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Effects of Molecular Structures on the Near-Infrared Optical Properties of Polyimide Derivatives and Their Corresponding Optical Waveguides

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ABSTRACT: Polyimides have been demonstrated to be a potential candidate as optical waveguide materials. Previous studies were focusing on the reducing the optical loss by decreasing the C−H bonding density of the molecular structure. The tuning of the near-infrared (NIR) overtone absorption position from the polarizability of the bridge group in polyimides is rarely studied. In this study, a series of polyimides prepared from pyromellitic dianhydride (PMDA) and diamines with various bridge groups were used to investigate the structure−NIR optical property relationships. The bridge groups include $-SO_2-$, $-S-$, $-O-$, and $-CH_2-$. Both the experimental and ab initio calculation on the model compounds and polyimide derivatives revealed that the stronger the electron-withdrawing ability of the neighboring bridge group, the shorter the aromatic C−H bond length. This results in the shifting of the overtone frequencies of the C−H bond to higher frequencies. Such bridge effects played an important role in the optical loss of the corresponding polyimide waveguides. It was found that the optical loss was resulted from both the C−H bonding density and the shifting of the overtone absorption by the bridge group. It indicates that tuning of NIR optical loss from the molecular structures of polyimides could be achieved.

Introduction

Polymers have emerged as a new class of optical waveguide materials because of the advantages of the structural flexibility, low cost, easy processability, and integration.[1−3] For polymers to be used for optical waveguides, the following properties should be considered, such as optical loss, refractive index, birefringence, thermal stability, and mechanical properties. Several polymers had been tested as optical waveguide materials, including acrylic polymers, polyimides, perfluorocyclobutetene, polycarbonates, fluorinated poly(vinyl ether), epoxy, polysiloxanes, and hyperbranched polymers.[1−5]

Among the polymers for optical waveguide applications, polyimides are one of the most potential candidates because of their excellent thermal stability and mechanical properties. The optical loss of the polyimide-based waveguides is resulted mostly from the C−H higher harmonic (overtone) vibrational absorption loss; scattering loss from the ordering structure, pinholes, or voids; and electronic absorption loss from a charge-transfer complex. The reduction of the C−H overtone vibrational absorption loss by the chemical substitution of halogen groups has been widely studied by several groups.[1−3,6−8] The scattering loss could be significantly reduced by adjusting curing conditions. Kowalczyk et al.[9] studied the loss mechanism in fluorinated polyimide waveguides. They concluded that the primary waveguide loss mechanism was from absorption, not scattering. The electronic absorption loss from a charge-transfer complex might not be important in the near-infrared (NIR) region.

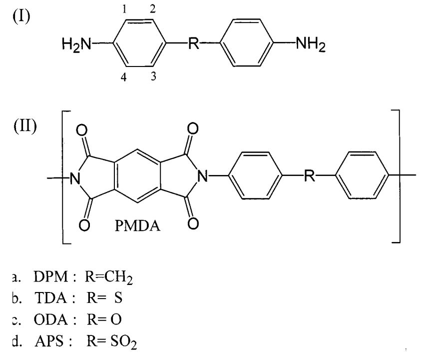

Figure 1. Chemical structures of the studied diamines and polyimides.

Although the optical loss reduction of polymer optical waveguides by halogenation has been addressed by several reports,[1−3,6−8] the tuning of the C−H NIR overtone absorption position from the polarizability of the bridge or side group in polyimides is rarely studied. For simple compounds of halogenated benzenes, the C−H NIR overtone absorption band could be tuned by the substitution of the electron-withdrawing groups, such as fluorine.[10] McCulloch et al.[8] studied several organic model solvents and showed that there is no direct relationship between the optical loss of the deuterated or fluorinated solvents and their corresponding C−H number density. The variation of the overtone absorption by polarized chemical substitution might account for the above deviation. If the C−H NIR absorption band could be tuned by chemical substitution, the optical window for optical communication was shifted. This would be very important for controlling the optical loss of polymer optical waveguides besides the current approach of reducing the C−H number density.

In this study, a series of polyimides from pyromellitic dianhydride (PMDA) and bridged diphenyl diamines (**I**) were prepared for investigating the structure−NIR optical property relationships, as shown in Figure 1. The bridge groups include $-SO_2-$, $-S-$, $-O-$, and $-CH_2-$. The NIR absorption of the studied diamines (**I**, in Figure 1) was studied both experimentally and theoretically in order to understand the intrinsic NIR absorption band of the corresponding polyimides. The theoretical ap-

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proach was based on the ab initio calculations and Morse potential function. The effect of the polarizability of the bridged group on the NIR absorption band was analyzed. Optical planar waveguides were prepared from the synthesized polyimides using silicon dioxide and 3-aminopropyltrimethoxysilane (APrTMOS) as the cladding and adhesion promoter, respectively. The optical loss of the prepared polyimide waveguide was measured by a cutback method at 1310 nm. The optical loss of the prepared waveguide was analyzed and correlated with the NIR absorption of the studied polyimides.

Experimental Section

Materials. Pyromellitic dianhydride (PMDA, Acros, 99%), 4,4′-oxydianiline (ODA, Acros, 99%), 4,4′-diaminodiphenylmethane (DPM, TCI, 98%+), 4,4′-thiodianiline (TDA, Aldrich, 98%), and 4-aminophenyl sulfone (APS, Aldrich, 98%) were purchased and dried under reduced pressure at 30 °C for 24 h prior to use. Anhydrous *N*,*N*-dimethylacetamide (DMAc, Aldrich, 99%), 3-aminopropyltrimethoxysilane (APrTMOS, Acros, 99%), and deuterated dimethyl sulfoxide (DMSO-d_6, Acros, 99+ atom % D) were used as received.

Preparation of Poly(amic acid)s (PAAs). The synthesis of poly(amic acid)s (PAA) was followed by a similar method reported in the literature.[11] The preparation of the amic acid of PMDA/ODA (**IIc** in Figure 1) was used as an example. 1189.2 mg of ODA (6 mmol) was dissolved into 14154.8 mg of dry DMAc with vigorous stirring under nitrogen. After the diamine dissolved completely, 1308.7 mg of PMDA (6 mmol) was slowly added into the solution over a period of 20 min. The solution was stirred and allowed to react at room temperature over 24 h to give a viscous and homogeneous PAA solution. The molecular weight distributions M_w (M_n) of the prepared PAA characterized by GPC were 26 310 (16 079), 25 542 (14 127), 31 477 (18 721), and 15 660 (9954) for PMDA/DPM (**IIa**), PMDA/TDA (**IIb**), PMDA/ODA (**IIc**), and PMDA/APS (**IId**), respectively.

Preparation of Polyimide (PI) Thin Films. 0.1% (v/v) of APrTMOS aqueous solution used as an adhesion promoter was spin-coated on a double-side polished silicon wafer at 3000 rpm for 10 s and cured at 105 °C for 90 s. 15 wt % of the prepared PAA solution was filtered by a 0.2 μm filter prior to use and then spin-coated on top of the APrTMOS film at 3000 rpm for 20 s. The PAA film was then cured in a nitrogen-purged furnace box through the following conditions: 70, 150, and 250 °C for 1 h and then 300 °C for another 2 h. The cured polyimide thin film was uniform and had the thickness of several micrometers for the FTIR structural characterization.

For the optical characterization of the NIR absorption spectra, polyimides with a film thickness more than 50 μm were required. In this case, 30 wt % of the prepared PAA solution was poured to a Teflon tray, followed by a similar curing process for several days to obtain a free-standing PI film.

Preparation of Optical Planar Waveguides. The silicon dioxide cladding layer was prepared as below. A silicon wafer was cleaned and thermally oxidized in a circular furnace purged with water vapor and nitrogen at 1200 °C for 11 h to give a uniform silicon dioxide film of 1.5 μm on the wafer surface. The sample for the optical propagation loss measurement was prepared from 15 wt % of the prepared PAA solution on top of the above silicon dioxide. 0.1% (v/v) of APrTMOS was used as the adhesion promoter before the polyimide film coated. In the prepared waveguides, the polyimide and silicon oxide were used as the guiding and cladding layers, respectively.

Characterization. Spectra of the studied diamines were recorded by dissolving diamines into DMSO-d_6 (1 wt %) with a dismountable liquid cell (0.1 mm spacing, KBr window) for the mid-IR region (Jasco FT/IR-410) and a set of quartz cells (5 mm spacing) for the NIR region (Jasco V570). Infrared spectra of the prepared polyimide films were recorded by a DIGILAB FTS3500GX spectrometer from 400 to 4000 cm^{-1} at a resolution of 1 cm^{-1}. The NIR absorption spectra for the prepared polyimide free-standing films were also recorded by a DIGILAB FTS3500GX from 4000 to 10 000 cm^{-1} at a resolution of 1 cm^{-1} with 1024 scans. The NIR absorptions of the prepared polyimide films were normalized by dividing with their film thickness.

The molecular weights of PAAs were characterized by a gel permeation chromatograph (GPC) equipped with PLgel 5 μm MIXED-C and D columns and a RI detector. The refractive index and film thickness of the prepared polyimde film were measured by a prism coupler Metricon model 2010 at the wavelength of 1319 nm. An atomic force microscope (Digital Instrument, Inc., model DI 5000 AFM) was used to probe the surface morphology of the coated films. The root-mean-square roughness (R_q) and average roughness (R_a) of the studied films were determined. The optical propagation losses at 1310 nm were measured by a cutback method with a module set up the same as in the previous work.[5d]

Theoretical Analysis on the Bond Length and Harmonic Frequencies of the Studied Diamines. The position of the C−H harmonic vibration absorption bands of the studied diamines could be estimated by the following analysis. According to the Morse potential theory,[12] the vibrational energies of isolated oscillators can be expressed as

$$\frac{E_n}{hc} = \left(n+\frac{1}{2}\right)\omega_e - \left(n+\frac{1}{2}\right)^2 \frac{{\omega_e}^2}{4D_e} = \left(n+\frac{1}{2}\right)\omega_e - \left(n+\frac{1}{2}\right)^2 x_e\omega_e \tag{1}$$

The vibrational frequencies are then obtained from eq 1

$$\nu_{n\leftarrow 0} = E_n - E_0 = \omega_e - n(n+1)x_e\omega_e \tag{2}$$

where n, ω_e, and x_e are the vibrational quantum number, harmonic frequency, and anharmonicity, respectively. $n = 1$, 2, and 3 represent the vibration number of the fundamental frequency and the first and second overtone, respectively. The anharmonicity, x_e, can be represented as the following equation

$$x_e = \frac{\omega_e}{4D_e} \tag{3}$$

where D_e is the equilibrium dissociation energy of the chemical bond, which is obtained from

$$D_e = D_0 + \frac{1}{2}\omega_e - \frac{1}{4}x_e\omega_e \tag{4}$$

For the case of the C−H bond, if the ground-state dissociation energy D_0 and the equilibrium harmonic frequency ω_e of the C−H oscillators could be obtained, $\nu_{n\leftarrow 0}$ and x_e could then be determined from eqs 2−4. The D_0 of the C−H bond could be obtained by the correlation of $D_0 = -1311.9R_e + 1523.4$,[13] where the units of D_0 and R_e are cm^{-1} and pm, respectively. The equilibrium bond length R_e and harmonic frequencies ω_e of the aromatic C−H bonds (1−4 in structure **I** of Figure 1) of the studied diamines were calculated first by ab initio calculations. All the geometries of the studied diamines were optimized to the local minima which were confirmed by the frequency calculations at the Hartree−Fock HF/6-31G* level of theory and were performed on Gaussian98.[14] The average absolute error of the calculated bond length in comparison with the experiment was examined to be 1.4 pm for the AH oscillators (where A is atom other than hydrogen).[15] However, it could be used to predict the correct trend of variations for similar structures at even smaller basis set.[10,13] To check the validation of our HF/6-31G* calculation, we checked the C−H bond length of benzene with that reported in the literature. The obtained C−H bond length of the benzene was 1.076 Å, which was the same as that reported in the literature.[16]

Results and Discussion

Effects of the Bridge Group of the Studied Diamines on Bond Length and Overtone Fre-

Table 1. Calculated Bond Lengths (in pm) of the Studied Diamines[a]

	C^1−H	C^2−H	C^3−H	C^4−H	R_e[b]
DPM (**Ia**)	107.68	107.63	107.68	107.67	107.66
TDA (**Ib**)	107.64	107.47	107.46	107.64	107.55
ODA (**Ic**)	107.64	107.44	107.45	107.64	107.54
APS (**Id**)	107.57	107.33	107.33	107.57	107.45

[a] Numbering of carbon is given in **I** of Figure 1. [b] R_e was obtained from the arithmetic average of C^1−H, C^2−H, C^3−H, and C^4−H.

quency. The ab initio calculation bond lengths of the studied diamines at the gas phase are shown in Table 1. The order of the average C−H bond length (1−4 in the **I** of Figure 1) for the studied diamines is DPM (**Ia**) > TDA (**Ib**) > ODA (**Ic**) > APS (**Id**). The electron-withdrawing strength of the bridged group on the C−H bond of the phenylene ring in Figure 1 is in the order of $-SO_2-$ > −O− > −S− > $-CH_2-$.[17] This result suggests that the stronger the electron-withdrawing bridged group neighboring to the C−H bond, the shorter the C−H bond length. The explanation on the above relationship is as below. The electron density is drawn from the C−H bond of the aromatic ring by the neighboring electron-withdrawing group. Thus, the hydrogen atom has to move close to the carbon in order to share the remaining electrons and results in a decrease of the C−H bond length. A similar conclusion has been obtained in the literature[17] for several hydrocarbons. The sulfone group is realized to be a strong electron-withdrawing group. However, the ether (or sulfur) group is often considered to be an electron-donating group. The electronic effect of the ether group is generally considered by two aspects: one is the resonance donating effect, where the unpaired electrons partially participate in the resonance of aromatic π electrons; the other one is the inductively withdrawing effect, where the electronegative oxygen inductively polarized electrons distribution through the σ skeleton. The obtained order in the phenylene C−H bond length of the studied diamines suggests that the inductive effect of the neighboring bridge groups could be dominant. This could be realized that the σ_{2sp^21s} bonding of the aromatic C−H bond might be relatively insensitive to the resonant electron-donating effect participated to π electrons. Therefore, the inductively electron-withdrawing effect of the bridged group is dominated in the studied case.

The calculated overtone frequencies, $\nu_{2\leftarrow0}$ and $\nu_{3\leftarrow0}$, in the C−H (1−4 in **I** of Figure 1) of the studied diamines by HF/6-31G* are shown in Table 2. The obtained vibrational frequencies, $\nu_{1\leftarrow0}$, $\nu_{2\leftarrow0}$, and $\nu_{3\leftarrow0}$, of the studied diamines appear in the order of APS (**Id**) > ODA (**Ic**) > TDA (**Ib**) > DPM (**Ia**). It is in the same order as the electron-withdrawing ability of the bridged group but in the reverse order as the C−H bond length. The obtained relationship between bond length and vibrational frequency is the same as the literature based on experimentally or the ab initio theoretically results[10,13,18−20] for many hydrocarbons and benzene derivatives. Figure 2 shows the NIR absorption spectra of the studied diamines in deuterated DMSO-d_6 in the wavelength range 1640−1720 nm (5800−6100 cm^{-1}). The peak of the absorption band corresponds to the $\nu_{2\leftarrow0}$ of the C−H bond of the phenylene ring, **I** of Figure 1. The $\nu_{2\leftarrow0}$ of DPM (**Ia**), TDA (**Ib**), ODA (**Ic**), and APS (**Id**) obtained from this figure is 5906, 5942, 5960, and 5971 cm^{-1}, respectively. The order of the overtone frequency is the same as that from theoretical result. A similar conclusion is obtained in the relationship between the bridged group and the $\nu_{3\leftarrow0}$ of the C−H bond, as shown in Figure 3 and Table 2. The difference between the values of the HF/6-31G* calculation and experimental overtone frequencies comes from the systematic errors of the Hartree−Fock approaches and the gas-phase theoretical results. Note that the NIR spectra of the studied diamines were recorded at liquid phase. However, the trend in the relationship between the electron-withdrawing strength of the bridge group and the overtone frequency is the same.

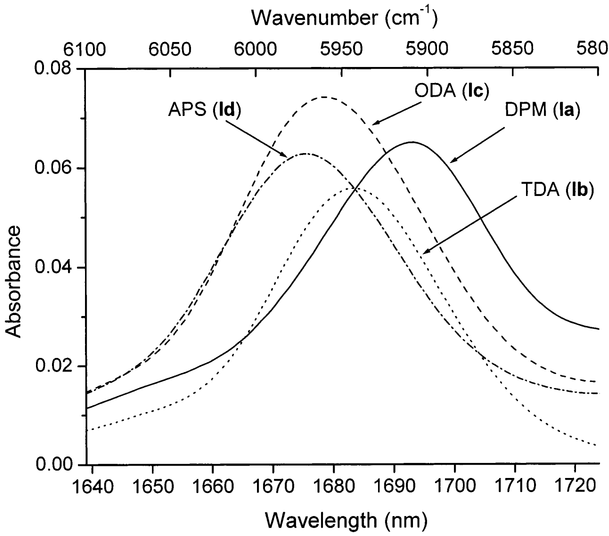

Figure 2. First overtone spectra of the C−H bond on the phenylene ring of the studied diamines: DPM (**Ia**), TDA (**Ib**), ODA (**Ic**), and APS (**Id**).

Optical Properties of the Prepared Polyimide Films. The NIR normalized absorption spectra of the prepared polyimide films, **IIa**−**IId**, in the range 1000−1800 nm are shown in Figure 4. There are three absorption bands shown in Figure 4: (a) the C−H stretching first overtone band around 1600−1800 nm, (b) the weaker combination band of the C−H stretching and deformation around 1330−1560 nm, and (c) the C−H stretching second overtone band around 1110−1200 nm. These three C−H vibration absorption bands are similar to those reported in the literature.[10] The

Table 2. Comparison of Calculated Frequencies and Experimental Results of the Studied Diamines and Polyimides

	diamine at HF/6-31G* (calcd)				diamine (exp)[a]				polyimide (exp)[b]			
	$\nu_{1\leftarrow0}$ (cm^{-1})	$\nu_{2\leftarrow0}$ (cm^{-1})	$\nu_{3\leftarrow0}$ (cm^{-1})	x_e	$\nu_{1\leftarrow0}$ (cm^{-1})	$\nu_{2\leftarrow0}$ (cm^{-1})	$\nu_{3\leftarrow0}$ (cm^{-1})	x_e	$\nu_{1\leftarrow0}$ (cm^{-1})	$\nu_{2\leftarrow0}$ (cm^{-1})	$\nu_{3\leftarrow0}$ (cm^{-1})	x_e
DPM (**Ia**)	3223	6315	9277	0.0195	3032	5906	8691	0.025	3076	5973	8756	0.027
TDA (**Ib**)	3234	6338	9314	0.0192	3039	5942	8741	0.021	3076	5977	8809	0.027
ODA (**Ic**)	3235	6341	9319	0.0191	3046	5960	8746	0.021	3080	6005	8851	0.024
APS (**Id**)	3240	6352	9337	0.0189	3076	5971	8768	0.028	3083	6023	8899	0.022

[a] Solution data in DMSO-d_6. [b] Film result.

Table 3. Properties of the Prepared Polyimdes and Their Corresponding Waveguides

	thickness (μm)	R_q (nm)	R_a (nm)	refractive index, n	R_{LL}/V_w (cm^{-3})^a	calcd C−H number density (10^{22}/cm^3)	optical loss (dB/cm)
silicon oxide	1.50			1.4457			
PMDA/DPM (**IIa**)	2.54	0.46	0.38	1.6748	0.338 41	2.64	2.36
PMDA/TDA (**IIb**)	2.28	0.62	0.45	1.6892	0.346 72	2.18	2.19
PMDA/ODA (**IIc**)	2.66	0.36	0.27	1.6774	0.338 45	2.26	2.61
PMDA/APS (**IId**)	2.41	0.28	0.22	1.6938	0.350 47	2.12	1.78

[a] R_{LL} = Lorentz and Lorenz molar refraction [mol^{-1}]; V_w = van der Waals molar volume [cm^3/mol].

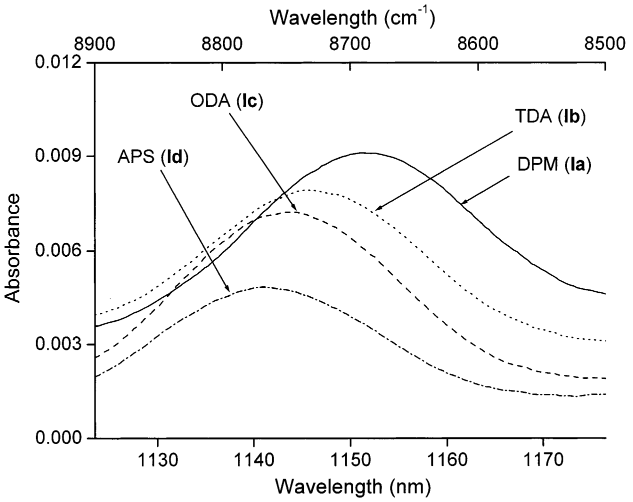

Figure 3. Second overtone spectra of the C−H bond on the phenylene ring of the studied diamines: DPM (**Ia**), TDA (**Ib**), ODA (**Ic**), and APS (**Id**).

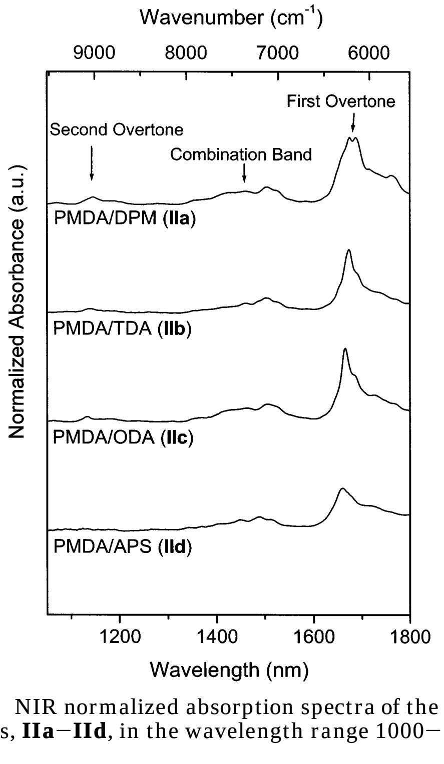

Figure 4. NIR normalized absorption spectra of the prepared polyimides, **IIa**−**IId**, in the wavelength range 1000−1800 nm.

corresponding peak positions of the overtone frequencies $\nu_{2\leftarrow0}$ and $\nu_{3\leftarrow0}$ from Figure 4 are listed in Table 3. The order of the peak positions of both the $\nu_{2\leftarrow0}$ and $\nu_{3\leftarrow0}$ is the same: PMDA/APS (**IId**) > PMDA/ODA (**IIc**) > PMDA/DPM (**IIb**) > PMDA/TDA (**IIa**). It is the same as those of the studied diamines. This concludes the importance of the electron-withdrawing ability of the bridged group on the NIR overtone absorption bands.

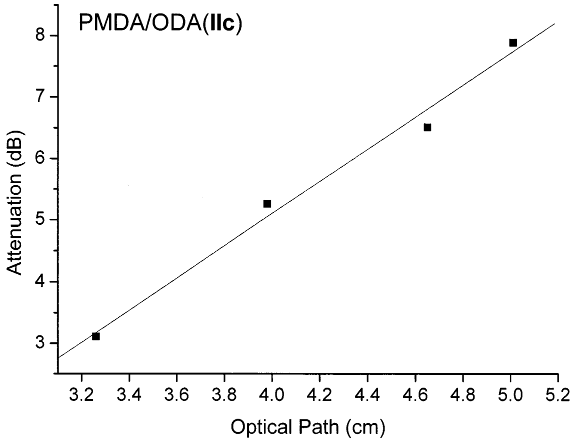

Figure 5. Illustration of optical loss of the PMDA/ODA (**IIc**)-based waveguide measured by the cutback method.

The refractive index and film thickness of the prepared polyimide film are listed in Table 3. The obtained refractive indices of the polyimide films were in the range 1.67−1.69, which was larger than that of the silicon oxide. Thus, the polyimide and thermal oxide could be used as the core and cladding of an optical waveguide. According to the Lorentz and Lorenz equation, the refractive index is generally proportional to the ratio of the molar refraction (R_{LL}) to the molar volume (V_w).[21] As shown in Table 3, the order of the R_{LL}/V_w is PMDA/APS (**IId**) > PMDA/TDA (**IIb**) > PMDA/ODA (**IIc**) > PMDA/DPM (**IIa**). This explains the order of the refractive indices of the studied polyimides.

Properties of the Planar Optical Waveguides from the Prepared Polyimides. The film thickness and surface roughness of the prepared polyimide film are in the ranges 2.28−2.66 μm and 0.22−0.62 nm, respectively, as shown in Table 3. The relatively small surface roughness in comparison with the film thickness suggests the insignificant surface roughness for scattering loss. The optical loss of the prepared waveguide at the wavelength of 1310 nm was measured by a cutback method. Figure 5 shows the relationship between the attenuation of the PMDA/ODA (**IIc**)-based waveguide with the waveguide length. The linear relationship between the attenuation and optical path indicates the accuracy of this measurement. The determined optical losses of the prepared waveguides at 1310 nm from the cutback method are listed in Table 3. The order of the optical loss on the prepared polyimide waveguide is PMDA/APS (1.78 dB/cm) < PMDA/TDA (2.19 dB/cm) < PMDA/DPM (2.36 dB/cm) < PMDA/ODA (2.61 dB/cm). Since the processing conditions for the various optical waveguides were the same and the insignificant surface roughness from the AFM result, the volume scattering loss could be neglect. Therefore, the order of the obtained optical loss is probably contributed from the following two factors: the C−H bonding density and the position of the C−H overtone

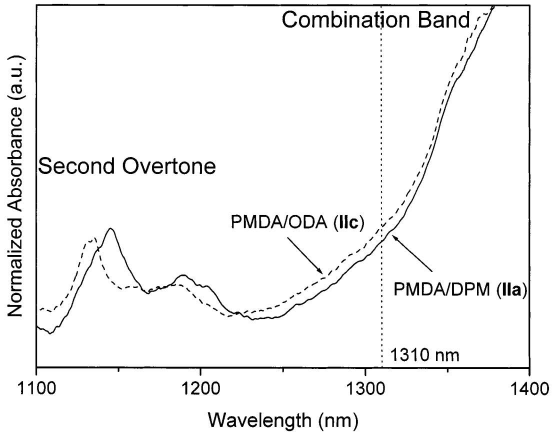

Figure 6. Band shifting on the normalized optical losses of PMDA/DPM (**IIa**) and PMDA/ODA (**IIc**) at the wavelength of 1310 nm.

bands. The C−H number densities of the prepared polyimides were evaluated by the group contribution additive method and listed in Table 3. The calculated C−H number densities of the prepared polyimides **IIa**−**IId** are 2.64, 2.18, 2.26, and 2.12 (units: 10^{22}/cm^3), respectively. The optical loss shown in Table 3 is roughly proportional to the C−H number density except for the case of the PMDA/DPM (**IIa**)-based optical waveguide. The relationship of the C−H number density and the optical loss of the **IIa** is different from the general trend reported in the literature.[1,2] Figure 6 shows the NIR normalized absorption spectra of the PMDA/DPM (**IIa**) and PMDA/ODA (**IIc**) film in the wavelength 1100−1500 nm. The optical loss at the wavelength of 1310 nm is primarily contributed by the combination band of the C−H stretching and deformation near 1400 nm but not the C−H second overtone band. As shown in Figure 6, the shifting of the combination band from the 1310 nm is more significant for the case of the PMDA/DPM (**IIa**) film than that of the PMDA/ODA (**IIc**) film. Thus, the lower optical loss of the PMDA/DPM (**IIa**) planar waveguide than that of the PMDA/ODA (**IIc**) is due to the shifting of the NIR absorption spectrum by the bridge group although the former has a higher C−H number density. The result suggests that the C−H bonding density and the position of the overtone vibrational band are both required for designing a new low loss waveguide materials.

Conclusions

In this study, a series of polyimides with various electron-withdrawing bridge groups of $-SO_2-$, $-S-$, $-O-$, and $-CH_2-$ were prepared to investigate the structure−NIR optical property relationships. Both the experimental and ab initio calculation on the model compounds and polyimide derivatives revealed that the stronger the electron-withdrawing ability of the neighboring bridge group, the shorter the aromatic C−H bond length. This results in the shifting of the fundamental and overtone frequencies of the C−H bond to higher frequencies. Such bridge effects play an important role on the optical loss of the corresponding polyimide waveguides. It was found that the optical loss was resulted from both the C−H bonding density and the shifting of the overtone absorption by the bridge group. Thus, tuning of optical loss could be achieved from the molecular structure of polyimides for optical waveguide applications.

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