temperature range 150–250°C, simultaneously with progress of the imidization reaction.

In the case of rigid linear polyimide, the film had a very low *TEC* in the machine direction even though the draw ratio was small. But it did not decrease below -1×10^{-5} K^{-1}, even if the draw ratio became larger than 20%. By contrast, the larger the draw ratio, the larger the *TEC* in the transverse direction became. That is, this polyimide had a negative *TEC* in the molecular chain direction, and a higher *TEC* in the perpendicular direction. Also, this polyimide film had a very high modulus in the molecular chain direction and a very small value in the perpendicular direction.

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