Polymers for Optical Communications

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Abstract
Optical fibres based on silica (amorphous SiO_2) are the primary medium used for optical communication, although amorphous polymers can also be used as materials for optical communication by utilising their characteristics. Plastic optical fibres (POFs) exhibit a significantly higher optical transmission loss compared with silica; however, they have useful features such as large core diameter, high aperture, excellent flexibility, lightweight, ease of processing, easy handling because of the use of visible light, and low system cost, including conventional light-emitting diode (LED) and organic LED sources. Polymers are a suitable material for short-distance optical communication, wherein low cost and ease of handling are often in high demand. Moreover, optical circuit devices for combining, splitting, and switching control of optical signals are necessary, for which the fabrication of polymer optical waveguides (PWGs) and related devices may be a vital technology. In this article, the structure, characteristics, and optical properties of various types of polymeric optical materials applicable to POFs and PWGs are outlined.

Keywords: Optical polymers; Optical transparency; Plastic optical fibre; Polymer optical waveguide; Processability

1 Introduction

In the 1980s, optical signal transmission systems based on optical communication networks (OCNs) fundamentally changed the conventional communication system that combines copper wires and electricity. Basically, the OCN adopts a communication system that uses semiconductor lasers and light-emitting diodes to convert electrical signals into light, transmits them through optical fibre, and converts the light into electrical signals using photodiodes. Figure 1 shows a schematic view of the broadband passive optical network (B-PON) system, which is a telecommunications technology based on OCNs for delivering

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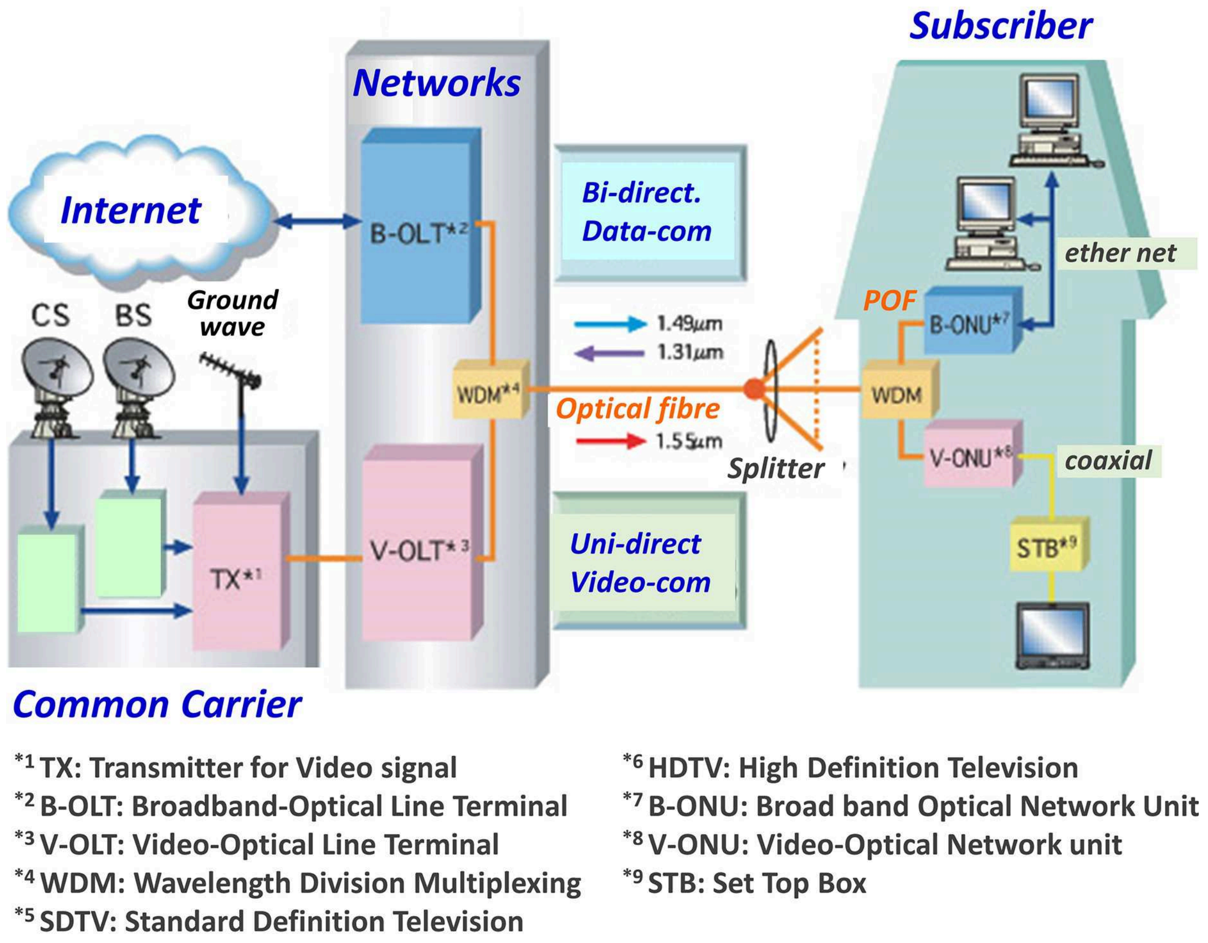
broadband network access to end customers. The transmission wavelengths used for optical telecommunications (such as 1.31, 1.49, and 1.55 µm) are not in the visible region but in the near-infrared (NIR) region owing to the transparency and refractive index dispersion of the silica optical fibre (Effenberger and El-Bawab 2009). Because of the high transmission loss and multimode operation, plastic optical fibre (POF) can be introduced in the subscriber's network, wherein the transmission length is shorter than 100 m.



*1 TX: Transmitter for Video signal
*2 B-OLT: Broadband-Optical Line Terminal
*3 V-OLT: Video-Optical Line Terminal
*4 WDM: Wavelength Division Multiplexing
*5 SDTV: Standard Definition Television
*6 HDTV: High Definition Television
*7 B-ONU: Broad band Optical Network Unit
*8 V-ONU: Video-Optical Network unit
*9 STB: Set Top Box

Figure 1: Scheme of broadband passive optical network system (B-PON) developed by NTT Corp. Silica-based optical fibres are used for the long-distance transmission; however, POF is useful in the subscriber system

In 1964, Du Pont Inc. (USA) succeeded in developing POF with poly(methyl methacrylate) (PMMA) as the core material and a fluoropolymer as the cladding material (DuPont de Nemours & Co. 1978a,b). Based on the basic research of Nippon Telegraph and Telephone Public Corp. (now NTT, Japan) (Oikawa et al. 1979; Kaino et al. 1981b, 1984), Mitsubishi Rayon Co. Ltd. (1974a,b) (now Mitsubishi Chemical Corp., Japan) developed and commercialised POF consisting of PMMA core and fluoropolymer cladding in 1978 (called 'Super Esca'), leading the way to commercial production. Since then, several new types of POF have been developed. In 1986, Asahi Kasei Corp. (Japan) and Toray Industries Inc. (Japan) entered the market, and novel technologies and market development occurred in most

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areas of Japan. These POFs have been mainly used at visible wavelengths because of their lower optical transmission in the NIR region.

2 Optical polymers and their characteristics

For polymers applicable to OCN systems, particularly for applications of POFs and polymer optical waveguides (PWGs), the following physical properties are necessary: (a) excellent transparency at optical communication wavelengths, (b) intrinsically amorphous nature, (c) suitable and controllable refractive index, (d) extremely small birefringence, (e) suitable formability and processability, (f) flexibility and good mechanical properties, (g) thermal stability and long-term durability, and (h) low moisture absorption.

The following polymers have been used as optical materials: (1) **PMMA**; (2) poly (cyclohexyl methacrylate) (**PCHMA**); (3) polystyrene (**PS**); (4) **AS resin** (copolymer consisting of styrene and acrylonitrile); (5) **MS resin**, a copolymer consisting of methyl methacrylate (MMA) and styrene; (6) polycarbonate (**PC**); (7) poly(4-methylpentene) (**TPX**); (8) polyvinylchloride (**PVC**); (9) norbornane-based cyclic olefin resin (**ARTON**); and (10) amorphous cyclo-olefin polymer (COP, **Zeonex**). The characteristic features of the representative optical polymers are briefly explained below, and their physical properties are summarised in Table 1.

Table 1: Physical properties of typical optical polymers applicable to POF (Kawai 1995)[a]

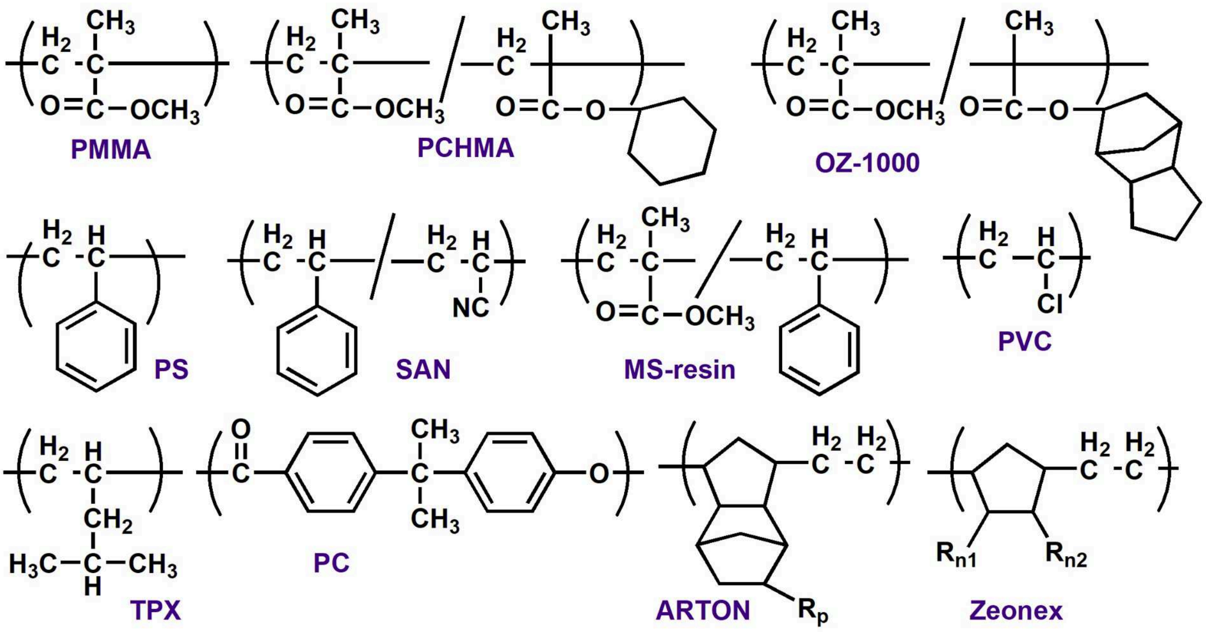
Polymer	*PMMA*	*PCHMA*	*OZ-1000*	*PS*	*AS resin*	*TPX*	*PC*	*ARTON*	*Zeonex*
Refractive index (n_D)	1.492	1.496	1.500	1.502	1.567	1.466	1.584	1.510	1.530
Abbe number	58	57	57	31	35	61	31	92	91
Optical transparency (%)	94	93	94	91	90	90	92	92	91
Saturated moisture absorption (%)	2.0	1.2	1.0	0.1	0.7	0.1	0.4	0.5	< 0.1
Distortion temp. (°C)	100	91	105	90	93	90	130	160	123
Specific gravity	1.19	1.17	1.16	1.06	1.07	0.87	1.20	1.08	1.01

[a] OZ-1000, TPX, ARTON, and Zeonex are the registered trade names of Hitachi Chemical Co. Ltd (now, Showa Denko Materials Co. Ltd., Japan), Mitsui Chemicals Inc. (Japan), JSR Corp. (Japan), and Zeon Corp. (Japan), respectively.

- **PMMA** is a typical isotropic plastic material with excellent transparency and weatherability, low birefringence, and good mouldability and mechanical strength. As a typical optical material, PMMA is used in lenses, POFs, and optical disc substrates. However, it absorbs water relatively easily, its surface is easily scratched, and solvent cracks are easily generated by acetone.
- **PCHMA** has well-balanced optical properties, such as transparency, refractive index, and dispersion properties; however, it has poor mechanical strength and impact resistance. The properties are controlled by varying the copolymerisation ratio.
- **PS** has a lower transparency than PMMA; however, it has excellent mouldability, mechanical properties, and low water absorption. Nevertheless, PS tends to cause

birefringence, has low heat resistance, and has difficulties in chemical resistance and weather resistance.

- The birefringence of PS can be suppressed by copolymerisation with acrylonitrile or MMA (**AS resin** and **MS resin**, respectively). The water absorption is less than that of PMMA. AS resin is used for lenses and is intended to improve the heat resistance and chemical resistance of PS.
- **PVC** has excellent water resistance, chemical resistance, and flame resistance; however, it is inferior in terms of mouldability, heat resistance, and durability. PVC is not an amorphous polymer.
- **TPX** is a crystalline polymer that is transparent because the specific gravities and refractive indices of the crystalline and amorphous phases are close to each other. It has excellent water resistance, excellent chemical resistance, and low birefringence. However, the moulding range is narrow owing to its crystallinity.
- **PC** is an engineering plastic with appropriate transparency and excellent heat and impact resistance. It also has low water absorption. However, it has a large birefringence and poor mouldability, and it lacks surface hardness.
- **ARTON** is an amorphous cyclo-olefin polymer (COP) developed by JSR Corp. (Japan) with good optical properties, dimensional stability, and heat resistance. It has polar groups in its molecular chain, providing good adhesion, bonding, and miscibility.
- **Zeonex** is another type of COP developed by Zeon Corp. (Japan). It is synthesised from hydrocarbon monomers that contain no polar groups. It has well-balanced properties such as good transparency, low birefringence, low moisture absorption, and heat resistance (Scheme 1).



Scheme 1

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3 Structures of POF

Figure 2 shows an overview of the structures of optical fibres and their light propagation modes (Abdel-Baki and El-Diasty 2013). There are three major types of optical fibres used in practical applications: (1) step-index multimode (SI-MM) fibres, (2) graded-index multimode (GI-MM) fibres, and (3) step-index single-mode (SI-SM) fibres. The SI type basically consists of a two-layer structure combining a polymer with a higher refractive index as the core material and a polymer with a lower refractive index as the cladding material. The incident light is transported through repeated total reflection at the interface. The GI type is designed with a gradual distribution of refractive indices such that the refractive index gradually increases towards the centre and the light travels towards the higher refractive index. The SI type is designed to propagate only single-mode light by making the diameter of the fibre ultrafine – for example, <10 μm. The typical and most popular POF has an SI-MM structure, in which a PMMA core with a diameter of ~1 mm is surrounded by a thin layer of a fluoropolymer with a diameter of 5 μm.

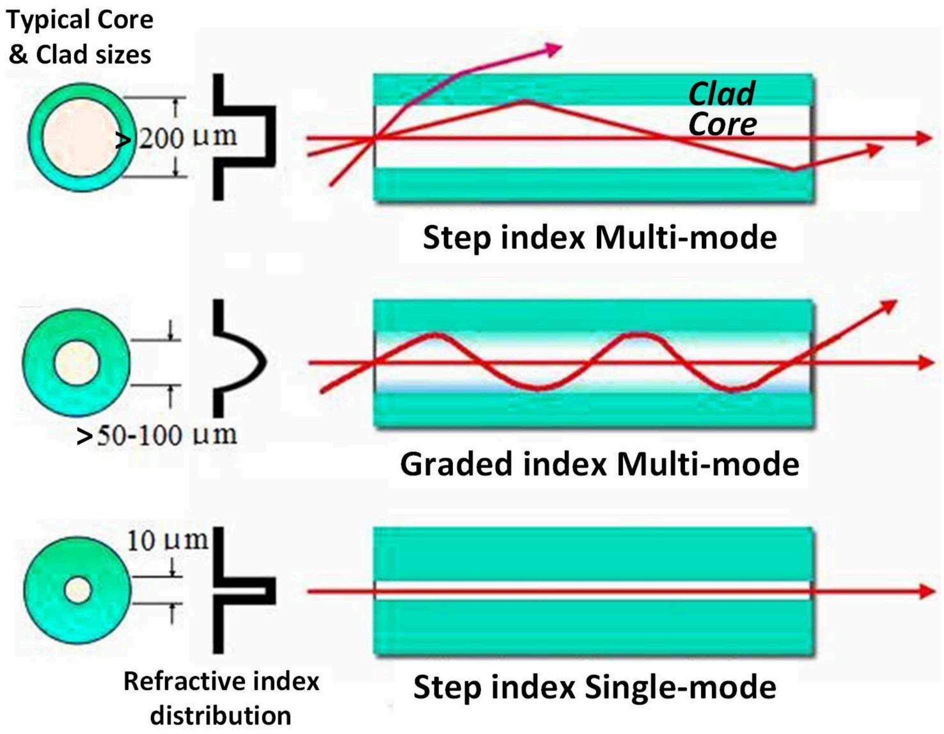

Figure 2: Three major types of optical fibre: (a) SI-MM, (b) GI-MM, and (c) SI-SM

4 Transmission losses of POF

Optical transparency is the most important property of POFs as well as other optical devices. The transmission loss of POFs can be divided into losses based on (1) the core polymer, (2) the interface between the core and the cladding polymers, and (3) the cabling polymer (Kaino et al. 1984; Emslie 1988; Koike and Koike 2011). The losses based on the core polymer are the most essential, and they can be divided into intrinsic and extrinsic losses. The intrinsic loss is further divided into absorption and scattering losses, as listed in Figure 3.

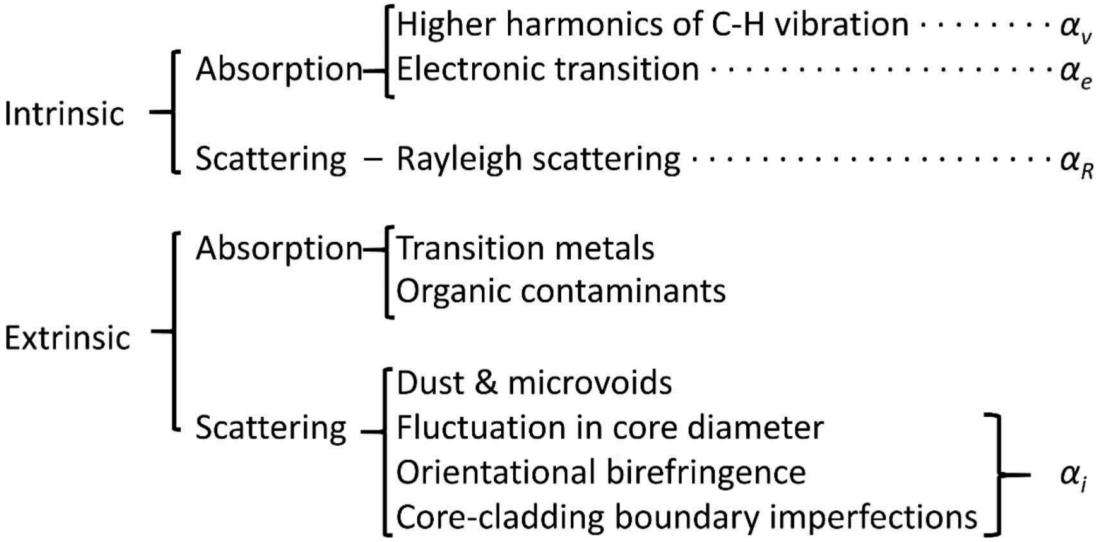

Figure 3: Loss factors of POFs

4.1 Absorption loss

There are two types of intrinsic absorption losses: (I) infrared (IR) vibrational absorption of polymers (harmonic vibrations of covalent bonds in polymer structures) and (II) ultraviolet (UV) absorption originating from electronic transitions. Generally, polymers exhibit a variety of molecular vibrational absorptions in the IR region. The chemical bonds, such as C–C, C–O and C=O, have little effect on the visible and NIR range because their fundamental vibrations are located at longer wavelengths in the IR region (>5 µm). However, the C–H bond, which is a constituent group of most polymers, has a fundamental vibration at ~3 µm; thus, its harmonic absorption appears between the visible and NIR regions (400–1,700 nm). The core polymer of the POF is basically made of PMMA. Figure 4 (redrawn by Ide and Tearda (1987)) illustrates the relationship between the molecular vibration absorption spectrum of PMMA and the loss (Kaino 1986). From the NIR to the visible regions, the harmonic nV_0 of the infrared stretching vibration of the aliphatic C–H bond and the combined vibration $nV_0 + \delta$ of the infrared bending vibration δ appear. The absorption intensity of the harmonics decreases as the order (n) increases; however, up to the seventh harmonic, it has a significant effect on the optical loss, while electronic transition absorption can be observed mainly in the UV region. In accordance with Urbach's rule (Urbach 1953), the logarithm of the absorption intensity is linearly proportional to the reciprocal of the wavelength; thus, the effect is more pronounced in the UV region but also extends to the visible region. As shown in Figure 4, the effect of the electronic transition in PMMA is negligible at more than 500 nm. For PS, however, the effect remains at 22 dB/km at 555 nm and 2 dB/km at 672 nm (Kaino et al. 1981a), and the loss is larger than that of PMMA because of the side chains of the phenyl group. Therefore, there is a low-loss window

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between the overtones of the C–H vibrational absorption, due to which the visible wavelengths are used for conventional POFs, except for perfluoropolymers.

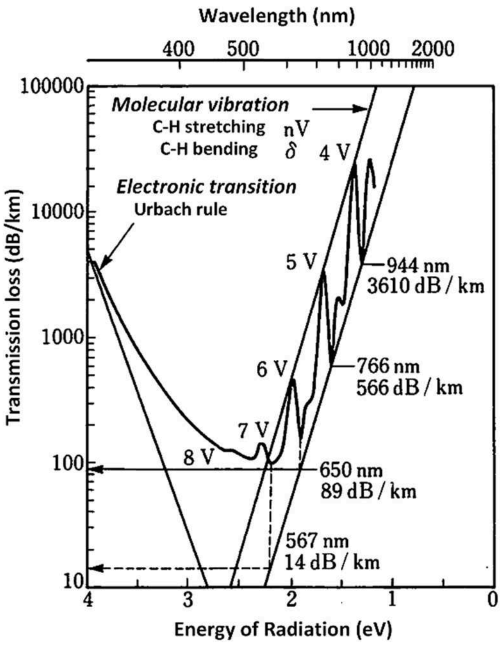


Figure 4: Optical transmission loss spectrum of PMMA. The losses are caused by the electronic transitions (<500 nm) and the higher harmonic vibrations of C–H bonds (>500 nm)

4.2 Scattering losses of POF

Transparent polymers applicable to POF are generally amorphous, and their light scattering is primarily caused by microscopic density fluctuations. Even for the same polymer solid, the internal density fluctuation differs depending on the moulding conditions and thermal histories, resulting in different scattering losses. The scattering loss of a polymer can often be minimised by heat treatment at temperatures above the glass transition temperature (T_g) for a long time to achieve the lowest internal density fluctuation. However, in typical moulding processes, larger density fluctuations are present, and 'excess scattering loss' is added to the intrinsic scattering loss, which increases rapidly towards shorter wavelengths.

5 Polymers used for POFs (Emslie 1988; Zubia and Arrue 2001)

5.1 PMMA-based polymers

All POFs commercialised by major companies (Mitsubishi Rayon, Asahi Kasei, and Toray) are PMMA core fibres. PMMA is characterised by good visible transmission and mechanical properties, low material cost, large diameter, and continuous production from raw material to fibre in a completely sealed system. The window with the lowest loss at 35 dB/km is ~567 nm, and the second lowest at 106 dB/km is ~650 nm (Kaino et al. 1984). The loss limit of 100 dB/km can be divided into the molecular vibration absorption of 88 dB/km and a Rayleigh scattering contribution of 12 dB/km. Therefore, a window of 570 nm is optimal in terms of loss, but a window of 650 nm is actually adopted considering other characteristics. The T_g of PMMA is 110°C, which is sometimes insufficient for practical use from the viewpoint of heat resistance. To improve heat resistance, a copolymer of MMA and maleimides, especially *N*-isopropyl maleimide, was developed by Toray Industries with improved heat resistance, a T_g of 129°C, and a transmission loss of 218 dB/km. The decrease in the transmission loss is smaller than that of PC. A method to increase the heat resistance using cross-linked PMMA as the core was also studied by Hitachi Cable Ltd. (now Hitachi Metals Ltd., Japan).

5.2 PC-based polymers

PC has been considered a heat-resistant POF material because of its excellent transparency and relatively high T_g of 145°C. In addition, PC has excellent impact resistance, moisture absorption resistance, bending strength, and tensile elongation. However, the loss is large at 1,200 dB/km (680 nm) and 800 dB/km (765 nm) (Yamashita and Kamada 1993). This is because of its susceptibility to Rayleigh scattering and the large absorption of electronic transitions based on the phenyl and polar ester groups. A POF with a modified PC core and silicone polymer cladding has also been investigated. The transmission loss is 600 dB/km (660 nm) and 450 dB/km (760 nm), which is lower than that of unmodified POFs, and the thermal life is four times longer.

5.3 Norbornane-based polymers

Fujitsu Ltd. (Japan) developed an optical fibre using a norbornene-based polymer, ARTON, developed by JSR Co. The features of this polymer are as follows: (1) the T_g at 171°C is higher than that of PC;(2) the birefringence is small; (3) the optical transmittance in the visible region is high; and (4) the water absorption is small. However, its disadvantage is that it has a large loss of 800 dB/km, which could be caused by the scattering loss.

5.4 Deuterated polymers

To develop POFs for long-distance transmission, there have been attempts to reduce the transmission losses. One method is to replace hydrogen (H) atoms in the C−H bonds that form polymer structures with heavier atoms (Groh 1988). By replacing H atoms with deuterium (D) atoms, vibrational absorption can be shifted to longer wavelengths due to the twofold atomic weight. In this case, replacing the H atoms in PMMA with D atoms has no significant effect on other physical properties. As shown in Figure 5 (redrawn by Ide and Tearda (1987)), the complete deuteration of PMMA reduces the losses to 20 dB/km (680 nm), 25 dB/km (780 nm), and 50 dB/km (850 nm) (Kaino et al. 1983). However, this polymer also shows an increase in loss with moisture absorption, which is caused by the harmonic absorption by, for example, the sixth overtone of the O–H vibration of the H_2O molecule (Scheme 2).

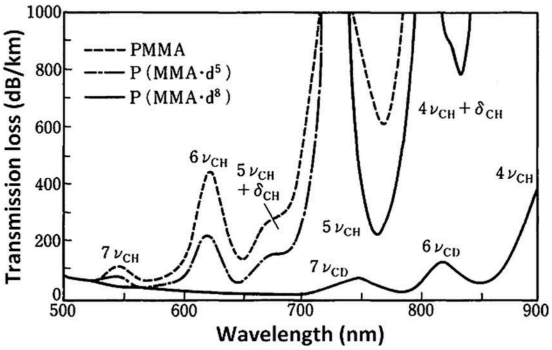
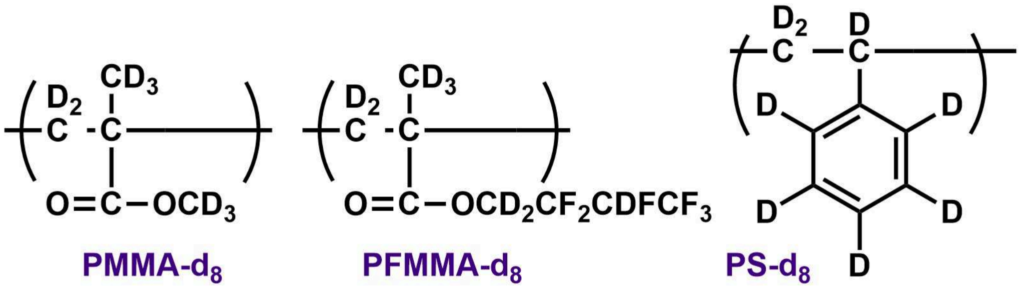


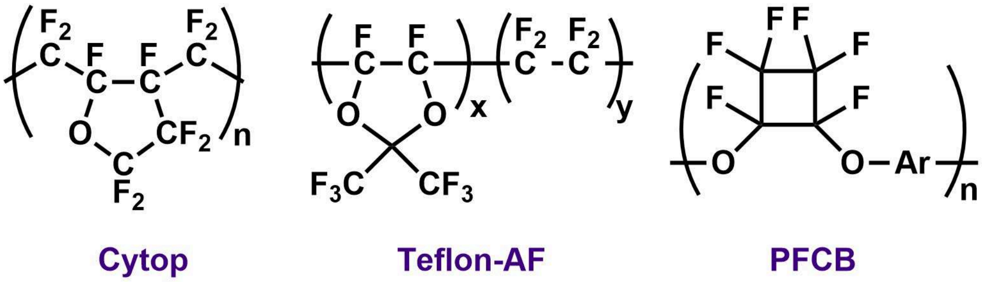
Figure 5: Reduction of transmission losses of PMMA induced by replacement of H atoms by D atoms



Scheme 2

5.5 Fluoropolymers

In addition to D atom, fluorine (F) atom has been used to replace the H atoms in the C–H bond with heavier elements. Replacement by F atoms can shift the absorption to significantly higher wavelengths than replacement by D atoms because of its atomic weight of 19 (Groh 1988). When a perfluoropolymer is used as the core, there are almost no harmonics in the range of 600–900 nm, and the theoretical limit of the loss value could be several dB/km. However, the refractive index of acrylic polymers becomes smaller than 1.42 when completely replaced with F, and the choice of cladding material is limited due to the aperture problem. Cytop, Asahi Glass Co., Ltd. (now AGC Inc., Japan), which is commercially available as a fully fluorinated polymer for GI-POF, consists of only C−F, C−C, and C−O bonds without C–H bonds (Yamabe 1992). Therefore, it has no strong absorption overtones at the communication wavelengths. The material has high durability and chemical resistance, and the material dispersion of Cytop is lower than that of silica. The GI-POF made from Cytop (Lucina, AGC Inc.) has a low loss of 0.05 dB/km over a wide range of 650–1,300 nm and a transmission speed of 10 Gbps, 10 times faster than PMMA SI POF (Nihei et al. 1997). Meanwhile, Teflon-AF, developed by Du Pont Inc. (USA), is another family of amorphous fluoropolymers based on the copolymerisation of 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole (PDD) with TFE (Smart et al. 1995; Resnick and Buck, 1999). Depending on its composition, its T_g can be controlled between 80°C (~20 per cent PDD) and 335°C (~100 per cent PDD). Teflon-AF is well suited for fibre optical applications owing to its exceptional transparency and processability. Du Pont Inc. made an exclusive agreement with Mitsubishi Rayon Co. Ltd. for the development of high-temperature POFs (Scheme 3).



Scheme 3

6 Polymer optical waveguides (PWGs)

An optical waveguide is a thin film formed on a substrate, such as silicon (Si), fused silica (SiO_2), or polymers, with a core that confines the optical signal and a cladding that surrounds the core in the form of a two-dimensional line or circuit. Optical fibres can be considered as a waveguide; however, while optical fibres in optical signal transmission are equivalent to coaxial cables in electrical signal transmission, optical waveguides can be called ‘optical wiring plates’ and are mainly used in optical integrated circuits and waveguide optical devices. Figure 6 shows a schematic of an optical networking unit used in fibre to the home (FTTH), wherein optical signals of three different wavelengths are propagated simultaneously (Ueda et al. 2001). When semiconductor optical devices, such as laser diodes and photodiodes, are integrated into a waveguide circuit, the waveguide materials must have high thermal stability over the soldering temperature (>280°C).

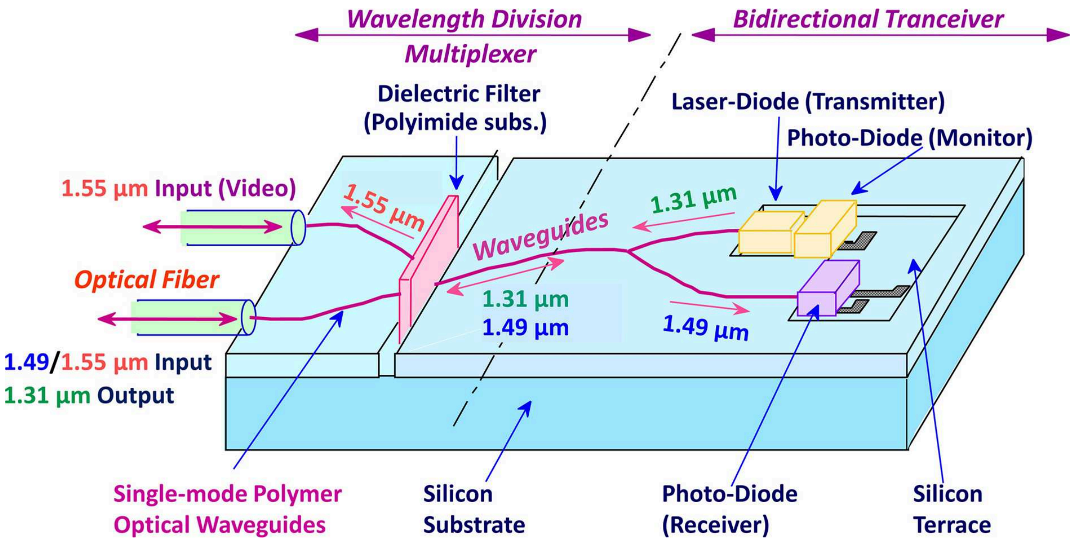


Figure 6: Schematic view of optical networking unit designed for B-PON system. The optical fibres, laser diode, photodiode, and dielectric filter are connected by single-mode optical waveguides

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Inorganic glass-based optical waveguides have been widely accepted (Takahashi 2003); however, they cannot be fabricated without a rigid support substrate. If optical waveguides can be formed in a flexible plastic film with a thickness of 0.1–0.3 mm, they can be used for optical transmission between liquid-crystal display panels and cameras to control large-scale integrated circuits in cell phones and for interboard wiring that has traditionally relied on 1:1 connection of coaxial cables or optical fibres. In particular, polymer waveguides (PWGs) can be used for optical interconnection because they have a minimum bending radius of less than a few millimetres and are resistant to degradation, even after repeated bending; therefore, their applications are expected to expand greatly if mass production becomes possible.

The cross-sectional structures of the optical waveguides are shown in Figure 7. For practical applications, it is essential to form channel-type structures of (b) or (c) that confine light in a direction parallel to the substrate surface. While inorganic glass-based waveguide materials such as silica and multicomponent glass present difficulties when fine patterns are fabricated, polymers allow a wide range of material selection according to the required performance, and various polymers have been developed. In the shorter-wavelength range (0.6–1.0 μm), where optical LAN applications are possible, many polymers exhibit high transparency, and deuterated PMMA PWGs show a low waveguide loss (0.011 dB/cm at 0.68 μm) (Yoshimura et al. 1998). UV-cured epoxy PWGs with heat resistance at ~200°C have also been developed (Enbutsu et al. 1998, 1999).

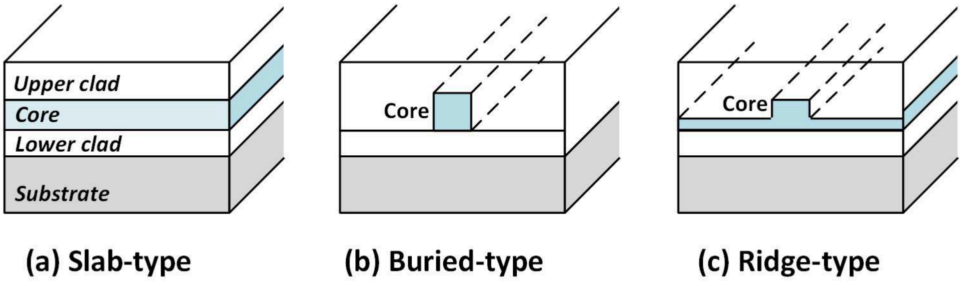

Figure 7: Three types of optical waveguide structures: (b) and (c) are suitable for practical use

Table 2 summarises the propagation loss and thermal resistance of typical PWG materials. In the longer-wavelength range of NIR (1.0−1.7 μm) for advanced optical interconnection using ultrafast modulated surface-emitting lasers, ordinary polymer materials have high optical loss because of the absorption caused by harmonic vibrations of C−H bonds, as explained above. To solve this problem, deuterated PMMA (Yoshimura et al. 1998) and fluorinated polyimides (FPIs) (Kobayashi et al. 1998) have been synthesised as new materials for PWGs to reduce the optical propagation loss significantly. In addition, the temperature dependence of the refractive index is large because the coefficients of thermal expansion of polymers are more than two orders of magnitude larger than those of inorganic glasses. Therefore, new PWG devices, such as temperature-tuneable wavelength-selective filters, have been developed to exploit the large thermo-optic (TO) effect (Han et al., 2018).

Table 2: Optical losses and thermal stability of typical polymer waveguide materials

Materials	*Loss of channel waveguide (dB/cm)*			*Thermal stability*	
	0.85 µm	*1.3 µm*	*1.55 µm*	*Material*	*Waveguide*
Fluorinated polyimide (Kobayashi et al. 1998)	–	0.2	0.4	400	350
Perfluorinated polyimide (Kagei et al. 2002)	–	0.15	0.18	>300	–
BCB polymers (Fischbeck et al. 1997b)	–	0.3	1.5	420	–
Deuterated silicone resin (Watanabe et al. 1998)	–	0.12	0.4	420	250
Deuterated PMMA (Yoshimura et al. 1998)	<0.02	0.1	1.5	150	80
UV-curable siloxane (Utaka et al. 2002)	–	0.3	0.6	–	–
UV-curable epoxy resin (Enbutsu et al. 1998, 1999)	0.08	0.5	4.7	–	200
UV-curable acrylates (Koshobu et al. 2002)	0.1	0.2	0.24	150	–
Amorphous perfluoropolymer (Cytop) (Matsukura et al. 2002)	–	0.2	0.17	108	–

As shown in Figure 8, although the conventional fabrication method of PWGs is a combination of photolithography and reactive ion etching (RIE), other methods include direct exposure, photobleaching, selective polymerisation, and imprinting based on UV-curing resin or compression moulding at high temperatures. The RIE method is similar to that used for silica glass optical waveguides and is used for single-mode optical waveguides that require high processing accuracy. However, it is difficult to reduce the cost because of the long working time owing to the large number of processes and the high cost of manufacturing equipment. In contrast, direct exposure, photobleaching, and selective polymerisation methods, which use photocurable or photosensitive resins to form embedded waveguides only by photolithography, are polymer-specific methods that can form core-cladding structures without using photoresists or vacuum processes. For example, in the direct exposure method using fluorinated epoxy resin, multimode PWGs with a large core diameter of ~50 µm can be fabricated in a short time.

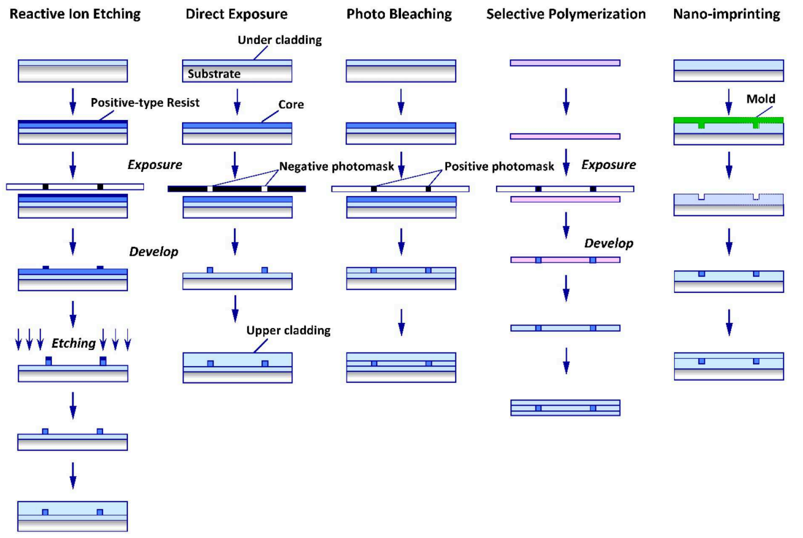

Figure 8: Schematic of PWG fabrication processes: all except RIE are polymer-specific methods that can form core-cladding structures

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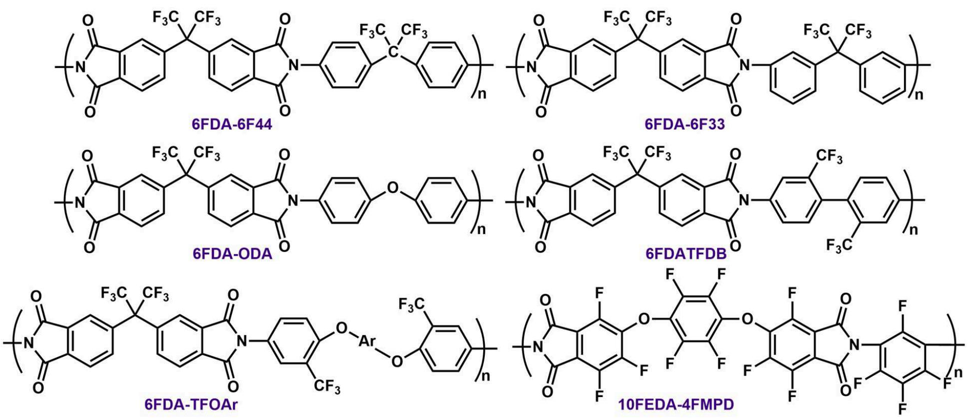
In addition to the cost-effective patterning techniques and compatibility with other materials, polymers have inherently higher negative TO coefficients (change in refractive index with temperature, *dn/dT*) and lower thermal conductivity compared with silica. These properties are attractive for waveguide components and integrated optical systems, especially for applications where optical interconnects, TO functions, thermal tunability, low power consumption, and temperature compensation are required. Thermo-optical switches (TOSs), variable optical attenuators (VOAs), tuneable waveguide device arrayed waveguide gratings (AWGs), and temperature-insensitive AWGs have been demonstrated and commercialised in devices that utilise these properties.

7 Polymers developed for PWGs

7.1 Fluorinated polyimides

Polyimides (PIs) have been recognised as superengineering plastics for more than fifty years due to their thermal stability (in general, T_g is higher than 250°C, and 5 per cent decomposition temperatures are higher than 400°C), mechanical toughness, pliability, and outstanding electrical properties (that is, high insulation and low dielectric constants). Hence, PIs have been widely used in the fields of electronics and aerospace applications. These fields require high transparency over the NIR region, low hygroscopicity, and solder temperature resistance (270–300°C). These properties enable PIs to be hybridised and/or monolithised with semiconductor components for optoelectronic applications.

In 1964, Roger (1967) at DuPont Inc. first synthesised a fluorinated polyimide (FPI) from an acid dianhydride (6FDA) and diamine (4,4'-6F) containing hexafluoro-isopropylidene (6F) units. The FPI films are colourless, transparent, and soluble in polar organic solvents. St. Clair et al. at NASA synthesised various kinds of FPIs from 6FDA and a variety of aromatic diamines containing ether (−O−) linkages. The absorption edges for the FPIs derived from 6FDA and diamines with ether, sulphone $\left(-SO_2^-\right)$, and 6F linkages were significantly shifted to wavelengths shorter by 100−150 nm than the conventional PIs. In addition, these FPIs are amorphous and soluble in polar solvents. They serve as typical FPIs because of their good thermal resistance (represented by T_g of more than 300°C) and a good balance of physical properties. Reuter et al. (1988) at IBM Corp. reported the optical properties of three kinds of FPI (6FDA-6F44, -6F33, -ODA), focusing on PWG materials for the first time. The FPIs exhibit optical transmission losses less than one-tenth those of nonfluorinated PIs at 0.63 μm because absorption edges are shorter by 20−50 nm through fluorination. Reuter et al. (1988) at IBM reported that the increase in optical losses caused by annealing is decreased at 0.83 μm rather than at 0.63 μm. Meanwhile, Matsuura et al. (1993a,b, 1999) at NTT Corp. reported that the optical transmission loss of 6FDA/TFDB (0.16 dB/cm) was maintained after annealing at 350°C for 1 hour at 1.3 μm, which originated from its higher T_g at ~335°C. In particular, single-mode PWGs made from this FPI showed no increase in optical loss, even after heat treatment at 380°C for 1 hour. One major difficulty related to FPIs is their high birefringence, which originates from the orientation of the phenyl and imide rings during thermal imidisation on the substrates. The introduction of one or two ether linkages in the main chain (6FDA-ODA (Matsuura et al. 1999), 6FDA-TFOAr (Han et al. 2000)) effectively reduced the birefringence (Scheme 4).



Scheme 4

The optical transmission loss spectrum of the FPI of 6FDA/TFDB in the NIR region is shown in Figure 9 (broken line) (Kagei et al. 2002). The absorption peaks that cause optical losses larger than 0.1 dB/cm are the second ($2\nu_{\mathrm{CH}}$: 1.65 μm) and third ($3\nu_{\mathrm{CH}}$: 1.15 μm) harmonics of aromatic C−H bonds, the coupling vibrations ($2\nu_{\mathrm{CH}} + \delta_{\mathrm{CH}}$: 1.40 μm) of $2\nu_{\mathrm{CH}}$ and the C−H bending vibration, and the second harmonics ($2\nu_{\mathrm{OH}}$: 1.44 μm) of the O−H bond resulting from absorbed moisture. Although the optical loss at ~1.55 μm is <0.5 dB/cm, the absorption caused by the tailing of $2\nu_{\mathrm{CH}}$ is essential to this material. Because FPIs contain plural phenyl C−H bonds in the main chains, the optical losses caused by the harmonic vibrations in the range of 1.30−1.55 μm are not negligibly small. In 1992, Ando et al. (1992, 1993, 1999) proposed and synthesised perfluorinated polyimides (PFPIs) to reduce the optical absorption losses of FPIs significantly. As expected from the structure with no H atoms in the structure (10FEDA-4FMPD), no absorption peaks are observed throughout the NIR region except for the absorption near 1.48 μm originating from absorbed water and the fourth harmonic of the asymmetrical stretching vibration of the imide carbonyl (C=O) group, as in Figure 9 (solid line). Excellent optical transparency is attained in the 1.53−1.58-μm region. The loss of the optical waveguide is as low as ~0.1 dB/cm at 1.55 μm (Kagei et al. 2002). This material is also heat resistant at higher than 300°C, so it can withstand a lead-free solder reflow process, which is sufficient for optical devices with short transmission distances.

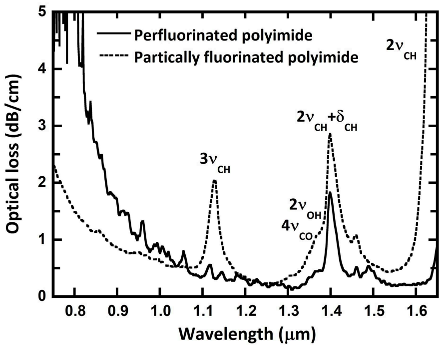
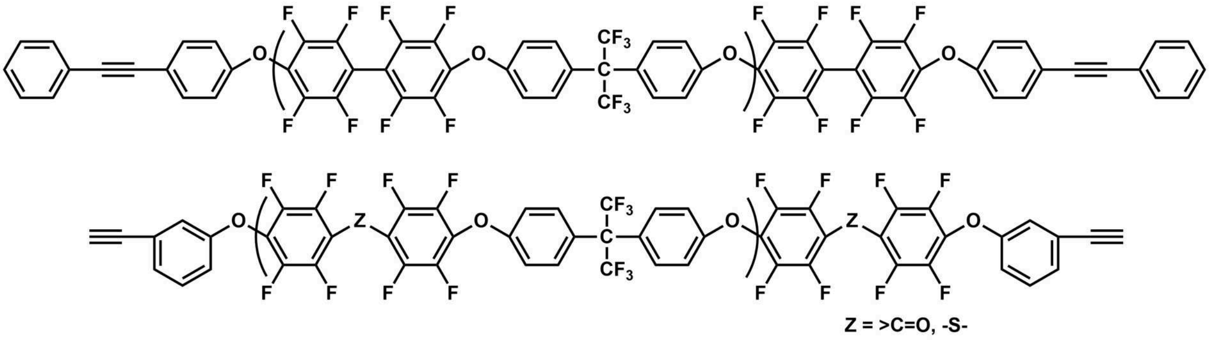


Figure 9: Optical transmission loss spectra of partially fluorinated (FPI) and perfluorinated (PFPI) polyimides in the NIR region. The absorption peaks originated from the harmonic vibrations of C–H and C=O bonds and that of O–H from moisture

7.2 Fluorinated polyethers and poly(ether ketone)s

Fluorinated poly(arylene ether)s (PAEs) and poly(arylene ether ketone)s (PAEKs) tend to be less birefringent than FPIs after being spin-coated and baked because of their flexible ether and ketone linkages in the polymer backbones. The incorporation of 6F units into the polymer backbone leads to polymers with increased fluorine content, solubility, thermal stability, and T_g, while also leading to lower crystallinity, dielectric constant, and moisture uptake. Examples of fluorinated PAEs bearing cross-linkable phenyl ethynyl terminal moieties are introduced at the chain ends. A very low propagation loss (0.2 dB/cm) was reported for a channel waveguide based on this polymer (Lee et al. 1998). However, a slightly higher birefringence of ~0.007 was induced by the skeletal structure and high-temperature curing process at ~320°C. An improvement in birefringence and curing temperature has been reported in a PAEK system containing a kinked decafluorobenzophenone in the polymer backbone and cross-linkable meta-substituted ethynylphenol groups at the chain ends (Lee et al. 1999) (Scheme 5).



Scheme 5

7.3 Perfluorocyclobutyl (PFCB) polymers

Several monomers for synthesising PFCB polymers have been developed, and the resultant copolymers were characterised by Dow Chemical (USA) in the early 1990s. Both thermoplastic and thermosetting PFCB polymers exhibit high T_gs values and optical transmission. A 1,1,1-tris(4'-trifluorovinyloxyphenyl)ethane-based polymer, which was originally designed as a dielectric material for semiconductor devices (Smith et al. 2000), has been applied to PWGs. However, because the homopolymer has a refractive index in the range of 1.487–1.49, either cores or claddings of waveguides have to be made of other materials. Waveguide devices, such as TOSs and VOAs, in which PFCB was used as the core and cladding material, have been reported (Fischbeck et al. 1997a; Lee et al., 2000). In one rib waveguide configuration, the bottom buffer was thermally grown silica and the core was PFCB. The waveguiding PFCB polymer showed a propagation loss of 0.25 dB/cm in the range of 1.515–1.565 μm.

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7.4 *Cytop and Teflon-AF*

Asahi Glass Co. used Cytop to make GI-MM POFs (Lucina) for short-range data communication applications. A single-mode waveguide with a low loss on the order of 0.1 dB/cm at 1.55 µm was fabricated using Cytop as the core material, which has excellent optical transmittance not only in the 1.55-µm band but also over a wide bandwidth up to short (Zhao et al. 2000; Matsukura et al. 2002). Opportunities also exist for Teflon-AF to be used in optical waveguide systems. One example is the TOS, in which Teflon-AF has been used as an overcladding layer (Keil et al. 1994, 1995).

7.5 *Polysiloxanes (silicone resins)*

Polysiloxanes are polymers whose backbones consist of alternating silicon and oxygen (−Si−O−) bonds. For application in waveguide components operating at 1.55 µm, the major concern remains the optical absorption of the organic groups attached to the silicon atoms. One approach is to introduce a deuterated phenyl group ($-C_6D_5$) into the polymers (Usui et al. 1996; Watanabe et al. 1998; Utaka et al. 2002). The deuterated MMA results in a higher optical propagation loss at 1.55 µm because of the harmonics of aliphatic C−D vibrations. However, the transmission loss spectra of d-phenyltrichlorosilane and d-phenyl-substituted polysilicone in Figure 10 indicate that the vibrational overtone absorption of the aromatic C–D bond narrowly escapes the 1.55-µm region (Watanabe et al. 1998). Nevertheless, for a specific silicone resin, the loss ~0.7 dB/cm at 1.55 µm is higher than 0.5 dB/cm for the wavelength region from 1.545 to 1.622 µm (Toyoda et al. 1999). A lower loss for silicone waveguides can be reached by increasing the d-phenyl substituent.

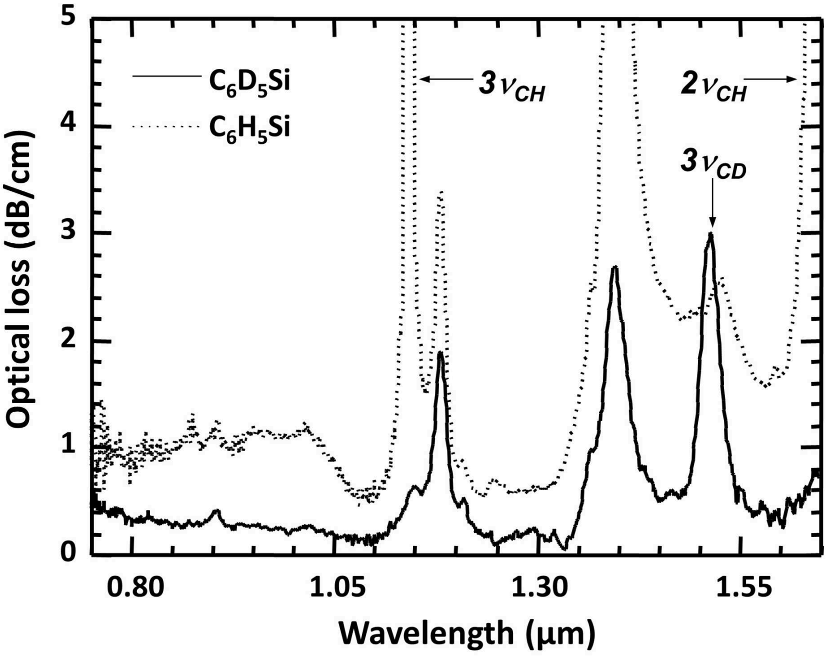

Figure 10: Optical transmission loss spectra of polysiloxane and deuterated polysiloxane in the NIR region: the absorption peaks originate from the harmonic vibrations of C–H and C–D bonds

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8 Conclusion

Owing to the beneficial characteristics of polymer materials, such as flexibility, lightweight, high impact strength, good processability, low production cost, and a wide range of processing methods, they have been used in various optical components such as optical films for displays, optical discs, optical lenses, optical fibres, and touch panels. Polymers have become indispensable materials in the field of optical technology, including optical communication applications, wherein various types of optical polymers have been developed and applied to POFs and PWGs by utilising the abovementioned characteristics. In particular, the introduction of multiple deuterium (D) and fluorine (F) atoms into polymer structures significantly reduces the optical transmission losses in the NIR region, and the use of silicone polymers and polyimides significantly enhances the thermal stability of PWG materials. In addition, the high negative TO coefficients and low thermal conductivity render the polymers beneficial for applications where optical interconnects, TO function, thermal tunability, low power consumption, and temperature compensation are required. Polymers are promising materials for POFs and PWGs and are applicable in short-distance optical communication and optical interconnections.

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