Polymers in optical telecommunications.
1. Passive components

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1. INTRODUCTION
Despite the obvious lull over the last few years it can be said that optical telecommunications and their associated technologies have had a fundamental effect on the engineering and social history of the second half of the twentieth century. Though it is true that the main role in this has been played by the optical fibres made from ultra-pure inorganic glass, there have also been significant developments in the field of polymers. An important application of polymers is in coatings and cables, but the production of optical media from polymers has also emerged and made some progress, and today a number of plastic optical fibres are commercially available. These have become very important in a specialised but important sector of the optical telecommunications market, the local area networks (LAN). In the present communication we would like to briefly describe the polymers used in optical fibres and PLC (planar lightwave circuits). We are not particularly concerned with the polymers employed in traditional optical devices (e.g. lenses) – though naturally many overlaps will occur. Later in another article we shall mention the polymers used in the sensorics and active components.

2. BASIC CONCEPTS
One of the most important physical factors involved in optical telecommunications, whether we are speaking of optical fibres or planar lightwave circuits is the total reflection (ref. 1). When a ray of light passes from a medium with a higher refractive index into a medium with a lower refractive index, there is a critical angle \( \sin \theta_c = \frac{n_2}{n_1} \) (where \( n_1 \) is the refractive index of the medium from which the ray exits, and \( n_2 \) is the refractive index of the medium it passes into), above which the ray is totally reflected back into the medium having the higher refractive index. Using this principle, the light ray carrying information can be kept inside the boundaries of the light-conducting core which has a higher refractive index, even if the path of the ray is not straight. In the case of optical fibres the light-conducting core and the light-reflecting coating also (in the simplest cases) are cylindrical, whereas in the case of waveguides they form a prism, defined by basically perpendicular strips, but the longitudinal axis can change direction. The geometric properties of the light-conducting core determine how many kinds of wave lengths of radiation (technically speaking, how many modes) the given structure can transmit. (Of course the wave propagation can be described not only by the greatly simplifying radiation image but also by the much more accurate Maxwell equations, but the two descriptions in this case lead to the same result). In long-distance telecommunication (e.g. in intercontinental telecommunications cables) it is more expedient to use fibres in which altogether one wavelength can propagate (so-called monomodal fibres), while in local networks (LAN) multi-mode fibres are also widely used. The insertion of monomodal fibres is more difficult, since the exceptionally small (microns in diameter) wave-conducting cores must be fitted very precisely together, but it is not necessary to allow for errors such as those arising from the differing propagation characteristics of the higher-mode fibres.
A characteristic of the fibres (or waveguides) mentioned so far is that the refractive index changes stepwise at the boundary surfaces (step-index, SI fibres). However, there are also solutions where the refractive index can be gradually changed along a geometrical dimension (e.g. in the case of optical fibres the radius) between two boundary values (these are called fibres with a gradually changing refractive index, or graded index, GI fibres). In this case also total reflection takes place, except that it is not by a sudden change in direction but by the light ray propagating along a curved path. If the tempo of the change is well chosen (in the case of fibres for example parabolically) then radiations at different wavelengths curve to a differing degree, but essentially stay together and propagate along the optical fibre, so that there is no widening of the signal resulting from the differentiation of the wavelengths. This is particularly important in the case of local networks using non-monochromatic (i.e. not consisting of a single wavelength) light sources (e.g. LEDs or light-emitting diodes). The geometric relations characterising the different fibre types fibre types and their ray paths are shown in Figure 1.

3. REQUIREMENTS OF POLYMERS EMPLOYED FOR THE PRODUCTION OF PASSIVE ELEMENTS

When choosing polymers for the production of passive components the most important optical characteristics are the refractive index and the absorption (signal-transporting capacity). The refractive index is determined from the Clausius-Mosotti relation (ref. 2), primarily by the molecular refraction (including the atomic and molecular polarisability), thus the refractive index of polymers containing aromatic or larger arrangements of atoms is higher, while that of polymers containing less polarisable atoms (e.g. fluoropolymers) is generally lower. For this reason fluorine-containing polymers are frequently employed for the outer layer of fibres, the purpose of which is to reflect the ray. Generally finding the right refractive index or choosing a polymer with an appropriate refractive index does not cause problems.

Weakening of the signal along the fibre (which generally is given in units of dB/m or dB/km) is determined by several kinds of absorption and dispersion mechanisms (refs. 3 – 7). To determine the absorption mechanism it is necessary to know the wavelength of the electromagnetic radiation being transported, which is generally in the far visible and the medium infrared range (600 – 1600 nm). Using colourless materials as the relaying agent we do not have to take account of absorption resulting from electron transition, and the most that can happen is that metal ions occurring as trace impurities at the edge of the visible or UV absorption band (of which the absorption coefficient generally decreases exponentially as it moves away from the middle of the band) gives an absorption background that gradually decreases with increasing wavelength. This can be reduced by purifying the monomers employed. The wavelength used is also distant from the infrared range, where the molecular vibrations cause absorption, but there is present an absorption mechanism which is difficult to remove and which is characteristic of the near infrared region: the upper harmonic and combination vibrations (ref. 8). These vibrations as measured by normal spectroscopic methods do not cause strong absorption (since basically they are classified among the so-called prohibited transitions and only appear because of the anharmonicity of the vibrations), but with the longer pathways found in fibres they can cause significant absorption. Figure 2 shows for example the absorption of polymethyl methacrylate fibre in the visible range. The absorption maximum appearing in the range between 600 and 650 nm is an overtone of the stretching vibration of the C-H bond, which can be found with a greater or lesser intensity in all such organic materials containing...
In the course of development attempts have been made to reduce the number of C-H bonds by using deuterated (e.g. perdeutero-PMMA) or halogenated (ref. 9) monomers. The result of this was as shown in Table 1 (ref. 10), but the deuterated and halogenated monomers are much more expensive than the commercial monomers employed in the production of bulk plastics.

In addition to the absorption mechanisms there are numerous dispersion mechanisms which also reduce the transmissibility of the signals. Among these are some (so-called internal scattering mechanisms) which are characteristic of the material itself and cannot be eliminated under ideal processing conditions, such as the Rayleigh scattering, which results from fluctuations in density (in the case of copolymers there is a combined fluctuation). The external scattering mechanisms (e.g. bubbles, particle scattering, fluctuation of the core diameter, birefringence arising from the molecular orientation and its fluctuation, and core/coating interface defects) can be reduced by improving the processing technology.

Many other properties apart from the optical characteristics are also important in polymers used for optical applications. One of these is the heat stability, which is determined primarily by the glass transition temperature. Considering that increasingly polystyrene, poly(methyl methacrylate) and polycarbonate are used in commercial plastic optical fibres (ref. 11), the heat stability is fairly restricted (Table 2). This can be improved to a certain extent by using crosslinked or speciality polymers (e.g. polyimides), but these are fairly expensive.

In addition to heat stability the hydrolytical and thermal stability are also important (which means that the optical and other characteristics are stable in time), as is good processability (melt viscosity), and good adhesion to other materials.

In the case of polymers used for the production of integrated plastic optics (refs. 7 and 12) other considerations also arise, associated for example with photolithographic processability. The path length of integrated polymer-optics is much shorter than with fibres, hence it is possible to use polymers made from monomers with higher losses or which are more expensive (Table 3).

The losses indicated are thus much higher than those given in Tables 1 and 2, since most of the integrated optics are used at the wavelengths (1300 – 1600 nm) employed for inorganic glass fibres, as those must be connected to long-distance communication networks. (For interest it may be noted that the absorption of good quality quartz glass fibres in the range 1300 – 1600 nm is less than 1 dB/km).

Acrylates and methacrylates are very versatile in their processing properties. They can be crosslinked by radical initiators, electromagnetic radiation or corpuscular radiation. In the case of radical polymerisation the molecular weight can be easily regulated, but with photopolymerisation stress-free optical products can be obtained. Between 400 and 700 nm they are fairly transparent, but above 800 nm they show increasing absorbance owing to high harmonic vibrations of the C-H. By choosing appropriate comonomers the refractive index, impact resistance, glass transition temperature and other properties can be varied over a wide range.

### Table 1. Some stages in the development of plastic optical fibres up to 1995 (ref. 1)

<table>
<thead>
<tr>
<th>Company</th>
<th>Core</th>
<th>Coating</th>
<th>Minimum loss, dB/km</th>
<th>( \lambda ), nm</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Du Pont</td>
<td>PMMA</td>
<td>Fluoropolymer</td>
<td>500</td>
<td>650</td>
<td>1968</td>
</tr>
<tr>
<td>Toray</td>
<td>PS</td>
<td>PMMA</td>
<td>1100</td>
<td>670</td>
<td>1972</td>
</tr>
<tr>
<td>Du Pont</td>
<td>PMMA-d(_8)</td>
<td>–</td>
<td>180</td>
<td>790</td>
<td>1977</td>
</tr>
<tr>
<td>Mitsubishi Rayon</td>
<td>PMMA</td>
<td>Fluoropolymer</td>
<td>300</td>
<td>650</td>
<td>1978</td>
</tr>
<tr>
<td>NTT</td>
<td>PMMA</td>
<td>Fluoropolymer</td>
<td>55</td>
<td>568</td>
<td>1982</td>
</tr>
<tr>
<td>NTT</td>
<td>PS</td>
<td>–</td>
<td>114</td>
<td>670</td>
<td>1982</td>
</tr>
<tr>
<td>NTT</td>
<td>PMMA-d(_8)</td>
<td>–</td>
<td>20</td>
<td>650</td>
<td>1983</td>
</tr>
<tr>
<td>Mitsubishi Rayon</td>
<td>PMMA</td>
<td>Fluoropolymer</td>
<td>110</td>
<td>570</td>
<td>1983</td>
</tr>
<tr>
<td>Asahi Chemical</td>
<td>PMMA</td>
<td>Fluoropolymer</td>
<td>80</td>
<td>570</td>
<td>1985</td>
</tr>
<tr>
<td>Fujitsu</td>
<td>PC</td>
<td>Polyolefin</td>
<td>450</td>
<td>770</td>
<td>1986</td>
</tr>
<tr>
<td>NTT</td>
<td>P(5F3DSi)</td>
<td>Fluoropolymer</td>
<td>178</td>
<td>850</td>
<td>1986</td>
</tr>
<tr>
<td>Hitachi</td>
<td>Thermosetting</td>
<td>Fluoropolymer</td>
<td>600</td>
<td>650</td>
<td>1987</td>
</tr>
<tr>
<td>Hoechst Celanese</td>
<td>PMMA</td>
<td>Fluoropolymer</td>
<td>130</td>
<td>350</td>
<td>1991</td>
</tr>
<tr>
<td>Bridgestone</td>
<td>Silicone</td>
<td>Silicone</td>
<td>800</td>
<td>650</td>
<td>1993</td>
</tr>
</tbody>
</table>

PMMA – poly(methyl methacrylate), PS – polystyrene, PC – polycarbonate, P(5F3DSi) – poly(5-fluoro-3-deutero-styrene)
Table 2. Some characteristics of polymers most frequently used for the production of commercial plastic optical fibres (ref. 11)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Refractive index</th>
<th>Loss/wavelength, dB/km/nm</th>
<th>Glass transition temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>1.49</td>
<td>70–100 dB/km/570 nm</td>
<td>105°C</td>
</tr>
<tr>
<td>PMMA</td>
<td></td>
<td>125–150 dB/km/650 nm</td>
<td></td>
</tr>
<tr>
<td>Polycarbonate, PC</td>
<td>1.58</td>
<td>700 dB/km/580 nm</td>
<td>150°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600 dB/km/765 nm</td>
<td></td>
</tr>
<tr>
<td>Polystyrene, PS</td>
<td>1.59</td>
<td>90 dB/km/580 nm</td>
<td>100°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70 dB/km/670 nm</td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Characteristics of polymers used for the production of integrated polymer optics (ref. 7)

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Polymer</th>
<th>Optical loss, dB/km, nm</th>
<th>Other characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allied Signal</td>
<td>Acrylate</td>
<td>2,000 [840]</td>
<td>Birefringence 0.0002 [1550] Crosslinked, Tg 25°C Environmentally stable</td>
</tr>
<tr>
<td></td>
<td>Fluorinated acrylate [Ultradel]</td>
<td>20,000 [1,300]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>50,000 [1,550]</td>
<td></td>
</tr>
<tr>
<td>Amoco</td>
<td>Fluorinated polyimide</td>
<td>40,000 [1,300]</td>
<td>Birefringence 0.025</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100,000 [1,550]</td>
<td></td>
</tr>
<tr>
<td>Dow Chemical</td>
<td>Benzocyclobutene [Cyclotene]</td>
<td>80,000 [1,300]</td>
<td>Tg &gt; 350°C</td>
</tr>
<tr>
<td></td>
<td>Perfluorocyclobutene [XU 35121]</td>
<td>150,000 [1,500]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>25,000 [1,300]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>25,000 [1,550]</td>
<td></td>
</tr>
<tr>
<td>Du Pont</td>
<td>Acrylate [Polyguide]</td>
<td>18,000 [800]</td>
<td>Laminated layer</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20,000 [1,300]</td>
<td>Excimer with laser</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60,000 [1,550]</td>
<td>Mechanically processable</td>
</tr>
<tr>
<td>General Electric</td>
<td>Polyether-imide [Ultem]</td>
<td>24,000 [830]</td>
<td>Heat stable</td>
</tr>
<tr>
<td>JDS Uniphase Photonics*</td>
<td>[Beambox]</td>
<td>60,000 [1,550]</td>
<td>Heat stable</td>
</tr>
<tr>
<td>NTT</td>
<td>halogenated acrylate</td>
<td>2,000 [830]</td>
<td>Birefringence 6 x 10^-6 [1310]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7,000 [1,310]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>170,000 [1,550]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>deuterated polysiloxane</td>
<td>17,000 [1,310]</td>
<td>Environmentally stable</td>
</tr>
<tr>
<td></td>
<td></td>
<td>43,000 [1,550]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>fluorinated polyimide</td>
<td>TE**: 30,000</td>
<td>Environmentally stable</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TM**: 70,000 [1,310]</td>
<td></td>
</tr>
</tbody>
</table>

* previously Akzo Nobel Photonics
**TE: transverse electrical mode, TM: transverse magnetic mode

The breaking elongation of PMMA is high (13%), hence it is quite tough. By adding polyfunctional comonomers the acrylates can be easily crosslinked, which increases their heat resistance. Polystyrene is more rigid than PMMA, but can be controlled during polymerisation, and the structure can be readily modified by comonomers. Polycarbonate has high impact strength, but it cannot be produced by radical polymerisation and is sensitive to ambient stress cracking.

Formerly, halogenated monomers and the polymers made from them attracted considerable interest, but one of the problems with these is that partly halogenated monomers only reduce but do not eliminate the absorption caused by CH harmonic vibrations, while with perfluorinated monomers there is the problem that it is hard to find a material with an even lower refractive index for coating them. Another problem with halogenated acrylates is the relatively low glass transition
temperature (ref. 9). Another interesting attempt has been made to reduce the amount of C-H vibrations: fibres consisting of a strongly crosslinked polysiloxanate ring were made with the aid of lanthanide metal ion catalysts (these latter are also useful in that they also serve as light amplifiers).

4. BRIEF HISTORY OF THE PRODUCTION OF POLYMER OPTIC FIBRES (POF) (REF. 5)

In the seventies two companies were the most active in the development and manufacture of polymer optical fibres (POF): Du Pont in the USA and Mitsibishi Rayon in Japan. In 1974 Mitsubishi patented melt fibre drawing technology (UK 1431157), which can be used to manufacture a PS or PMMA based fibre with a fluorinated polymer coating. In the same year they patented a continuous production process (UK 1449950), which used a high-purity acrylate core and fluoroacrylate coating. The product was marketed as Eska Extra, and had a minimum loss of 125 dB/km at 567 nm. Du Pont experimented firstly with deuterated acrylate fibres, but later withdrew from this market. The Japanese company NTT later reduced the thickness to 567 nm with a loss of 55 dB/km for PMMA core fibres, but in the case of perdeutero PMMA the “record” was 20 dB/km.

Since purity is a basic requirement in fibre manufacture, bulk polymerisation processes are more popular than e.g. emulsion, suspension or other polymerisation methods, since the monomer can easily be purified by distillation. Bulk polymerisation can only be used with monomers where there is no danger of precipitation, where the monomer breaks down the forming polymer, hence most development has concentrated on PMMA and PS.

The production methods include continuous processes and processes employing batch polymerisation followed by continuous extrusion, and there are also processes starting with performs that copy the manufacturing technology for optical glass fibres. In he continuous polymerisation methods the monomer + polymer system is degassed as it becomes viscous, a part of the monomer residue is removed during extrusion, and the coating is applied by continuous coextrusion. The advantage of the continuous method is that it gives a high production capacity, and the disadvantage is that it is not simple, and can give rise to degradation of the melt and metal contamination. With the batch methods firstly the high-purity polymer is prepared in a separate stage by bulk polymerisation, and this is then processed by extrusion. Such a process for example was patented by NTT in 1981 (GB 2089325). This method is simpler than continuous polymerisation and involves less chance of impurities. The stretching process starting with a preform is theoretically very simple: a larger diameter bulk-polymerised cylinder is heated at the end (in the case of PMMA to 200 – 250°C) and the fibre at the right viscosity is wound onto it. The fibre thickness is determined by the winding speed. The coating component can be present in the preform or it can be applied from the outside during the fibre drawing process. Using this technology it is easier to produce low-loss fibres, since the heat degradation is lower, and it is easier to work out the continuously changing refractive index profile (even in the perform).

5. DEVELOPMENT OF POLYMER FIBRES WITH A GRADUALLY CHANGING REFRACTIVE INDEX

In the 80s, particularly in Japan a lot of effort was devoted to developing methods of manufacturing fibres with a predetermined refractive index profile. One of the earliest attempts consisted of swelling a partially polymerised perform with a monomer having a lower refractive index, then polymerising the whole system (ref. 14). Later they introduced the so-called random interfacial gel polymerisation technique (ref. 15), in which a PMMA tube is filled with a mixture of two monomers. The M1 monomer has a lower refractive index and lower molecular weight, and M2 has a higher refractive index and weight. Polymisation is initiated at 80 – 100°C, and this starts from the PMMA wall, which is preferentially swollen by the monomer M1. Because of the gel effect the polymerisation proceeds inwards from the outside and since the monomer M1 diffuses more readily into the gel, a concentration gradient is formed. When selecting the monomers (here methyl methacrylate and benzyl methacrylate were used) it is necessary to consider not only the refractive indices but also the copolymerisation constants, so that approximately random copolymers are formed. Later (refs. 16 and 17) the method was modified, replacing the monomer M2 with a non-reactive molecule such as bromobenzene with a higher refractive index. Since the mobility of the non-reactive molecules is relatively high, it was necessary to investigate particularly the problem of heat stability (ref. 18) and possibilities of improving it. Refractive index modifying additives had to be found which do not soften the PMMA matrix and which diffuse at lower rate into the matrix (molecules with a more rigid structure). Finally a series of aromatic compounds were tested, including triphenyl phosphate, diphenyl sulphone, benzyl benzoate and diphenyl sulfoxide which were found to be effective.

6. ORGANIC-INORGANIC HYBRIDS AS THE PROMISE FOR THE FUTURE

The boundary between organic and inorganic chemistry has become increasingly indistinct in recent years. Reasons for this include the development of metal-organic chemistry, ceramic-precursor polymers and of sol-gel technology.
Sol-gel technology appeared firstly as an alternative glass production technology. The essence of this technology is that compounds having the composition M(OR)n (where M is a metal or semi-metal, and R is an alkyl or aryl group) are hydrolysed. During this process hydroxides (sols or gels) having the composition M(OH)n, are first formed, and then by condensation mixed oxy-hydroxyl gels, then after drying and heating ceramics and glasses having a well-defined composition can be obtained. In this way high-purity or special-composition bulk glasses, or rather coatings or fibres can be produced. (The difficulty of diffusion prevents the production of solid bulk glasses in greater thicknesses). The idea is very simple, but the practical execution is more of an art than a science, since the quality of the product is affected by many parameters.

The other rapidly developing technology was the development of metal-organic coupling agents or adhesion promoters. These silane and more rarely titanate compounds also contained alkoxy groups as reactive organic groups, and so were useful in that they react with any glass surfaces containing an inorganic silanol group or any plastics and form a bridge between otherwise incompatible phases. An essential step in this reaction is that the alkoxy groups of the coupling agent hydrolyse and the silanol groups condense with each other and with the inorganic surface.

The most recent development has been to use coupling agents or molecules with similar structures as materials in their own right rather than for modification of inorganic fillers: the functional groups on the surface of nanoclusters formed by the effect of hydrolysis (e.g. epoxy groups, isocyanate groups, amine groups, unsaturated functional groups) were reacted with the type of liquid resins with which they are capable of reacting. In this way depending on the ratio of organic to inorganic materials nano-reinforced polymers or inorganic glasses made impact-resistant by organic material are formed which already show practically no organic glass transition. The optical applications of the idea are obvious: the refractive index and mechanical properties of the material are continuously changeable and can be planned, heat stability is better than with pure polymers, and so on.

With hydrolysis of tetraethoxy silicate and parallel radical polymerisation of acrylate monomers for example low shrinkage, crack-free, transparent monolithic optical materials can be produced (ref. 19). The method can be extended also to fluorine-containing monomers (ref. 20). Elastic transparent optical gels can be prepared by functionalising perfluorinated polyether-diol with mercaptopropyltrimethoxysilane and crosslinking with tetraethoxy silane. By reacting perfluoroalkyl silanes, vinyltrimethoxy silane and tetraethoxy silane transparent, crack-free, water-repellent gels can be produced. Numerous patents describe these or comparable systems for the manufacture of optical coatings, fibres or even lenses, and the use of organic-inorganic hybrids is extending also to integrated optics.

7. PRINTED OPTICAL CIRCUITS

It is interesting to note that in addition to rapid prototype production ink-jet technology has also been successful in the sphere of micro-optics (ref. 21). During the process a 25 – 50 µm diameter optical polymer melt was added by drops to predetermined optical substrates, and in this way 40 – 1000 µm optical components (lenses, waveguides) can be formed flexibly and cheaply (not using lithographic methods). The method is also suitable for the automated manufacture of graded index elements. Micродrops “fired” at temperatures above 200°C immediately fuse on impact and form homogenous products.

8. CONCLUSIONS

The data presented above show that polymers have contributed significantly to the rise of optical information technology, and if this rate of development continues there is no doubt that they will also replace inorganic glass in other spheres.

REFERENCES

21. W.R. Cox and T. Chen, Optics and Photonics News, 12, No.6, 2001, p.32. (No date given)