Solution-processable Low-CTE Transparent Heat-resistant Plastic Substrate Materials in Display Devices

Masatoshi Hasegawa, Tomohiro Ishigami, Junichi Ishii

Department of Chemistry, Faculty of Science, Toho University
2-2-1 Miyama, Funabashi, Chiba 274-8510, Japan
TEL & FAX: +81-47-472-1869, E-mail: mhasegaw@chem.sci.toho-u.ac.jp

Introduction

We have so far developed various polyimide (PI) systems showing low linear coefficients of thermal expansion (CTE) and studied the low CTE generation mechanism. The results revealed that low CTE characteristics are closely related to a high level of PI main chain orientation to the film plane (XY) direction, which is induced upon thermal imidization process. An indispensable structural factor for the prominent imidization-induced in-plane orientation is the PI backbone linearity/stiffness. Therefore, low-CTE PI systems themselves are usually insoluble in common organic solvents. In other words, highly soluble PIs are limited to non-crystalline systems consisting of highly distorted main chains and bulky side groups/substituents (typically, CF_3 group). From this situation, it is believed that simple casting process (without imidization) using stable PI solutions usually causes no significant in-plane orientation. In the present work, we show that highly transparent soluble PI systems give rise to considerably low CTE upon simple solution casting process of stable PI varnishes without imidization process.

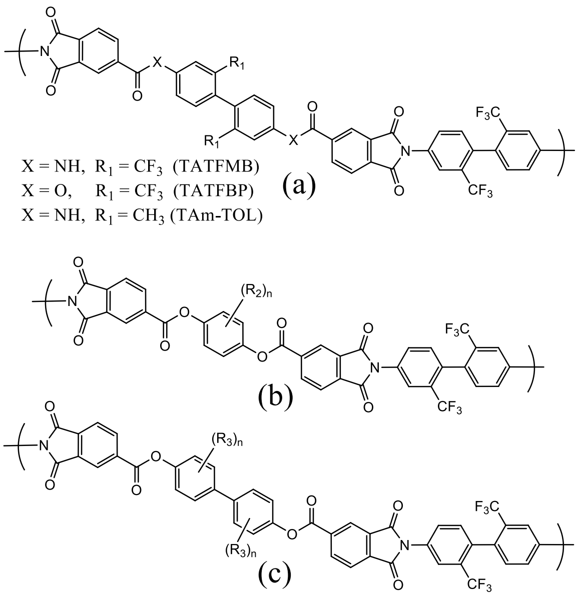

Fig.1 Structures of polyimide systems studied.

Experimental Section

In this work, some novel tetracarboxylic dianhydrides were synthesized, purified, and analyzed. Poly(amic acid)s (PAAs) with high molecular weights were readily obtained by the equimolar polyaddition of these tetracarboxylic dianhydrides and a rigid fluorinated diamine (TFMB). An excess of a cyclodehydration reagent (Ac_2O/pyridine) was added into the PAA solutions and stirred at room temperature for 24 h to ensure complete imidization. The homogeneous PI solutions formed were slowly poured into methanol to obtain fibrous PI powder. It showed excellent solubility even in less hygroscopic solvents [e.g., γ-butyrolactone (GBL) and cyclopentanone (CPN)] and allowed the formation of stable PI varnishes with a high solid content. PI films were prepared by coating/drying the PI solutions on a glass substrate at 60 + 150 + 250 ºC for each 1 h. The optical, thermal, and mechanical properties of the PI films were evaluated. The molecular structures of some PIs examined in this work are shown in **Fig. 1**.

Results and Discussion

Table 1 lists the properties of systems (a). The chemically imidized TATFMB/TFMB powder sample was soluble even in CPN. The PI film prepared by solution casting of the stable PI varnish provided an almost colorless flexible film achieving excellent combined properties, for example, a very high T_g of 328 ºC, a considerably low CTE (9.9 ppm/K), and good film toughness (the elongation at break, $\varepsilon_b = 27$ %), although there was room for further improvement of the film transparency (light transmittance at 400 nm, $T_{400} < 50\%$). On the other hand, the thermally imidized counterpart did not show low CTE characteristics. A poly(amide-imide) derived from trimellitic acid anhydride chloride (TMAC) and TFMB, which possesses the same chemical composition as the TATFMB/TFMB system, resulted in a slightly colored very brittle film ($\varepsilon_b = 0\%$). An effect of the CF_3 groups in TATFMB on the properties was also investigated. The corresponding CH_3-substituted TA*m*-TOL/TFMB system caused intensive film coloration (T_{400} = 0%). Thus, these comparative results revealed the importance of the film preparation route (chemical or thermal cure), chain sequence, and the great role of the CF_3 groups in TATFMB.

Table 1 Properties of TATFMB/TFMB and related systems.

Tetracarboxylic dianhydride or Acid chloride	Cure	η_{inh} (PAA) (dL/g)	Color of PI films	Solvent for re-dissolution	CTE (ppm/K)	T_g (ºC)	T_{400} (%)	ε_b (%)	W_A (%)
TATFMB	Chemical	3.22	Colorless	CPN (> 7 wt%)	9.9	328	43.4	27	0.81
TATFMB	Thermal			DMAc	37.8			5	
TMAC	Chemical	0.61	Pale-Yellow	DMAc	23.9	278	18.4	0	
TA*m*-TOL	Chemical	1.32	Yellow	DMAc (10 wt%)	38	259	0	11	1.67

Table 2 Properties of TATFBP/TFMB-based systems.

Tetracarboxylic dianhydride	Cure	η_{inh} (PAA) (dL/g)	Color of PI films	Solvent for re-dissolution	CTE (ppm/K)	T_g (ºC)	T_{400} (%)	ε_b (%)	W_A (%)
TATFBP	Chemical	1.34	Colorless	CPN (> 15 wt%)	32.5	261	70.7	13	0.03
TATFBP (70) X-DA (30)	Chemical	1.62	Colorless	DMAc (> 12 wt%)	12.6	277	74.8	7	

Table 2 lists the properties of TATFBP/TFMB-based homo and copolymer systems. The change from the amide to the ester linkages gave rise to significantly enhanced film transparency (T_{400} = 70.7%) in addition of drastically reduced water absorption (W_A = 0.03%). However, the incorporation of ester linkage was less effective to decrease CTE, probably owing to a decrease in the main chain rigidity. Then, an aromatic tetracarboxylic dianhydride (X-DA) was used as a comonomer. The copolymerization approach successfully reduced the CTE (12.6 ppm/K) unexpectedly without sacrificing high film transparency (T_{400} = 74.8%). In the present work, the development of novel solution-processable low-CTE colorless PI materials was also extended to other systems depicted in **Fig. 1(b)** and **(c)**. The detailed properties will be discussed in this report. We also propose the mechanism of "casting-induced in-plane chain orientation".

Fig. 2 shows a CTE−T_{400}−solubility diagram for various PI systems. One notices that even poly(ether sulfone) (PES) as a typical high-temperature engineering plastic is beyond the present purpose as well as a popular soluble transparent PI system (6FDA/TFMB, #1). The results of conventional thermally cured insoluble PI systems (#6−12) suggest how simultaneous achievement of high transparency and low CTE is difficult. Semi-cycloaliphatic s-BPDA/CHDA and the CBDA/TFMB systems are rare cases possessing low CTE and high transparency (#6, 7). However, these systems show no solution-processability. On the other hand, some of poly(ester imide)s depicted in **Fig. 2(b)** simultaneously achieved low CTE, high transparency, and good solution-processability (#2, 3, 5) as indicated from the data points plotted within "Target Area-II" applicable to the plastic substrate in electronic paper devices (external-light reflection mode), although "Target Area-I" applicable to LCD (backlight-transmission mode) is difficult to achieve at the current stage.

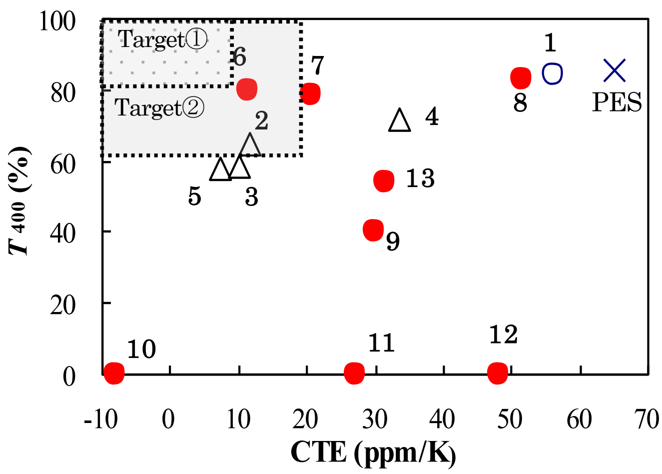

Fig.2 CTE−T_{400}−solubility diagram.