Polyimides Derived from 2,2′-Bis(trifluoromethyl)-4,4′-diaminobiphenyl. 4. Optical Properties of Fluorinated Polyimides for Optoelectronic Components

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ABSTRACT: Optical loss and refractive indices of fluorinated polyimides and copolyimides are studied for application to optoelectronic components. These polyimides and copolyimides are prepared from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA), pyromellitic dianhydride (PMDA), and 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (TFDB). The polyimide 6FDA/TFDB prepared from 6FDA and TFDB cured at 350 °C has an optical loss of 0.7 dB/cm at 0.63 μm, and this is the lowest of all polyimides cured at high temperature. Direct measurement of the optical loss of a polyimide at 1.3 μm was achieved for the first time by using a 6FDA/TFDB block with unequal length, width, and thickness. The optical loss was also low, 0.3 dB/cm. 6FDA/TFDB, PMDA/TFDB, and their copolyimides cured on a silicon substrate at 350 °C have two different refractive indices, an in-plane refractive index (n_{TE}) and an out-of-plane refractive index (n_{TM}). The n_{TE} of the copolyimide at 1.3 μm can be controlled between 1.523 (6FDA/TFDB) and 1.614 (PMDA/TFDB) by changing the 6FDA/TFDB content. It decreases monotonically with increasing 6FDA/TFDB content. The n_{TM}, on the other hand, can be controlled between 1.514 (6FDA/TFDB) and 1.521 (copolyimides with 60 mol % 6FDA/TFDB), but it has a maximum value at a 6FDA/TFDB content of 60 mol %. These polyimides and copolyimides prepared on a silicon substrate have birefringences between 0.008 (6FDA/TFDB) and 0.123 (PMDA/TFDB). Low optical loss and precise refractive index control are very important characteristics for optoelectronic components, especially at the telecommunication wavelength of 1.3 μm.

Introduction

Optical polymers are attractive for economical and practical optoelectronic devices and interconnections in optical communication systems. In particular, polymer optical waveguides have been investigated for use as flexible interconnections and in optoelectronic integrated circuits (OEICs).[1]

Organic polymers such as poly(methyl methacrylate) (PMMA), poly(styrene) (PS), and poly(carbonate) (PC) have excellent optical transparency in the visible wavelength, and they are used as materials for a variety of optical components. Optical waveguides using these polymers have also been studied.[2,3] However, these polymers do not have sufficient thermal stability at high temperature. High thermal stability should have the first priority in optical waveguides used in OEICs in order to provide compatibility with high-performance IC fabrication processes.[1] Precise control of the refractive index is essential for fabricating single-mode optical waveguides with core/cladding systems and for optical interconnections between different materials. Low optical loss in the near-infrared wavelengths of 1.3 and 1.55 μm is required for optical telecommunication systems.

On the other hand, polyimides have excellent thermal stability, and they have been investigated as waveguide materials. Sullivan[4] fabricated thermally-stable ridge waveguides using a polyimide with an optical loss of 0.3 dB/cm at 0.83 μm. Reuter et al.[5] have reported the optical loss of commercial fluorinated polyimides containing hexafluoroisopropylidene ($-C(CF_3)_2-$) groups and estimated the optical loss below 0.1 dB/cm at 0.63 μm using optimized conditions. However, the optical loss increases to around 3 dB/cm with a high curing temperature of 300 °C, because scattering centers are produced and charge transfer complexes are formed by the ordering and the production of voids and pinholes during imidization. Optoelectronic applications require polyimides with low loss and high thermal stability. The relationship between optical loss and polyimide chemical structure and the relationship between optical loss and preparation conditions have been reported for 0.63 and 0.83 μm, but the optical loss at the telecommunication wavelength of 1.3 μm has not been directly measured using the output intensity of the propagating light (rather than using light scattered from the polymide surface).

We have already reported[6–8] on the fluorinated polyimides derived from 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (TFDB). The polyimide 6FDA/TFDB prepared from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and TFDB has a high optical transparency in the UV–visible region in addition to a low dielectric constant, low water absorption, and low refractive index due to the high fluorine content of 31.3%. On the other hand, the polyimide PMDA/TFDB prepared from pyrometallitic dianhydride (PMDA) and TFDB has a relatively high refractive index due to its low fluorine content of 23.0%.[6] Furthermore, we have reported the control of properties such as the refractive index at 589.3 nm (using sodium D-line light) by controlling the polymer blend and the copolymerization of these two types of fluorinated polyimides.[8] These properties—high optical transparency and refractive index controllability—are very suitable for optoelectronic applications.

This paper studies the optical loss and refractive indices, in-plane refractive index (n_{TE}) and out-of-plane refractive index (n_{TM}), of the fluorinated polyimides 6FDA/TFDB and PMDA/TFDB and their copolyimides cured at a high curing temperature of 350 °C at a telecommunication

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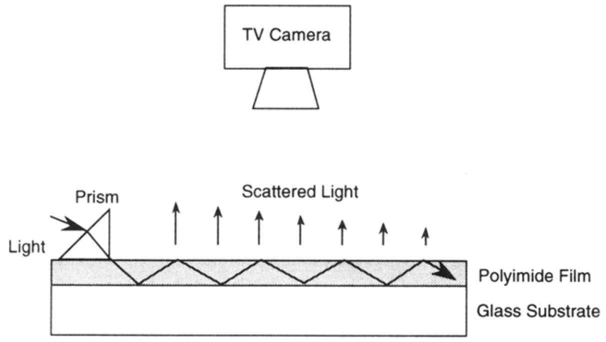

Figure 1. Experimental setup for measuring optical loss at 0.63 μm.

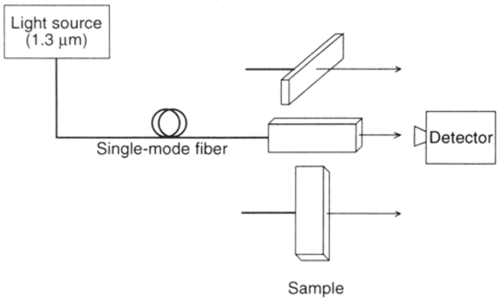

Figure 2. Experimental setup for measuring optical loss 1.3 μm using a 6FDA/TFDB polyimide block.

wavelength of 1.3 μm in addition to that at a visible wavelength of 0.63 μm.

Experimental Section

Measurements. The optical losses at 0.63 μm were measured from the scattered light.[9] The experimental setup is illustrated in Figure 1. Light from a 0.63-μm helium–neon laser was coupled through a prism into the 10-μm-thick polyimide films on a quartz glass substrate. The light scattered from the film surface was detected by a Hamamatsu C-1000 TV camera. The optical loss was calculated from the plot of the scattered light intensity against the propagation length. The attenuation of scattered light is directly proportional to the optical loss in the polyimide film.

The UV–visible spectra were measured with a Hitachi U-3500 photometer. The 10-μm-thick polyimide films on a quartz glass substrate were used as samples.

The optical loss at 1.3 μm was measured using a laser diode as a 1.3-μm light source. The experimental setup is illustrated in Figure 2. The sample was a 6FDA/TFDB polyimide block 24.7 mm long, 14.8 mm wide, and 2.1 mm thick. The light was introduced into the polyimide block from each direction using a single-mode fiber with a mode-field diameter of 8 μm. The transmission loss was measured from the difference between input and output light intensities using an Anritsu MA9611A detector and ML9001A optical power meter. The optical loss excluding connection loss was calculated from the slope in the plot of transmission against propagation length.

The near-infrared absorption spectrum was measured with a Nihon-Bunkou Mac-1 spectrophotometer for a 160-μm-thick polyimide film. A 34-μm-thick film was used as a reference. The beam was linearly polarized and incident upon the film at a Brewster angle of about 57°.

The n_{TE} and n_{TM} were measured with a Metricon PC-2000 prism coupler using light from a 0.63-μm helium–neon laser, a 1.3-μm laser diode, and a 1.5-μm laser diode. The samples were polyimide films about 5 μm thick on a silicon substrate. The birefringences (Δn) were calculated using the following relationship:

$$\Delta n = n_{TE} - n_{TM}$$

Polyimide Preparation. The polyimides and a fluorinated copolyimide used in this study are shown in Figure 3. The poly(amic acid) precursor solutions were prepared from the dianhydride(s) PMDA, 6FDA, or both PMDA and 6FDA and the diamine TFDB or 2,2′-dimethyl-4,4′-diaminobiphenyl (DMDB) in *N,N*-dimethylacetamide (DMAc). They were spin-cast onto a quartz glass substrate (50 mm long, 70 mm wide, and 2 mm thick) or a silicon substrate (76.2 mm diameter and 0.38 mm thick) to give a thin layer of solution and then heated to 250, 300, or 350 °C in a dry nitrogen atmosphere or an air atmosphere. The heating conditions of each sample are listed in Table 1. Polyimide layers from 2 to 30 μm thick were obtained in this process by optimizing the spinning speed. More details of these preparations are given in our previous papers.[6-8] This heat treatment (curing) promoted imidization and converted poly(amic acid)s into polyimides.

The 6FDA/TFDB polyimide block used for the optical loss measurement at 1.3 μm was prepared from a poly(amic acid) solution. It was cast on a silicon substrate and then heated to 350 °C in a dry nitrogen atmosphere. This thick polyimide layer was peeled from the silicon, and a polyimide block (24.7 mm long, 14.8 mm wide, and 2.1 mm thick) was cut out from it.

Results and Discussion

Optical Loss of Homopolyimides at 0.63 μm. The optical losses of several homopolyimides at 0.63 μm cured at 350 °C in a dry nitrogen atmosphere were measured. For example, a plot of the scattered light intensity against the propagation length of a 6FDA/TFDB film on a quartz glass substrate is shown in Figure 4. Although some data points are scattered by contamination absorbed during the poly(amic acid) preparation or polyimide film formation, the plot gives a straight line. The slope represents the optical loss of a 6FDA/TFDB polyimide film. The optical losses of several polyimides are listed in Table 2. 6FDA/TFDB has the lowest optical loss of 0.7 dB/cm of all polyimides. Compared with 6FDA/TFDB, either PMDA/TFDB prepared with PMDA instead of 6FDA or 6FDA/DMDB prepared with DMDB instead of TFDB has a higher optical loss of about 5 dB/cm, and PMDA/DMDB prepared with nonfluorinated PMDA and DMDB has the highest optical loss of 36 dB/cm. The optical loss of polyimide decreases when $-C(CF_3)_2-$ groups are introduced into the polyimide main chain, or trifluoromethyl ($-CF_3$) groups into the biphenyl group as the side chain. Reuter et al.[5] have reported that the optical loss of polyimides as waveguide materials decreases with increasing the number of $-C(CF_3)_2-$ groups. The relative optical loss of these polyimides agrees well with the coloration and light absorption in our previous paper.[6] St. Clair et al.[10,11] studied less-colored polyimide films to introduce $-C(CF_3)_2-$ groups to separate chromaphoric groups to reduce electronic interaction between color-causing centers, and to lower the color intensity of the resulting polymer.

We have not investigated the optical loss on the end group effect or molecular weight dependence in detail yet. However, the end group effect of the polyimides used in this study will be negligible, because their molecular weights are sufficiently high. The degree of polymerization can be expected from their highly intrinsic viscosities, 6FDA/TFDB of above 1.0 dL/g and PMDA/TFDB of above 1.7 dL/g.

Optical loss at 0.63 μm of Fluorinated Copolyimides. The optical loss at 0.63 μm of the copolyimides prepared from PMDA, 6FDA, and TFDB cured at 350 °C is shown in Figure 5. The optical loss of copolyimides falls between those of PMDA/TFDB (4.3 dB/cm) and 6FDA/TFDB (0.7 dB/cm) homopolyimides. The high optical loss with large PMDA/TFDB content results from the large light absorption due to electronic transfer. It decreases monotonically with increasing 6FDA/TFDB content and is not

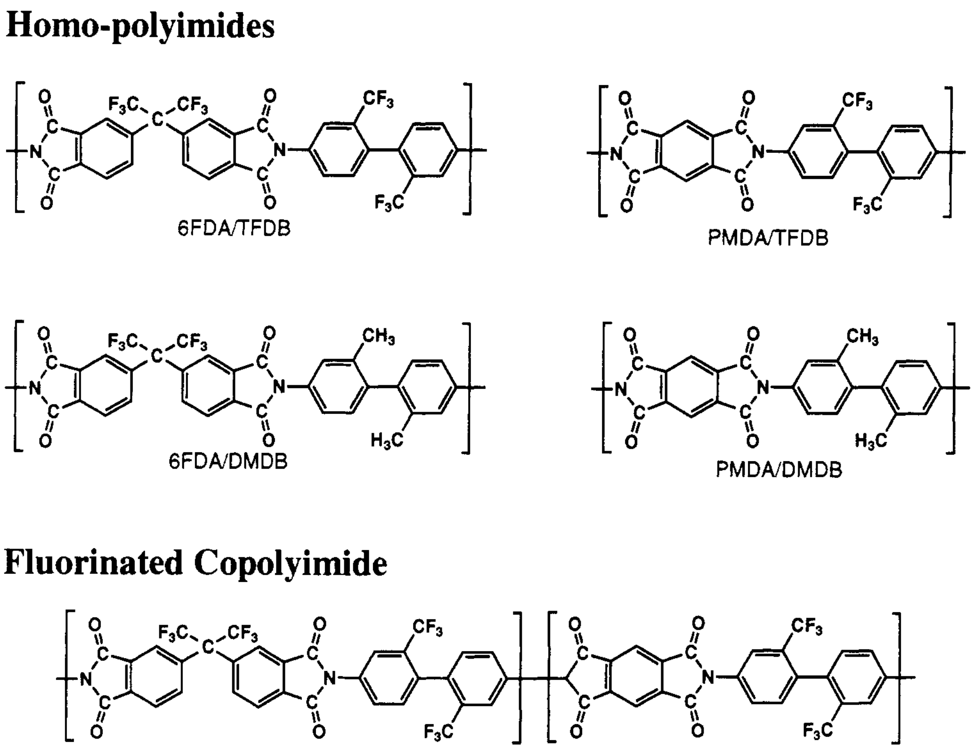

Figure 3. Structure of polyimides and a fluorinated copolyimide.

Table 1. Curing Conditions of Polyimides

max curing temp, °C	curing conditions
250	70 °C × 2 h + 160 °C × 1 h + 250 °C × 1 h
300	70 °C × 2 h + 160 °C × 1 h + 250 °C × 0.5 h + 300 °C × 1 h
350	70 °C × 2 h + 160 °C × 1 h + 250 °C × 0.5 h + 350 °C × 1 h

increased by copolymerization. This result indicates that these copolyimides are optically homogeneous, and copolymerization of PMDA/TFDB and 6FDA/TFDB does not increase the amount of light scattered at 0.63 μm. On the other hand, the polyimide blend film prepared from the mixture of 50 wt % 6FDA/TFDB and 50 wt % PMDA/TFDB poly(amic acid) solution could not be measured due to the large amount of scattered light caused by inhomogeneity of the polyimide blend.

Dependence of Optical Loss at 0.63 μm on Curing Conditions. As described in the Introduction, the optical loss at 0.63 μm of commercial fluorinated polyimides depends on the curing conditions, it increases with increasing curing temperature, except for 6FDA/TFDB, which has a constnat optical loss independent of curing temperature. The optical losses at 0.63 μm of 6FDA/TFDB and PMDA/TFDB cured at various maximum curing temperatures and in various atmospheres are shown in Figure 6. 6FDA/TFDB has a constant optical loss between 250 and 350 °C in a nitrogen atmosphere. PMDA/TFDB cured at a low temperature of 250 °C has rather a low optical loss of 1.3 dB/cm, but the loss increases with increasing maximum curing temperature. The UV–visible spectra of polyimides with different maximum cure temperatures in a nitrogen atmosphere are shown in Figure 7. All 6FDA/TFDB polyimides with different maximum cure temperatures have almost the same cut-off wavelength of about 400 nm; however, the cut-off wavelength of PMDA/TFDB is shifted to longer wavelengths with increasing the maximum cure temperature. Remarkable optical loss increase of PMDA/TFDB with increasing the maximum cure temperature is based on this cut-off wavelength shift. This shift is based on an electron transition increase, and it is caused by tight molecular packing due to high temperature curing. Compared with PMDA/TFDB, 6FDA/TFDB has less interaction between polyimide molecules do to the loose packing with the structure containing the $-C(CF_3)_2-$ group after high temperature curing. These results agree with the results for coloration of poly(amic acid) and the polyimide films. In 6FDA/TFDB, both the poly(amic acid) film just after solvent removal at 70 °C in a vacuum and the polyimide film after 350 °C curing are colorless. In PMDA/TFDB, however, the poly(amic acid) film before curing is colorless, and the polyimide film after curing is slight yellow. However, a similar increase in optical loss at 0.63 μm has

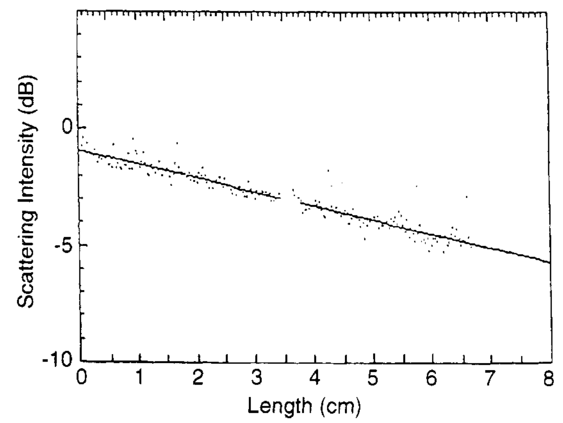

Figure 4. Dependence of scattered light intensity on the propagation length in a 6FDA/TFDB polyimide film. Light wavelength: 0.63 μm.

Table 2. Optical Loss of Various Polyimide Films at 0.63 μm

polyimide	optical loss, dB/cm	polyimide	optical loss, dB/cm
PMDA/DMDB	36.0	PMDA/TFDB	4.3
6FDA/DMDB	5.5	6FDA/TFDB	0.7

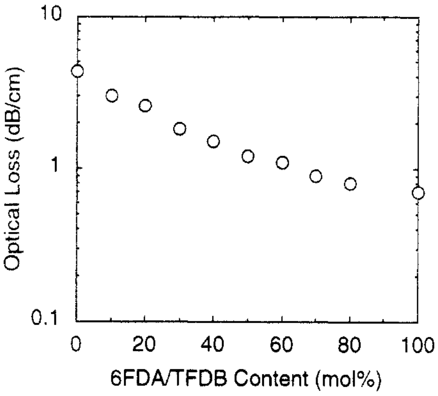

Figure 5. Optical loss of fluorinated copolyimides. Light wavelength: 0.63 μm.

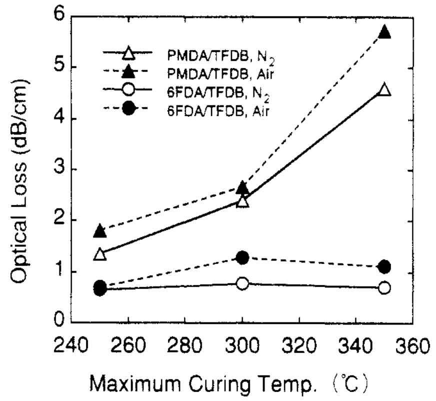

Figure 6. Dependence of optical loss on the maximum curing temperature. Light wavelength: 0.63 μm.

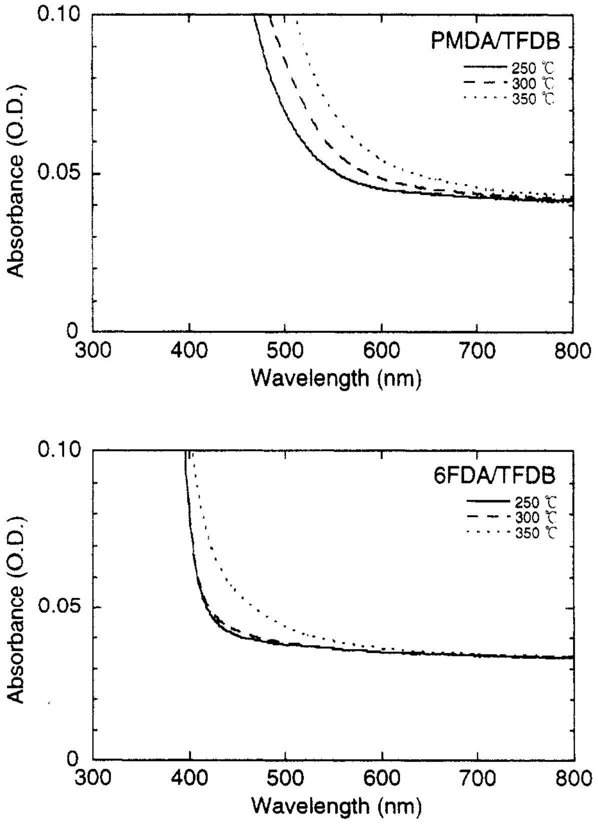

Figure 7. UV–visible spectra of polyimides with different cure temperatures.

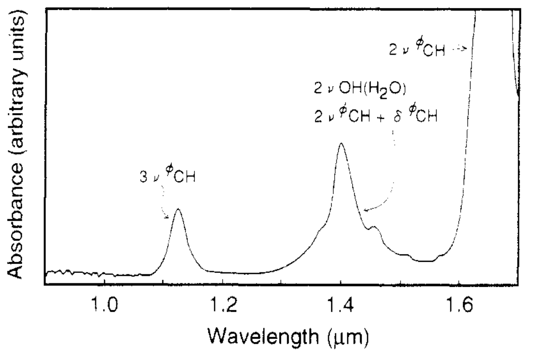

Figure 8. Light absorption spectrum of a 6FDA/TFDB polyimide film.

also been observed in other fluorinated polyimides. Reuter et al.[5] have reported that the polyimide containing two $-C(CF_3)_2-$ groups, 6FDA/3,3′-6F or 6FDA/4,4′-6F, prepared from 6FDA and 2,2-bis(3-aminophenyl)hexafluoropropane (3,3′-6F) or 2,2-bis(4-aminophenyl)hexafluoropropane (4,4′-6F) has an optical loss of less than 1 dB/cm after being cured at 200 °C, but it increases to around 3 dB/cm after curing at 300 °C. They have pointed out that the increase in optical loss is caused by the refractive index fluctuations producing scattering centers and by formation of charge transfer complexes leading to increased aborption with ordering. 6FDA/TFDB may have less ordering than 6FDA/3,3′-6F or 6FDA/4,4′-6F polyimides cured at high temperatures of above 300 °C.

For both 6FDA/TFDB and PMDA/TFDB, the optical losses cured in a nitrogen atmosphere are lower than those cured in an air atmosphere. X-ray photoelectron spectroscopy (XPS) was performed to investigate the influence of oxygen on polyimide molecules during curing. However, polyimides cured in an air atmosphere have the same XPS spectra (O 1s, C 1s, N 1s, and F 1s) as polyimides cured in a nitrogen atmosphere in both 6FDA/TFDB and PMDA/TFDB. The optical loss increase cured in an air atmosphere seems to be caused by slight oxidation degradation or producing radicals.

Dependence of Optical Transparency on Wavelength. The light absorption spectrum measured for the 6FDA/TFDB polyimide film is shown in Figure 8. The absorption in the visible region is caused by electron transition, but the absorption in the near-infrared region is mainly caused by the harmonics and their coupling of the stretching vibration of chemical bonds. Carbon–hydrogen (C–H) and oxygen–hydrogen (O–H) bonds strongly affect the absorption. There is an absorption peak due to the third harmonic of the stretching vibration of the C–H bond ($3\nu^{\phi}_{CH}$, 1.1 μm), a peak due to the combination of the second harmonic of the stretching vibration and deformation vibration of the C–H bond ($3\nu^{\phi}_{CH}$, $+\delta^{\phi}_{CH}$, 1.4 μm), and a peak due to the second harmonic of the stretching vibration of the C–H bond ($2\nu^{\phi}_{CH}$, 1.65 μm). However, it has small light absorpiton at the telecommunication wavelengths of 1.3 and 1.55 μm. Furthermore, the number of hydrogen atoms in a unit volume of 6FDA/TFDB is much lower than for other transparent polymers, PMMA, PS, and PC (Table 3), and these hydrogen atoms are only that bonded to benzene rings. The wavelength of 1.3 or 1.55 μm will be used for optical telecommunication, so 6FDA/TFDB is expected to be applicable to optoelectronic materials.

Optical Loss at 1.3 μm. The optical loss of a 6FDA/TFDB polyimide block at 1.3 μm was directly measured using samples with different light propagation lengths. Transmission (dB) obtained from the difference between output and input light intensities versus propagation legnth is plotted in Figure 9. The optical loss without connection loss is 0.3 dB/cm calculated from this slope.

Table 3. Hydrogen Content in a Unit Volume of Optical Polymers

polymer	no. of hydrogens [*a*] per monomer unit	density [*b*]	mol wt [*c*] per monomer unit	([*a*] × [*b*])/[*c*]	ratio
PMMA	8	1.19	100	0.0952	3.9
PS	8	1.04	104	0.0800	3.3
PC	14	1.20	254	0.0661	2.7
6FDA/TFDB	12	1.47	728	0.0242	1.0

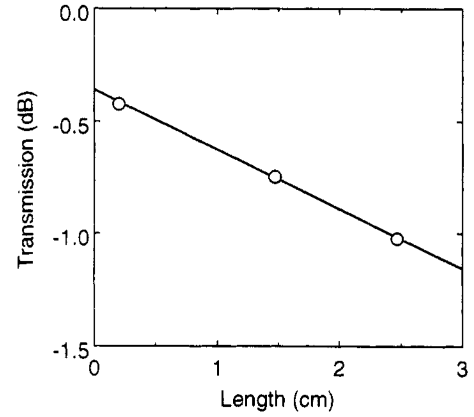

Figure 9. Transmission losses of a 6FDA/TFDB polyimide block.

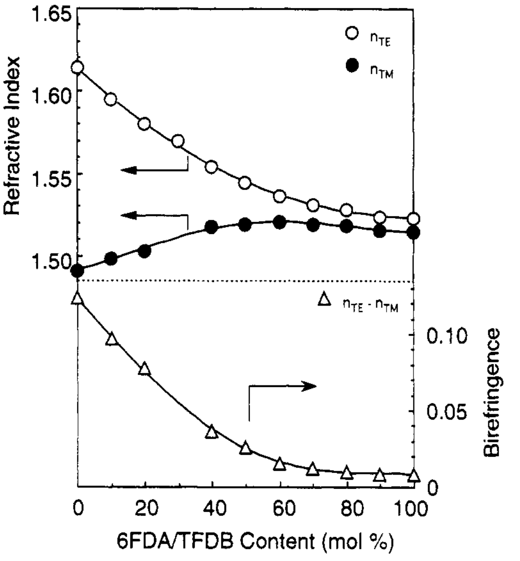

Figure 10. Refractive indices and birefringences of copolyimides. Light wavelength: 1.3 μm.

The previous optical loss measurement by using scattered light could not be could not be done at 1.3 μm because the scattered light intensity was very weak.

Besides the intrinsic material light absorption, there will be an optical loss of 0.3 dB/cm due to scattering by voids and fluctuation in the refrative index. The imidazation of poly(amic acid) to polyimide with the removal of the water may produce voids and refractive index fluctuations which will degrade transmission.

Refractive Index of the Copolyimides. The refractive indices n_{TE} and n_{TM} at 1.3 μm of 6FDA/TFDB, PMDA/TFDB, and their copolyimides cured at 350 °C on a silicon substrate in a dry nitrogen atmosphere are shown in Figure 10. The n_{TE} decreases with increasing 6FDA/TFDB content and can be controlled precisely between 1.523 and 1.614 by changing the 6FDA/TFDB content. In the high 6FDA/TFDB content region, the slopes of the curves are gentle, and more accurate refractive index control is achieved. The refractive index depends on molecular refraction and molecular volume and decreases with increasing fluorine content.[12] The n_{TE} decreases with increasing 6FDA/TFDB content, but it was a maximum at a 6FDA/TFDB content of 60 mol %. The n_{TM} can also be controlled between 1.514 and 1.521 by changing the 6FDA/TFDB content from 60 to 100 mol %. The n_{TE} is always higher than n_{TM} at the same 6FDA/TFDB content.

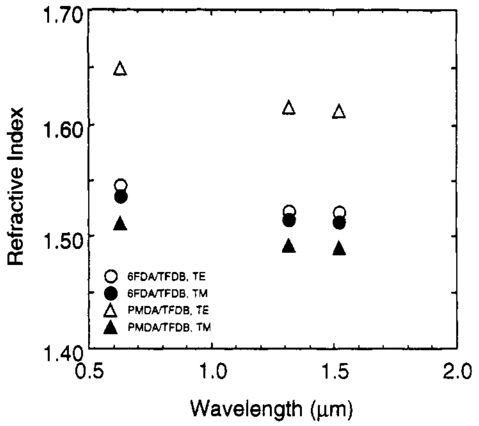

Figure 11. Dependence of refractive indices of 6FDA/TFDB and PMDA/TFDB polyimides on wavelength.

The difference between n_{TE} and n_{TM} is the birefringence; it is caused by the alignment of phenyl rings and imide rings during curing on a silicon substrate. The birefringence decreases with increasing 6FDA/TFDB content. PMDA/TFDB with the largest birefringence of 0.123 has a linear structure of phenyl rings and imide rings in the PMDA unit. They are located in the same plane, and it is easy to align PMDA/TFDB molecules. On the other hand, 6FDA/TFDB with the smallest birefringence of 0.008 has a bent structure of two phenyl rings linked by $-C(CF_3)_2-$ groups in the 6FDA unit. The two phenyl rings do not form a coplanar structure. The birefringence of the copolyimides decreases with increasing 6FDA/TFDB content and can be controlled between 0.008 and 0.123. There have been some reports on polyimides about the relationship between birefringence and chemical structure[5,13] and between birefringence and imidization conditions.[14,15] We are studying the relationship between birefringence and preparation conditions of the polyimide film (such as substrate and curing temperature). The results will be reported in other papers.

Dependence of Refractive Index on Wavelength. The dependence of refractive indices (n_{TE} and n_{TM}) on wavelength in 6FDA/TFDB and PMDA/TFDB polyimide films cured at 350 °C on a silicon substrate in a dry nitrogen atmosphere is shown in Figure 11. The n_{TE} and n_{TM} of both polyimides decrease monotonically with increasing wavelength. In the copolyimides, the relationship between refractive indices and 6FDA/TFDB content at 1.3 and 1.55 μm is similar to that at 0.63 μm shown in Figure 9. Precise refractive index control is achieved by copolymerization over a wide wavelength range from visible to near-infrared.

Conclusions

The optical loss and refractive indices of fluorinated polyimides, 6FDA/TFDB, PMDA/TFDB, and their copolyimides were measured at the visible and near-infrared wavelengths. The optical losses at 0.63 μm of fluorinated polyimides cured at 350 °C are 0.7 (6FDA/TFDB) and 4.3 dB/cm (PMDA/TFDB). The copolyimides are optically homogeneous, and their optical losses are not increased by copolymerization. The low optical loss of 6FDA/TFDB is constant independent of the maximum curing temperature. 6FDA/TFDB has a low optical loss of 0.3 dB/cm at a optical telecommunication wavelength of 1.3 μm. These polyimides and copolyimides cured on a silicon substrate have two different refractive indices, n_{TE} and n_{TM}. The n_{TE} of the copolyimides can be controlled between 1.523 and 1.614 by changing the 6FDA/TFDB content. The n_{TM} can also be controlled between 1.514 and 1.521. The low optical loss, thermal stability of the optical loss, and precise refractive index control are very important characteristics for optoelectronic components.

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References and Notes

(1) Izawa, T. ECOC-IOOC 91, 8th International Conference on Integrated Optics and Optical Fibre Communication IOOC '91, 1991, Web6-1.

(2) Schriever, R.; Franke, H.; Festl, H. G.; Kratzig, E. *Polymer* **1985**, *26*, 1426.

(3) Kurokawa, T.; Takato, N.; Katayama, T. *Appl. Opt.* **1980**, *19*, 3124.

(4) Sullivan, C. T. *SPIE Optoelectronic Materials, Devices Packaging, and Interconnects II* **1988**, *994*, 92.

(5) Reuter, R.; Franke, H.; Feger, C. *Appl. Opt.* **1988**, *27* (21), 4565.

(6) Matsuura, T.; Hasuda, Y.; Nishi, S.; Yamada, N. *Macromolecules* **1991**, *24*, 5001.

(7) Matsuura, T.; Ishizawa, M.; Hasuda, Y.; Nishi, S. *Macromolecules* **1992**, *25*, 3540.

(8) Matsuura, T.; Yamada, N.; Nishi, S.; Hasuda, Y. *Macromolecules* **1993**, *26*, 419.

(9) Okamura, Y.; Yoshinaka, S.; Yamamoto, S. *Appl. Opt.* **1983**, *22* (23), 3892.

(10) St. Clair, A. K.; St. Clair, T. L.; Shevket, K. I. *ACS Polym. Mater. Sci. Eng.* **1984**, *51*, 62.

(11) St. Clair, A. K.; St. Clair, T. L.; Slemp, W. S. *Proceeding of the Second International Conference on Polyimides, Recent Advances in Polyimide Science and Technology*; Weber, W., Gupta, M., Eds.; Society of Plastics Engineers: New York, 1987; p 16.

(12) Nakamura, K.; Murata, N.; Maruno, T. *Rev. Electr. Commun. Lab.* **1989**, *37* (2), 127.

(13) Prest, W. M.; Luca, D. J. *J. Appl. Phys.* **1979**, *50* (10), 6067.

(14) Russell, T. P.; Gugger, H.; Swalen, J. D. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1745.

(15) Nakagawa, K. *J. Appl. Polym. Sci.* **1990**, *41*, 2049.