Recent Progress on Polymer Waveguide Materials

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Polymer waveguides have a potential of achieving the economic requirement for low priced optical devices and of applying novel active devices. The developments of the polymer waveguide materials and their applications have been investigated since 1990s. The remarkable progress on the polymer waveguides is expected to realize acceptance of the polymer devices in the optical communication networks. We review the recent progress on the polymer waveguide materials in addition to the characteristics required for the waveguides.

Keywords: Optical waveguides, Polymer materials, Waveguide fabrication

1. Introduction
Recent rapid spread of personal computers and the Internet has accelerated expansion of information traffic. The increase of the information traffic which is so-called the Information Technology Revolution requires to construct optical access network systems in which optical fibers are installed from a central office to every home, “Fiber-To-The-Home (FTTH)”. In order to spread the FTTH network, a drastic cost reduction of optical components used in the network is required. For the cost reduction, optical devices based on planar lightguide circuits (PLCs) with optical waveguides are key components. However, the silica-based waveguides for the PLC platform are fabricated through a tedious and time-consuming process such as chemical vapor deposition (CVD) or flame hydrogen deposition (FHD) which requires high temperature treatment over 1,000°C [1]. Considerable interests have been focused on polymer waveguides because of having the advantages of low temperature process for fabrication, ease of control on optical and mechanical properties, and mass production possibility. In addition to those, the wet coating process of the polymer waveguides allows to fabricate at large areas, which will be utilized for the application of the optical interconnections [2]. Furthermore, the polymer materials can provide novel functionalities such as thermo-optic (TO) and electro-optic (EO) properties and have potentials of high-speed optical switches and modulators with a low driving voltage. In recent years, optical applications using other optical functions such as gratings formed optically have been also demonstrated [3]. Thus, the polymers can be integrated on the same chip and offer a versatile platform by adding various functionalities.

In this paper, we review polymer waveguide materials, which were reported to be utilized for single-mode optical components for optical telecommunication use, and their fabrication methods. Several required characteristics which are important for designing waveguides are also described.

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2. Characteristics Required for Waveguide Materials

Low insertion loss is the most important characteristic for single-mode optical components, so that absorption of the materials should be as small as possible in the near-infrared (near-IR) region from 1.3 μm to 1.6 μm. A precious control of refractive indices for the waveguide materials is also an essential factor to affect the insertion loss. High heat resistance is required for optical network units (ONUs) or transceiver modules [4] on which photo-diodes and laser-diodes are mounted, because of passing solder reflowing process of electric parts[5]. Moreover, the optical properties including the insertion loss are required to be maintained under harsh environments.

2-1. Refractive Index

An optical waveguide consists of a central core surrounded by a cladding layer, of which refractive index is lower than that of the core. The optical characteristics of the waveguides are affected by refractive indices of the core and the cladding. The number of modes is determined by the core size, Δn which represents the relative index difference between core and cladding, (n_{core}-n_{clad}/n_{core}), and the wavelength of the light [6]. The Δn of the waveguides should be controlled to be about 0.3% at the core diameter of 7 μm to support a single-mode of the transmission light for long distance communications. The waveguides operate with multi-mode which propagates light in many paths if Δn of the waveguides is larger. The existence of many different paths causes “smearing” of signal pulses. On the other hand, smaller Δn of the waveguides makes the light difficult to propagate in the core. The value of refractive index also affects the coupling loss between the single-mode fiber and the waveguide. The refractive index of core close to that of the fiber prevents the coupling loss from increasing, because mismatch of the refractive index between them causes an increase of reflection at the interface. The refractive index at 1.55 μm wavelength is therefore desirable to be 1.45 which is same as the index of the common single-mode fibers. However, the increase in the coupling loss caused by the mismatch can be improved by using UV curable adhesive of which the refractive index is in between the fiber and waveguide. Refractive indices of the waveguide materials relate to both molar volume, and polarizability molar refraction.

The refractive index can be estimated by these factors and is controlled by choosing organic substituents in the materials. In general, the polymer materials show relatively higher temperature dependence of refractive index compared to that of inorganic materials. Several optical devices which utilize higher thermal-optic (TO) effect (dn/dT) of the polymers have been demonstrated with lower energy consumption [7]. The refractive index of the polymers decreases with an increase of the temperature at a rate of -10^4/K, which is one order of magnitude higher than that of inorganic materials.

2-2. Propagation Loss

Propagation loss is defined as \(-10\log(P_o/P_i)\) [dB]; \(P_o\) and \(P_i\) represent the input power and the output power passed through the waveguides, respectively. The propagation loss caused by the materials in the waveguides is measured with a cut-back method. Low propagation loss at the near-IR region is required for the waveguide materials and is a key factor to determine the performance of the optical devices. The propagation loss is classified as intrinsic and extrinsic loss factors. The intrinsic loss mainly depends on vibrational overtone absorption of molecular bonding in the materials. The overtone absorption has been investigated theoretically and experimentally [8]. The good agreement between the experimental and theoretical explanations shows that the absorption wavelength is predictable from the position of the fundamental vibration and the anharmonicity constant. The stretching vibration of C-H, C=O, and O-H bonding influences the increase in the propagation loss in the near-IR region. The overtone of C=O bonding is found to show lower intensity compared to other overtones. Although other bonding such as C-O, C-C, or C=C also show overtone absorption in the near-IR region, the influence of those bonding can be neglected because strong overtone intensity is not expected. Fluorination and deuteration are effective methods to reduce C-H overtone absorption because substitution of C-F or C-D for C-H shifts the absorption band to higher wavelength as well as it makes the intensity weak. The overtone absorption of O-H bonding also influences the characteristics of transmission of the waveguides due to absorbed water as reported about optical fibers. The optical fibers with lower propagation loss are realized by reducing Si-OH content and reported as ultra low
fibers [9]. The fluorination is considered to be effective to reduce O-H vibrational absorption as well as C-H stretching absorption, because fluorine prevents moisture from penetrating into the polymer. In addition, the increase in the reduced mass of fluorine shifts the fundamental absorption to the longer wavelength region. As one of the other intrinsic loss factors, Rayleigh scattering is considerable and is inversely proportional to the fourth power of the wavelength. The polymer materials are required not to include impurities such as particles larger than the wavelengths.

The extrinsic loss factors include microvoids, core size, surface roughness of the core, orientational birefringence, and imperfection of core-cladding boundary [10]. These factors also affect the propagation loss of the waveguides, but most of factors will be avoided by the well-framed fabrication process or waveguide designs.

2-3. Polarization Dependent Loss
Polarization dependence loss (PDL) is measured as the peak-to-peak difference in transmission of the waveguides with respect to all possible states of polarization. The PDL leads to degradation of the transmission quality of optical communication network systems or even to failure of the systems. Low PDL is therefore required for the waveguides. Optical anisotropy of the materials causes PDL. Some aromatic polymers such as polyimides tend to show relatively high optical anisotropy. This is because of the strong preference of aromatic moieties to align with their planes oriented along the surface. The anisotropy is furthermore induced by the stress accumulated in the waveguides during the fabrication process or thermal treatment.

2-4. Heat Resistance
Optical devices are used under several circumstances, outside or inside the buildings, so that glass transition temperature of the polymers should be high enough not to deform and decompose the materials. At least, the Tg over 100 °C is preferable for the polymers. In some cases of the optical modules equipped with laser-diodes and photo-diodes, Silver-Tin alloy solder reflowing process is employed at the temperature over 250 °C. The polymers are therefore expected to have high heat resistance. The heat resistance is evaluated as thermal decomposition temperature by thermogravimetric analysis (TGA), and some of highly crosslinked polymers are reported to have decomposition temperature over 400 °C as described in the latter section.

2-5. Long-term Reliability
Long-term reliability is an essential factor for the polymer waveguides to keep the initial performance in various environments. In most cases, the waveguides are fabricated on the inorganic substrates such as silicon wafers or quartz glass plates which are stable at wide temperature ranges. For the polymer waveguides, both strong adhesion to the substrate and low coefficient of thermal expansion (CTE) are desirable to prevent boundary imperfections between the waveguides and the substrate because the imperfections make the propagation loss worse. As the standard evaluation method of the optical devices, Telecordia Standard Requirements (GR-1221-CORE) has been widely employed for the devices [11]. According to the Requirements, for examples, no changes in the propagation loss are expected after 1,000 cycles of thermal shock test, which is carried out at -40 °C to +85 °C, and 5,000 hours of heat damp test at 85 °C/ 85 %R.H.

3. Waveguide Fabrication Process
Several methods simpler than quartz waveguides have been reported for the fabrication of the polymer waveguides [1]. One of the common features for the polymer waveguides is to be able to make a waveguide layer by wet coating methods. The wet coating methods such as spin-coating, dipping, or casting can easily make films with high uniformity at the wide areas on the substrate. The possibility to fabricate the waveguide films by roll coating method is proposed for the sake of high productivity [12]. Regarding the core formation in the waveguides, several methods have been proposed: (A) photolithography with reactive ion etching (RIE) [13], (B) direct photolithography [14], (C) photo-bleaching [15], and (D) soft lithography including injection molding [16] or hot embossing [17] as shown in Figure 1.

(A) Photolithography with RIE has been widely employed for the fabrication of polyimide waveguides. The fabrication method is basically same as that for silica-based waveguides, and is able to achieve precise core patterns. A core layer is spin-coated onto an under-cladding layer formed on a silicon substrate and is cured at the temperature around 350 °C. A photo-resist is
(1) Under-cladding formation
(2) Core layer formation
(3) Etching mask layer formation
  ↓ UV ↓ UV ↓ UV
(4) Photolithography
(5) Development
(6) RIE
(7) Ashing
(8) Over-cladding formation

(A) Photolithography with RIE, (B) Direct photolithography,
(C) Photo-bleaching, (D) Injection molding

Figure 1. Fabrication methods of polymer waveguides.

consequently coated and photo-patterned through a positive photo mask in order to form core patterns. The core patterns are etched by O₂-RIE, and then, ashing is carried out to remove the residual photo-resist. Finally an over-cladding layer is formed by spin-coating and cured.

(B) Direct photolithography is a simple method to fabricate core patterns without any photo-resist coating and vacuum process as employed at (A). Polymer materials should have photosensitive property; either crosslinking or decomposition of the polymers through the photo reaction. The core materials are developed with a developer to make patterns after being exposed directly with UV light through a photo mask.

(C) Photo-bleaching takes advantage of decomposition of the chemical bonding, which leads to the change in refractive index. Both core and clad layers are made by employing the same materials in many cases. UV irradiation gives a contrast of the refractive index between exposed and unexposed parts. The methods need no developing processes as carried out at (B).

(D) Soft lithography including injection molding and hot embossing is proposed to be suitable for mass production and to be able to reduce the fabrication costs. Chou et al. reported that fine patterns at submicron-order level were fabricated through soft lithography using polydimethylsiloxane (PDMS) as a mold [18]. According to the injection molding method reported by Hosokawa et al. [19], a master stamper disk is firstly produced by using the semiconductor photolithographic process. UV curable clad resin on a glass substrate is pressed by the stamper and cured upon UV irradiation through the substrate. An under-cladding layer with grooves is formed by removing the stamper. Then, the grooves are filled with UV curable core resin and consequently cured upon UV light exposure. Finally the liquid clad resin is coated on the cured core resin, sandwiched by the substrate, and then cured.

4. Polymer Materials

Early investigations into conventional linear polymers such as polymethylmethacrylate (PMMA), polystyrene, and polycarbonate have demonstrated an excellent potential of these
materials for the waveguides in relatively short wavelengths (0.65 µm or 0.85 µm). However, the transparency of these polymers is not high enough to transmit optical signals at 1.55 µm. Various types of polymers for the waveguides has been proposed to improve propagation loss and thermal resistance as described below. The fluorination and the deuteration of the polymers are effective to decrease C-H vibrational absorption in the near-IR region as described in the former section. Development of photosensitive materials capable of direct photolithography and photo-bleaching materials are also reported to improve the processability of polymer waveguides.

4-1. Fluorinated Polyimides

Polyimides are known as flexible and thermally stable linear polymer materials and has been widely used in several industrial areas such as fibers [20], print circuit boards [21], and low dielectric materials [22, 23]. The glass transition temperature of the polyimides is reported to be over 300 °C and hence the polyimides can withstand for thermal process such as solder reflowing process. However, the polyimides have C-H vibrational absorption in the near-IR region. In order to increase the transparency in the region, a certain parts of hydrogen atoms in the molecules are replaced with fluorine atoms. The effect of the substitution on the propagation loss has been investigated in detail by Matsuura et al. [24]. They fabricated the single-mode waveguides with partly fluorinated polyimide as shown in Scheme 1; hexafluorobisphenol A dianhydride (6FDA) / bis(trifluoromethyl)iphenyldiamine (TFDB) / 6FDA / oxabiphenyldiamine (ODA) copolymers. The fabrication of the waveguides includes process through photolithography with RIE method. The refractive indices of both core and clad in the waveguides is controlled by changing the ratio of 6FDA/TFDB and 6FDA/ODA. The propagation losses at 1.31 µm and 1.55 µm are reported to be 0.3 dB/cm and 0.6 dB/cm, respectively [25]. The polyimide waveguides show excellent stabilities of the propagation loss at 85 °C/ 85 %R.H. Since the past ten years, several kinds of optical devices, such as optical splitters [26], thermo-optic (TO) switches [25], arrayed waveguide gratings (AWGs) [27], and WDM modules [28] fabricated by employing partly fluorinated polyimides, have been reported. To obtain lower propagation loss, all fluorinated polyimides in which all of hydrogen atom were replaced with fluorine atom have been demonstrated, and the propagation loss less than 0.1 dB/cm at 1.55 µm has been reported by Kagei et al. [29]. On the other hand, to eliminate the time-consuming RIE process and photo-resist coating, Mochizuki et al. have developed photosensitive polyimides for the waveguides [30]. The propagation loss of the waveguides fabricated through direct photolithography is 0.4 dB/cm at 1.55 µm.

Polyimides prepared from aromatic diamines and dianhydride has a tendency to orient because aromatic moieties of main chain of the polyimide are apt to stack by intermolecular. Then their structures are relatively rigid and two-dimensional plane in horizontally on the substrate, resulting is relative high PDL. The orientation of the polyimides causes the increase in the PDL. Maeda et al. suggested that PDL occurred by the internal stress arose from the difference of the coefficient of thermal expansion (CTE) between polyimide and silicon substrate when the substrate with polyimide film was cooled after post-baking. The reduction of PDL caused by the internal stress was confirmed by replacing silicon substrate with polyimide film in order to decrease the difference of the CTE between clad and substrate [31].

4-2. Perfluoro-polyolefines

It is reported that d4-PMMA (poly(methyl methacrylate) and deuterated polystyrene (d4-ST) show a low propagation loss in the near-IR region [32]. The substitution of hydrogen atoms to fluorine atoms on PMMA is also reported to be effective to decrease C-H vibrational absorption
and O-H absorption [33]. The productivity of the deuterated polymers is poor due to high cost of the raw materials. The investigation of waveguides with optically transparent amorphous perfluoropolyolefines such as Teflon® AF (perfluorodimethylxolane-tetrafluoroethylene copolymer) and Cytop® (poly(perfluoro(3-buteny1 vinyl ether))) have demonstrated low propagation loss and low PDL for these polymers [34]. The chemical structures are depicted in Scheme 2. The waveguides fabricated by Cytop® through photolithography with RIE method show low propagation loss at a wide wavelength region of 1.0 μm to 1.6 μm. The propagation losses at 1.31 μm and 1.55 μm are reported as 0.10 dB/cm and 0.12 dB/cm, respectively. Moreover, the fabrications of four-channel WDM modules and 1x8 optical splitters with low insertion loss by using Cytop® have been demonstrated [35].

4-3. Polysilanes

Polysilanes are thermally stable organometallic polymers in which silicon atoms are directly linked and repeated in one-dimension. It is noteworthy that the skeleton of polysilane is reactive against UV light [36]. The polysilanes have maximum absorption at UV region due to the relatively small transition energy of the Si-Si bonding. When the polysilanes are irradiated by UV light, the Si-Si bonding in the polymers is homolytically cleaved to produce two silyl radicals [37]. The radicals react with oxygen in the atmosphere to convert to disiloxane linkage which has smaller molecular refractive index than the disilane. This phenomenon has been known as “photo-bleaching of polysilanes” and recently it had been applied to the fabrication of the waveguides without developing process. For example, the photo reaction of polymethylphenylsilane, which has λmax absorption near 330 nm, has been investigated in detail [38, 39]. The refractive index of the polymer is decreased with the increase of irradiation of UV light. The fabrication of channel waveguides through this method using the polysilanes has been demonstrated by Imoto et al. [40]. The polysilanes are classified as two types as shown in Table 1: the linear polysilanes substituted by phenyl group which has large maximum absorption in the UV region, while they affords large PDL of the waveguides due to the stacking of phenyl groups in solid state. On the other hand, the branched polysilanes improve PDL due to the lower crystallinity of the polymer. The crystallinity of the linear polysilanes can be

<table>
<thead>
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<th>Structure</th>
<th>Structural feature</th>
<th>Crystallinity</th>
<th>Transparency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear type</td>
<td>Orientation</td>
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<td>Low</td>
</tr>
<tr>
<td>Branched type</td>
<td>Rigid</td>
<td>Low</td>
<td>High</td>
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improved by introducing a certain unit of branched polysilane moieties into the polymer structure. Methyl or phenyl groups on the polysilanes can be decomposed by baking at high temperature. Infrared spectroscopic study showed that the intensity of the peaks around 3,000 cm⁻¹, which were assigned to the stretch of C-H bonding, decreased during baking at 370 °C. The decrease in C-H content in the polymers leads to lower propagation loss. The propagation loss is reported to be 0.04 dB/cm at 1.55 μm by post-baking at 370 °C after core formation by photo bleaching. The optical splitters of 1×8 with fine core patterns have been demonstrated through photo-bleaching of the polysilanes and shown low insertion loss.

4-4. Polysiloxanes

The features of polysiloxanes consisting of three-dimensional Si-O-Si structures as shown in Scheme 3 are to possess excellent mechanical properties, heat resistance, and high transparency. In many industrial areas, organic-inorganic hybrid materials based on the polysiloxane structures have been widely developed and some of them have been commercialized as coatings and lenses [41]. The siloxane based organic-inorganic hybrid materials are prepared by “sol-gel reactions” involving hydrolysis and condensation of alkoxy silane or halogenated silane compounds. Alkoxy or halogen groups in the compounds are easily hydrolyzed and condensed in the presence of acid or base catalyst. Imamura et al. reported low propagation loss of the waveguides fabricated with polysiloxane starting from halogenated silanes [42]. Tamaki et al. have reported photo-patterenable sol-gel materials by taking advantage of residual silanol groups in the polymers [43-49]. It is also reported fine patterns, which are suitable for optical splitters, can be achieved through direct photolithography by controlling the amount of photo acid generators and amines as acid diffusion controllers. The refractive index of the materials is precisely tunable by changing organic parts in the polymers. The channel waveguides are fabricated with the polysiloxane at the processing time less than 4 hours. The propagation losses at 1.31 μm and 1.55 μm are reported to be 0.2 dB/cm and 0.3 dB/cm, respectively, and the PDL is less than 0.1 dB/cm. The polysiloxane materials are intrinsically amorphous and homogeneous, so that there is no tendency for intermolecular orientation. Figures 2 and 3 show the change in the insertion losses for the straight waveguides of which length is 15 mm after keeping under the different conditions (damp heat and the thermal shock). The changes are less than 0.5 dB even after 3,000 hours damp heat test and 500 cycles thermal shock test, indicating that the waveguides have excellent

Scheme 3. The structure image of polysiloxanes.
long-term durability at both wavelengths, 1.31 μm and 1.55 μm.

Deuterated polysiloxanes has been investigated to reduce the propagation loss by Inamura’s group [50]. The polysiloxanes are prepared from two monomers through the conventional synthesis method as shown in Scheme 4. The refractive index is varied over a wide range from 1.472 to 1.532 at 1.55μm by controlling d-phenyl content from 27 to 95 mol% in the copolymer. The propagation loss and the PDL are 0.23 dB/cm and less than 0.05 dB/cm at 1.55 μm, respectively, for the waveguides fabricated by using the core materials with 95-mol % d-phenyl content through photolithography with RIE method.

4-5. Fluorinated acrylates

The performance of the waveguides fabricated with perfluoroaCRYlate, which was prepared by replacement of hydrogen on polyethylene glycol diacrylate, is reported by Tardley et al. as shown in Scheme 5 [51]. The waveguides through photolithography with/without RIE process can be fabricated with the materials. The refractive indices in the wide range from 1.30 to 1.52 can be designed by copolymerizing or blending with other organic acrylates. The propagation loss of the waveguides is 0.25 dB/cm at 1.55 μm. The increase of the propagation loss is less than 0.1dB after long-term operation at 125 °C. Although other characterization for optical component with the material has not been reported, the result indicate that the heat resistance of acrylates is improved by introduction of fluorine to acrylate.

![Scheme 4. The conventional synthesis of deuterated polysiloxane.](image)

![Scheme 5. The chemical structure of fluorinated acrylates.](image)

5. Summary

The recently developed polymer materials for the waveguides in telecommunication use are reviewed in this paper. Much progress on the performance for the waveguide materials is recognized on propagation loss, heat resistance, long-term reliability, and simple fabrication process. The waveguide characteristic of polymer

<table>
<thead>
<tr>
<th>Materials</th>
<th>1.31μm</th>
<th>1.55μm</th>
<th>Heat-Resistance [°C]</th>
<th>Ref.</th>
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<td>400</td>
<td>[25]</td>
</tr>
<tr>
<td>All fluorinated polyimide</td>
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<td>0.10</td>
<td>-</td>
<td>[29]</td>
</tr>
<tr>
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<td>0.12</td>
<td>-</td>
<td>[35]</td>
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<tr>
<td>Polysiloxane</td>
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<td>0.04</td>
<td>-</td>
<td>[40]</td>
</tr>
<tr>
<td>Deuterated polysiloxane</td>
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<td>0.27</td>
<td>370</td>
<td>[45]</td>
</tr>
<tr>
<td>Fluorinated acrylates</td>
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<td>0.23</td>
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<td>[50]</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>0.25</td>
<td>125</td>
<td>[51]</td>
</tr>
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</table>
materials is summarized in Table 2. In several academic and industrial laboratories, active optical devices, which take advantage of unique functions of the polymers, have been also developed. These polymer waveguides are expected to be widely applied to many optical applications in the near future.

References
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