Polyimides Derived from 2,2′-Bis(trifluoromethyl)-4,4′-diaminobiphenyl. 3. Property Control for Polymer Blends and Copolymerization of Fluorinated Polyimides

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ABSTRACT: Fluorinated polyimide blends and copolyimides have been prepared from 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (TFDB), 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA), and pyromellitic dianhydride (PMDA). The fluorinated polyimide blends are made with two types of poly(amic acid)s; one is 6FDA/TFDB poly(amic acid) prepared from 6FDA and TFDB, and the other is PMDA/TFDB poly(amic acid) prepared from PMDA and TFDB. On the other hand, fluorinated copolyimides are prepared from TFDB diamine and two dianhydrides, 6FDA and PMDA. The coefficient of thermal expansion (CTE) increases with increasing 6FDA/TFDB content in the polyimide blend and increases with increasing 6FDA/TFDB unit content in the copolyimide. The CTE can be controlled between -5×10^{-6} and 8.2×10^{-5} °C^{-1} by polymer blend or copolymerization techniques. The copolyimide made with a 10 mol % 6FDA/TFDB unit content has almost the same CTE as the silicon substrate and thus has little stress after imidization by heating. On the other hand, the in-plane refractive index of their films decreases with increasing 6FDA/TFDB content in the polyimide blend and decreases with increasing 6FDA/TFDB unit content in the copolyimide. The refractive index can also be controlled between 1.554 and 1.647 at 589.3 nm by polymer blend or copolymerization techniques.

Introduction

We have recently reported on the fluorinated polyimides derived from 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (TFDB).[1] The polyimide prepared from 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and TFDB (6FDA/TFDB) has a low dielectric constant, low water absorption, low refractive index, and high optical transparency and is highly soluble in polar solvents due to its high fluorine content of 31.3%. On the other hand, the polyimide prepared from pyromellitic dianhydride (PMDA) and TFDB (PMDA/TFDB) has a relatively low fluorine content of 23.0% but has a low coefficient of thermal expansion (CTE) on account of its rigid-rod structure. Harris et al. have synthesized polyimides based on TFDB and studied their solubility and thermal stability.[2] Cheng et al. have formed a fiber made of the polyimide solution from 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) and TFDB and studied its mechanical properties.[3]

In other previous work, we have described low thermal expansion fluorinated polyimides which have a rigid-rod structure with trifluoromethyl side chains.[4] However, the CTE of these polyimides is determined by their structure, and it is impossible to control it precisely. We need polyimides which have the same CTE as aluminum, copper, silicon, or silicon dioxide for use as interlayer dielectrics in microelectronic devices. This feature is necessary to prevent the devices from cracking, peeling, and bending.

The applications of polyimides to optical interconnections are also being studied.[5,6] In this field, control of optical properties such as the optical transparency and the refractive index is very important. Materials with low optical loss and a controllable refractive index are required for optical waveguides in such devices as optoelectronic integrated circuits.

The polyimide PMDA/TFDB has a low CTE of -5×10^{-6} °C^{-1} and a high refractive index of 1.647, and 6FDA/TFDB has a high CTE of 8.2×10^{-5} °C^{-1} and a low refractive index of 1.554.[1] We have been investigating the polymer blend and the copolymerization of these two polyimides and how their properties can be controlled.

Studies have already been made of polyimide blends, copolyimides, and polyimide interpenetrating polymer networks (IPNs). Ohishi et al. have synthesized random and block copolyimides based on PMDA, *p*-phenylenediamine (PPD), and oxydianiline (ODA) and reported their mechanical properties.[7] Yamamoto et al. have synthesized polyimide blends and copolyimides based on PMDA, PPD, and ODA and discussed the CTE difference between polyimide blends and copolyimides.[8] Yokota et al. have prepared polyimide composite films by polymer blending and studied the mechanical properties of such blends.[9] Burks et al. have synthesized copolyimides with varying flexibilizing groups and studied their flow, mechanical, adhesive, and thermal properties.[10] Pater et al. have synthesized IPN polyimides to develop tougher polymers which ar more resistent to microcracking.[11]

This paper describes the preparation and characterization of polyimide blends and copolyimides based on the TFDB diamine with 6FDA and PMDA dianhydrides and investigates the relationship between the polymer components and their properties.

Experimental Section

Measurements. IR spectra were measured with a Hitachi 270–30 IR spectrometer.

Polymer decomposition temperatures were measured by thermogravimetric analysis (TGA) with a Shimadzu TGA-50 thermogravimetric analyzer. The TGA measurements were conducted with a heating rate of 10 °C/min in a nitrogen atmosphere.

Dielectric constants were measured with a YHP 4278 capacitance meter at a frequency of 1 MHz and a temperature of 23 °C. Samples were preconditioned at 1 Torr at 120 °C for 2 h to eliminate absorbed water.

The in-plane refractive indices were measured with an Atago 4T-Type refractometer at 20 °C using sodium D-line light with a wavelength of 589.3 nm.

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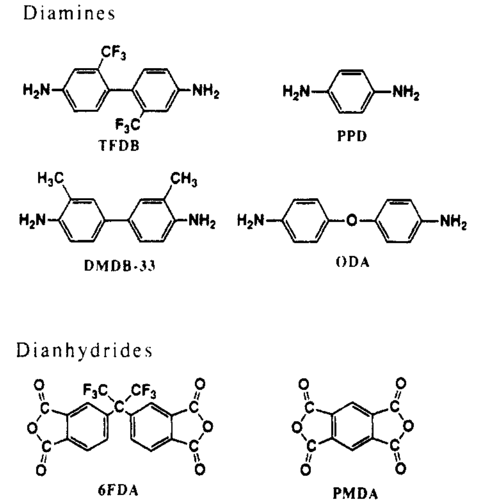


Figure 1. Diamines and dianhydrides.

The CTEs were measured by thermomechanical analysis (TMA) with a Sinku Riko TMA-7000 thermomechanical analyzer. Specimens were 5 mm wide, 15 mm long, and 15 μm thick. The measurements were carried out three times during elongation with a heating rate of 5 °C/min in a nitrogen atmosphere at a load of 3 g. After the first measurement (first run), the sample was cooled gradually to 25 °C in a nitrogen atmosphere, and then the second measurement (second run) was made. The same operation was carried out between the second run and the third run. The CTE values were determined as the mean at 50–300 °C.

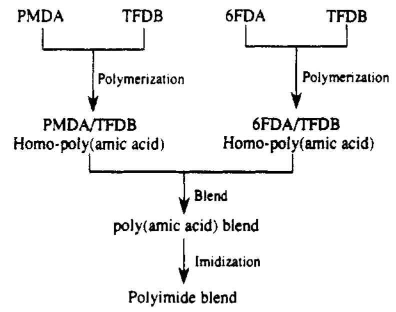
Materials. The diamines and dianhydrides used in this study are shown in Figure 1. TFDB was synthesized by the method given by Maki and Inukai[12] and was purified carefully by sublimation under reduced pressure. 6FDA was obtained from Hoechst Japan Ltd. and was purified by sublimation under reduced pressure. PMDA was obtained from Mitsui Toatsu Chemical Inc. and was purified by recrystallization from acetone. PPD and ODA were obtained from Wako Pure Chemical Industries, Ltd., and were purified by sublimation under reduced pressure. *o*-Tolidine (3,3′-dimethyl-4,4′-diaminobiphenyl, DMDB-33) was obtained from Kanto Chemical Co. Inc. and was purified by sublimation under reduced pressure. *N,N*-Dimethylacetamide (DMAc) was obtained from Aldrich Chemical Co. Ltd. Its water content was below 0.005% and its evaporation residue was below 0.0010%. It was used without further purification.

Preparation of Homopolyimides. 6FDA/TFDB Homopolyimide. Preparation of the Poly(amic acid). 6FDA (13.3274 g, 30.000 mmol) was dissolved in DMAc (206.4 g) to give a clear, colorless solution. TFDB (9.6072 g, 30.000 mmol) was then added to the solution while stirring vigorously. The solution was stirred at room temperature for 48 h and eventually became viscous. At this stage, 10% weight poly(amic acid) solution was obtained (intrinsic viscosity: 1.00 dL/g). The preparation was carried out in a dry nitrogen atmosphere.

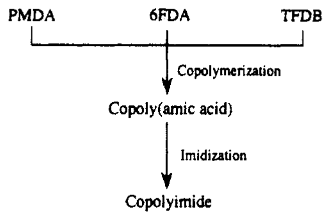
Conversion of the Poly(amic acid) into Polyimide. The poly(amic acid) solution was spin-cast onto a clean, dry silicon substrate to give a thin layer of solution. It was then heated to 350 °C in a dry nitrogen atmosphere using the following schedule: 70 °C, 2 h; 160 °C, 1 h; 250 °C, 0.5 h; 350 °C, 1 h. This heat treatment converted the poly(amic acid) into polyimide. Whereas the IR absorption peak due to the carbonyl stretching of the amide group appeared at about 1720 cm^{-1} in the poly(amic acid), the absorption peaks due to the carbonyl asymmetric and symmetric stretching of the imide group appeared at 1740 and 1790 cm^{-1} in the polyimide.[1] The polyimide film was tough and flexible and had excellent transparency.

PMDA/TFDB Homopolyimide. PMDA/TFDB poly(amic acid) solution (DMAc, 145.4 g, 10% weight) was prepared in the same manner as the 6FDA/TFDB poly(amic acid) except that PMDA (6.5436 g, 30.000 mmol) was used instead of 6FDA. The same method was also used to prepare the PMDA/TFDB polyimide film.[1]

Scheme I



a. Polyimide Blend



b. Copolyimide

Table I
Mass and Monomer Unit Moles of Poly(amic acid) Solutions in the Polyimide Blends

6FDA/TFDB content, mol %	PMDA/TFDB 10 wt % soln		6FDA/TFDB 10 wt % soln	
	g	mmol[a]	g	mmol[a]
0	53.8	10.0	0	0
15.0	45.8	8.50	11.4	1.50
19.0	43.6	8.10	14.5	1.90
26.0	39.8	7.40	19.9	2.60
41.3	31.6	5.87	31.6	4.13
58.5	22.4	4.15	44.7	5.85
100.0	0	0	76.4	10.00

[a] Monomer unit moles of poly(amic acid).

Other Homopoly(amic acid)s and a Homopolyimide. PMDA/PPD, PMDA/DMDB-33, and PMDA/ODA poly(amic acid) solutions (in DMAc, 10% weight) were prepared in the same manner as 6FDA/TFDB. The PMDA/ODA poly(amic acid) was then converted into polyimide in the same way as before.

Preparation of Polyimide Blends. Polyimide blends were obtained by mixing the DMAc solution of PMDA/TFDB homopoly(amic acid) with the DMAc solution of 6FDA/TFDB homopoly(amic acid) (Scheme Ia). These solutions were blended in various ratios and then stirred for 7 days in a dry nitrogen atmosphere. At this time, the mixture were clear in any blend ratio, and there was no phase separation. The masses of PMDA/TFDB and 6FDA/TFDB homopoly(amic acid) solutions are listed in Table I. These poly(amic acid) blends were then converted into polyimide blends in the same manner as the 6FDA/TFDB homopolyimide. All polyimide blend films were tough and flexible.

Preparation of Copolyimides. Copolyimides were prepared from the two dianhydrides, PMDA and 6FDA, and TFDB diamine (Scheme Ib). PMDA and 6FDA were dissolved in DMAc, and then TFDB was added to the solution while stirring vigorously. The masses of the dianhydrides, diamine, and DMAc are listed in Table II. The solution was stirred in a dry nitrogen atmosphere at room temperature for 48 h and eventually became viscous. At this stage, 10% weight copoly(amic acid) solutions were obtained. These copoly(amic acid)s were converted into copolyimides in the same manner as the 6FDA/TFDB homopolyimide. All the copolyimide films were tough and flexible.

Results and Discussion

Phase Behavior of Polyimide Blends. It is vitally important to ensure the components are mixed homoge-

Table II
Monomer Contents and Solvent of Homopolyimides and Various Copolyimides

6FDA/TFDB content,[a] %	PMDA g	PMDA mmol	6FDA g	6FDA mmol	TFDB g	TFDB mmol	DMAc, g
0	2.1812	10.000	0	0	3.2024	10.000	48.5
10	1.9631	9.0000	0.4442	1.000	3.2024	10.000	50.5
20	1.7450	8.0000	0.8885	2.000	3.2024	10.000	52.5
30	1.5268	7.0000	1.3327	3.0000	3.2024	10.000	54.6
40	1.3087	6.0000	1.7770	4.0000	3.2024	10.000	56.6
50	1.0906	5.0000	2.2212	5.0000	3.2024	10.000	58.6
60	0.8725	4.000	2.6655	6.0000	3.2024	10.000	60.7
70	0.6544	3.000	3.1098	7.0000	3.2024	10.000	62.7
80	0.4362	2.000	3.5540	8.0000	3.2024	10.000	64.7
90	0.2181	1.000	3.9982	9.0000	3.2024	10.000	66.8
100	0	0	4.4424	10.000	3.2024	10.000	68.8

[a] 6FDA/TFDB unit content in the copolyimides.

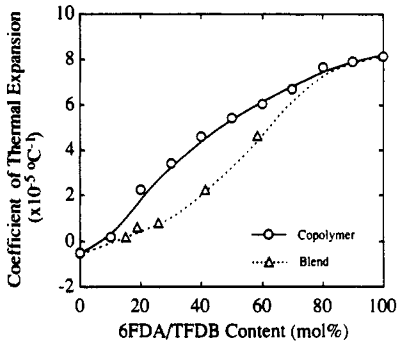


Figure 2. Coefficient of thermal expansion of copolyimides and polyimide blends. Temperature range, 50–300 °C; second run.

Table III
Phase Behavior of Poly(amic acid) Solutions (Polymer A:Polymer B = 1:1 (wt/wt))

polymer A	polymer B	phase
6FDA/TFDB	PMDA/TFDB	single
6FDA/TFDB	PMDA/DMDB-33	dual
6FDA/TFDB	PMDA/PPD	dual

neously when preparing polyimide blends. To obtain polyimide blends, PMDA/TFDB and 6FDA/TFDB poly(amic acid) solutions are mixed. Table III shows the phase behavior of the poly(amic acid) blend solutions containing relatively flexible 6FDA/TFDB and three types of rigid-rod polymers, PMDA/TFDB, PMDA/DMDB-33, and PMDA/PPD. The blend of the 6FDA/TFDB and the PMDA/TFDB solutions becomes single phase, but the others remain dual phase after stirring. In these mixtures, only the combination of PMDA/TFDB and 6FDA/TFDB enables the polyimide blend.

Thermal Expansion Control. The CTEs (second run) of the polyimide blends and copolyimides are shown in Figure 2. Almost all polyimide blends and copolyimide films were stressed when the films were cooled to room temperature after imidization by heating on a silicon substrate. The CTEs measured in the first run of TMA measurement are thus different from those of the second run. However, the CTEs measured in the second run are almost the same as those of the third run, because the film stress was released in the first run. The CTEs of both polyimide blends and copolyimides increase with increasing 6FDA/TFDB content and can be controlled between -5×10^{-6} and 8.2×10^{-5} °C^{-1} by changing the 6FDA/TFDB content. The PMDA/TFDB main chain consists of rigid phenyl rings and imide rings. This suggests that the rigid-rod structure is easy to order and that the ordering of PMDA/TFDB segments causes the low CTE. The presence of liquid-crystalline order in the rigid-rod polyimide gel from BPDA and TFDB in *m*-cresol has been reported by Harris et al. On the other hand, although 6FDA/TFDB is not flexible because of its high T_g of 335 °C, it is more flexible than PMDA/TFDB because of the presence of hexafluoroisopropylidene ($C(CF_3)_2$) groups, and its bent structure makes the molecular packing loose in the polyimide film.

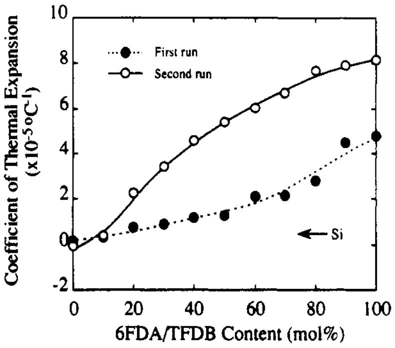


Figure 3. Coefficient of thermal expansion of copolyimides for first and second runs. Temperature range, 50–300 °C.

Polyimide blends have lower CTEs than copolyimides with the same 6FDA/TFDB content. The rigid PMDA/TFDB matrix may form a continuous phase in the polyimide blend. The polyimide blends may undergo exchange reactions in the mixing or imidization of poly(amic acid)s and block copolyimides form. On the other hand, the copolyimdie may exhibit microstructural inhomogeneities due to differences in monomer reactivity and also block copolyimides form. However, the CTE difference between polyimide blends and copolyimides (Figure 2) shows that the polymer structures are obviously different from each other.

Almost all polyimide films formed from poly(amic acid) solutions on silicon substrates have different CTE values for the first and second runs. Film stress arises during the heating cycle due to mismatch in the CTEs of the polyimide and the silicon substrate.[1] Figure 3 shows the CTEs measured in the first and second runs of the copolyimides. The difference in the CTEs between the first and second runs increases as the difference between the CTEs of the copolyimide and the silicon substrate increases.

In the copolyimides, the first- and second-run CTEs become identical at a 6FDA/TFDB content of about 10 mol %, at which point the polymer CTE is almost the same as that of the silicon substrate. TMA curves of copolyimides with 10 mol % 6FDA/TFDB unit and 100 mol % 6FDA/TFDB unit (6FDA/TFDB homopolyimide) are shown in Figure 4. The copolyimide with 10 mol % 6FDA/TFDB unit expands with the silicon substrate and has little stress after imidization. Its TMA curve of the first run is close to that of the second run. On the other

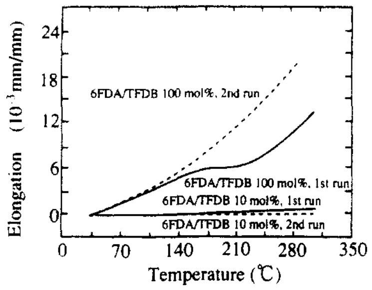


Figure 4. TMA curves of a copolyimide containing 10 mol % 6FDA and of 6FDA/TFDB homopolyimide.

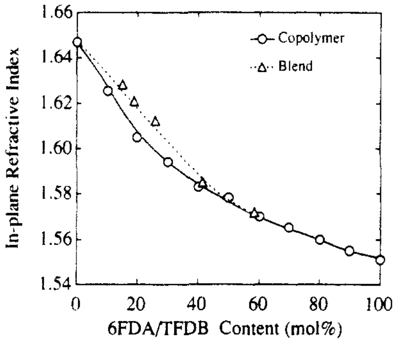


Figure 5. In-plane refractive indices (n_{TE}s) of copolyimide and polyimide blend films measured at 589.3 nm and 20 °C.

hand, the 6FDA/TFDB homopolyimide has quite different first- and second-run TMA curves.

Refractive Index Control. The in-plane refractive indices (n_{TE}) of polyimide blends and copolyimide films are shown in Figure 5. Both refractive indices decrease with increasing 6FDA/TFDB content and can be controlled between 1.647 and 1.556 at 589.3 nm by changing the 6FDA/TFDB content. At high 6FDA/TFDB contents, the curves slope gently, allowing precise refractive index regulation. Compared with the large difference in CTE, the refractive indices of copolyimides and polyimide blends are quite similar at all 6FDA/TFDB contents. The refractive index thus depends on 6FDA/TFDB content, but not the molecular formation, whether polymer blend or copolymer. The fluorine content of both polyimide blends and copolyimides increases with increasing 6FDA/TFDB content. The refractive index is expressed by the molecular refraction and the molecular volume and is known to decrease with increasing fluorine content.[14]

Solubility Studies. 6FDA/TFDB homopolyimide is soluble in organic polar solvents such as DMAc, acetone, tetrahydrofuran, and ethyl acetate, but PMDA/TFDB homopolyimide is insoluble in any solvent.[1] The solubilities of the corresponding copolyimides in DMAc are shown in Table IV. Those which were cured at 350 °C and contain less than 30 mol % 6FDA/TFDB unit were insoluble in DMAc. However, when the final cure temperature was reduced to 300 °C, copolyimides containing more than 20 mol % 6FDA/TFDB unit were completely soluble. The distortion of periodicity by copolymerization gives the high solubility, despite the large number of insoluble PMDA/TFDB units. The solubility differences at a 6FDA/TFDB content of 20–80 mol % result from the choice of final cure temperature, 300 or 350 °C. This suggests that rigid segments of PMDA/TFDB aggregate at 350 °C in the copolyimides, and this aggregation reduces the solubility.

Table IV
Solubility of Homopolyimides and Copolyimides[a]

6FDA/TFDB content, mol %	solubility	
	300 °C[b]	350 °C[b]
0	--	--
10	--	--
20	+	--
30	+	--
40	+	-
50	++	-
60	++	+
70	++	+
80	++	+
90	++	++
100	++	++

[a] Key: ++, fully soluble after 2 days; +, fully soluble after 5 days; –, partially soluble after 5 days; – –, insoluble after 5 days. [b] Final cure temperature at imidization. Solvent, DMAc. Concentration, 5% by weight.

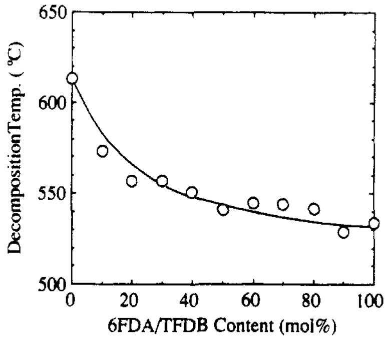


Figure 6. Decomposition temperature of copolyimides defined as 10% weight loss in a nitrogen atmosphere at a heating rate of 10 °C/min.

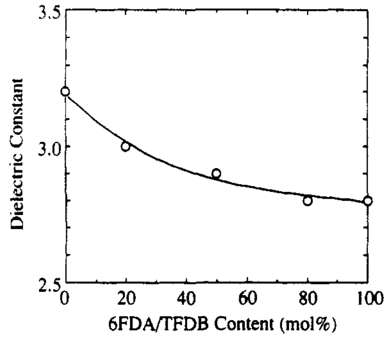


Figure 7. Dielectric constant of copolyimides at 1 MHz.

Thermal Stability. Figure 6 shows the polymer decomposition temperatures of the copolyimides. All have decomposition temperatures, defined as 10% weight loss in a nitrogen atmosphere, above 500 °C. The PMDA/TFDB homopolyimide with 0 mol % 6FDA/TFDB content has the highest polymer decomposition temperature at 613 °C. The decomposition temperature decreases with increasing 6FDA/TFDB content. Even a small amount of 6FDA/TFDB units is required to cause a substantial drop in the decomposition temperature.

The glass transition temperature (T_g) of 6FDA/TFDB homopolyimide is 335 °C, and PMDA/TFDB homopolyimide fails to exhibit a T_g below 400 °C by differential scanning calorimetry.[1] The T_g's of all investigated polyimide blends and copolyimides are above 335 °C.

Other Properties. Figure 7 shows the dielectric constant of the copolyimides. The dielectric constant decreases with increasing 6FDA/TFDB content as a result of the increased fluorine content.[15] Polyimides with a low dielectric constant have also been made by incorporating $C(CF_3)_2$ groups in both diamine and dianhydride units.[16] The 6FDA/TFDB homopolyimide has the highest fluorine content of 31.3% and the lowest dielectric constant of 2.8 at 1 MHz.

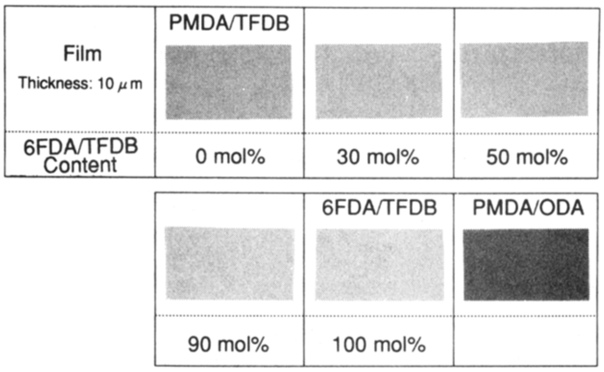


Figure 8. Color comparison of fluorinated copolyimide films and a nonfluorinated polyimide film.

The transparencies of several polyimide and copolyimide films is compared with that of a nonfluorinated polyimide, PMDA/ODA, in the photograph in Figure 8. The fluorinated homopolyimides and copolyimides are all more transparent than the nonfluorinated PMDA/ODA. The color of 10-μm-thick films gradually changes from bright yellow to colorless as the 6FDA/TFDB content increases. Less colored polyimide films have been made by incorporating $C(CF_3)_2$ groups into the polymers. These groups separate the chromophoric groups so as to reduce the charge transfer complex formation and thus lower the absorption in the visible spectrum of the resulting polymer.[17,18]

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