Optical and thermal properties of methyl methacrylate and pentafluorophenyl methacrylate copolymer: Design of copolymers for low-loss optical fibers for gigabit in-home communications

Kotaro Koike [a,b,*], Takahiro Kado [a,b], Zen Satoh [a,b], Yoshiyuki Okamoto [b,c], Yasuhiro Koike [a,b]

[a] Graduate School of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kouhoku-ku, Yokohama 223-0061, Japan
[b] Koike Photonics Polymer Project, ERATO-SORST, Japan Science and Technology Agency, Shinkawasaki Town Campus, 7-1 Shinkawasaki, Saiwai-ku, Kawasaki 212-0032, Japan
[c] Polymer Research Institute, Polytechnic Institute of NYU, 6 Metrotech Center, Brooklyn, NY 11201, USA

ARTICLE INFO

ABSTRACT

As a novel base material for low-loss graded index plastic optical fibers (GI POFs) in gigabit home networks, a copolymer of methyl methacrylate (MMA) and pentafluorophenyl methacrylate (PFPMA) was prepared and its thermal and optical properties were investigated. When the PFPMA content in the monomer feed was 0–50 mol%, both the glass transition temperature (T_g) and the decomposition temperature of the copolymer were higher than that for PMMA, which is the base material for many commercially available POFs. The transmittance of the copolymer was also found to be higher than that of PMMA since it has fewer C–H bonds per unit volume. As the core material of GI POFs, MMA-co-PFPMA (65/35 mol%), which had the highest T_g of 118 °C was utilized. A low-loss GI POF with an attenuation of 172–185 dB/km at the emission wavelengths of a high-speed light source (670–680 nm) was successfully obtained for the first time.

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1. Introduction

With rapidly increasing interest in fiber-to-the-home (FTTH) services and digital consumer electronics, the demand for high-speed home networks connecting several devices such as PCs, TVs, and other home electric appliances is increasing. Systems using a graded index plastic optical fiber (GI POF) [1,2] as the transmission medium and a vertical-cavity surface-emitting laser (VCSEL) [3] as the light source are expected to be the leading medium for realizing gigabit in-home communications, but there is still a big problem that needs to be solved. Given the laying distance in a house (30–50 m), the POF attenuation needs to be less than 200 dB/km. For GI POF based on poly(methyl methacrylate) (PMMA), which is the base material for most commercially available POFs, the wavelengths satisfying this requirement are limited to 570 and 650 nm because of C–H stretching vibrational absorption losses [4]. However, the emission wavelengths of long-life and inexpensive VCSEL are 670–680 nm. Thus, the development of

novel base materials with low-loss characteristics is one of the most pressing issues.

To decrease the C–H absorption losses, substituting hydrogen with heavier atoms such as deuterium or fluorine is an effective method. There have been previous reports on low-loss POFs consisting of perdeuterated PMMA (PMMA-d_8) [5] and perfluorinated polymer (CYTOP®) [6]. While they have excellent low-loss characteristics, these polymers are expensive and hence the fibers are overpriced for general consumers when the core diameter is as large as several hundreds micrometer. In addition, the high performance they provide is not necessary for the very short reach networks in houses, and less expensive materials with the required attenuations are desired.

Over the last few years, we have explored the potential of partially halogenated polymers. In past studies, we succeeded in preparing low-loss GI POFs with attenuations of less than 200 dB/km at 670–680 nm wavelengths [7,8]. However, some serious problems regarding thermal properties were not solved. To utilize GI POFs in a house, both low-loss characteristics and adequate thermal stability are necessary. One important requirement is a high glass transition temperature (T_g). The operating temperature limit required for a house is 70 °C. Since the temperature limit is generally T_g – 20 °C, the T_g for GI POF must be over 90 °C. Moreover, the difference in T_g between the base material and the actual core must be considered. The parabolic refractive index profile in the GI POF core region is

* Corresponding author. Koike Photonics Polymer Project, ERATO-SORST, Japan Science and Technology Agency, Shinkawasaki Town Campus, 7-1 Shinkawasaki, Saiwai-ku, Kawasaki 212-0032, Japan. Tel.: +81 445801597; fax: +81 445801433.
E-mail address: koutarou.k@z3.keio.jp (K. Koike).

formed by adding a low-molecular-weight dopant, which lowers the T_g by 10–20 °C through the plasticization effect [9]. Thus, the core base material should have a T_g of at least 110 °C, which is higher than that for PMMA. Another parameter is a high decomposition temperature. To produce inexpensive GI POFs, we will eventually have to continuously fabricate GI POFs using the co-extrusion process [10]. In this process, polymer bulks are melted at over 200 °C for several hours; polymers with low decomposition temperatures would degrade during the fabrication process. We have already clarified that GI POFs based on PMMA can be prepared without any thermal degradation by the co-extrusion process, and the decomposition temperature of PMMA is an indication.

In this paper, we report on a novel GI POF based on a partially fluorinated copolymer with lower loss and higher thermal stabilities than those of PMMA. For the core material, a copolymer of MMA and pentafluorophenyl methacrylate (PFPMA) was utilized. The T_g and 5% weight loss temperature of poly(PFPMA) are 130 °C and 317 °C, respectively [11], which are much higher than those for PMMA. One of the notable features of poly(PFPMA) is that its polymerization proceeds to a low conversion. In the co-extrusion process, the residual monomers lead to numerous bubbles that increase the attenuation of the fiber. Thus, we tried to reduce the amount of remaining monomer by utilizing copolymerization. There were two main reasons for choosing MMA as a comonomer of PFPMA. The first was their different reactivities to copolymerize. When MMA is M_1 and PFPMA is M_2, r_{12} and r_{21} are 0.56 and 1.30, respectively [12]. This indicates that PFPMA preferentially polymerizes; therefore, we believed that the amount of unreacted PFPMA would be reduced by the copolymerization with MMA. The second was their refractive indices. In general, copolymers tend to have extremely high scattering losses due to the large heterogeneous structure and the corresponding heterogeneity of refractive index. Consequently, copolymers have not been the leading candidate for POF base materials. However, in this copolymeric system, the increment in scattering loss is negligibly small since the refractive indices of both homopolymers are almost the same (PMMA: $n_D = 1.4914$, poly(PFPMA): $n_D = 1.4873$). Moreover, the percentage of C–H bonds per unit volume of poly(PFPMA) compared with that of PMMA is only 34%, so smaller absorption losses and lower attenuation can be expected.

2. Experimental

2.1. Materials

Methyl methacrylate, pentafluorophenyl methacrylate, and 2,2,2-trifluoroethyl methacrylate were purchased from Mitsubishi Gas Chemical Co. Inc., SynQuest Laboratories Inc. (Alachua, FL), and Tosoh F-Tech Inc., respectively. Methanol, chloroform, tetrahydrofuran (THF), benzoyl peroxide (BPO), *n*-butyl mercaptan (nBM), *n*-lauryl mercaptan (nLM), and diphenyl sulfide (DPS) were purchased from Wako Pure Chemical Industries Inc. Di-tert-butyl peroxide (DBPO) was purchased from NOF Corporation. Monomers were freshly distilled before use, and all other chemicals were used directly without further purification.

2.2. Polymer preparation

Monomer mixtures with DBPO as an initiator and nBM as a chain transfer agent were transferred into glass ampules and subjected to repeated freeze–pump–thaw cycles; this was followed by sealing under vacuum with flame. The polymerization reactions were carried out at 100–130 °C in oil baths for 48 h. The obtained bulks were dissolved in chloroform and precipitated from a large amount of methanol with vigorous stirring. The purified polymer
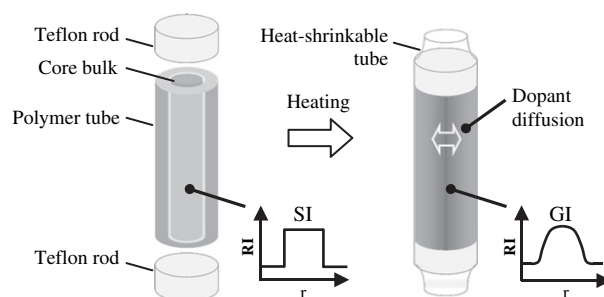

Fig. 1. Schematic diagram of the rod-in-tube method.

samples were dried under vacuum at 50 and 90 °C for 24 h at each temperature to allow the solvents to evaporate.

2.3. GI POF fabrication

In a batch process, GI POFs can be obtained by heat drawing preforms with GI profiles in their core regions. In a previous study, we prepared GI preforms using an interfacial-gel polymerization technique [4]. This method has the advantage of being able to precisely control the refractive index profile, whereas the scattering loss of the core region tends to greatly increase when the core and cladding consist of different materials. In the interfacial-gel polymerization technique, the core monomer is polymerized within the polymer tube (i.e., cladding layer of GI POF), and the inner wall of the polymer tube is slightly dissolved into the core solution during the polymerization process. When the dissolved and core polymers have different refractive indices, a large heterogeneous structure is formed, leading to an extremely high scattering loss. Therefore, this method is not appropriate for preparing GI POFs from various materials. In addition, the mechanism for forming a graded refractive index profile is different from that for the co-extrusion process. Thus, in this study, we prepared GI preforms using a rod-in-tube method. The schematic diagram is shown in Fig. 1. In the rod-in-tube method, a core rod with a dopant and a cladding tube are prepared separately. The core rod was prepared in the same manner without purification as mentioned in Section 2.2. For the dopant, DPS ($n_D = 1.633$) was added to the core solution. The cladding tube was prepared as follows. A glass tube containing monomers—0.20 mol% BPO as the initiator, and 0.28 mol% nBM as the chain transfer agent—was rotated on its axis at 3000 rpm in an oven at 70 °C for 3 h. The monomer mixtures were placed on the inner wall of the glass tube through centrifugal force and polymerized. After heat treatment at 90 °C for 24 h, a polymer tube was obtained as a cladding layer for a GI preform. The core rod was inserted into the tube, and both ends were closed with Teflon rods. The rod was then covered with a heat-shrinkable tube and heated in an oven at 150 °C for 24 h. During the heat treatment, the core rod and cladding tube adhered to each other; the dopant diffused into the cladding layer, forming the GI profile. This way, the scattering loss for the core region did not increase since both layers consisted of similar polymers. The mechanism of the dopant diffusion obeys Fick's law and is the same as for the co-extrusion process. The heat drawing for the GI preform was carried out at 220–240 °C, and the fiber diameter was controlled to be 600 μm.

Table 1
Preparation conditions for copolymer bulks.

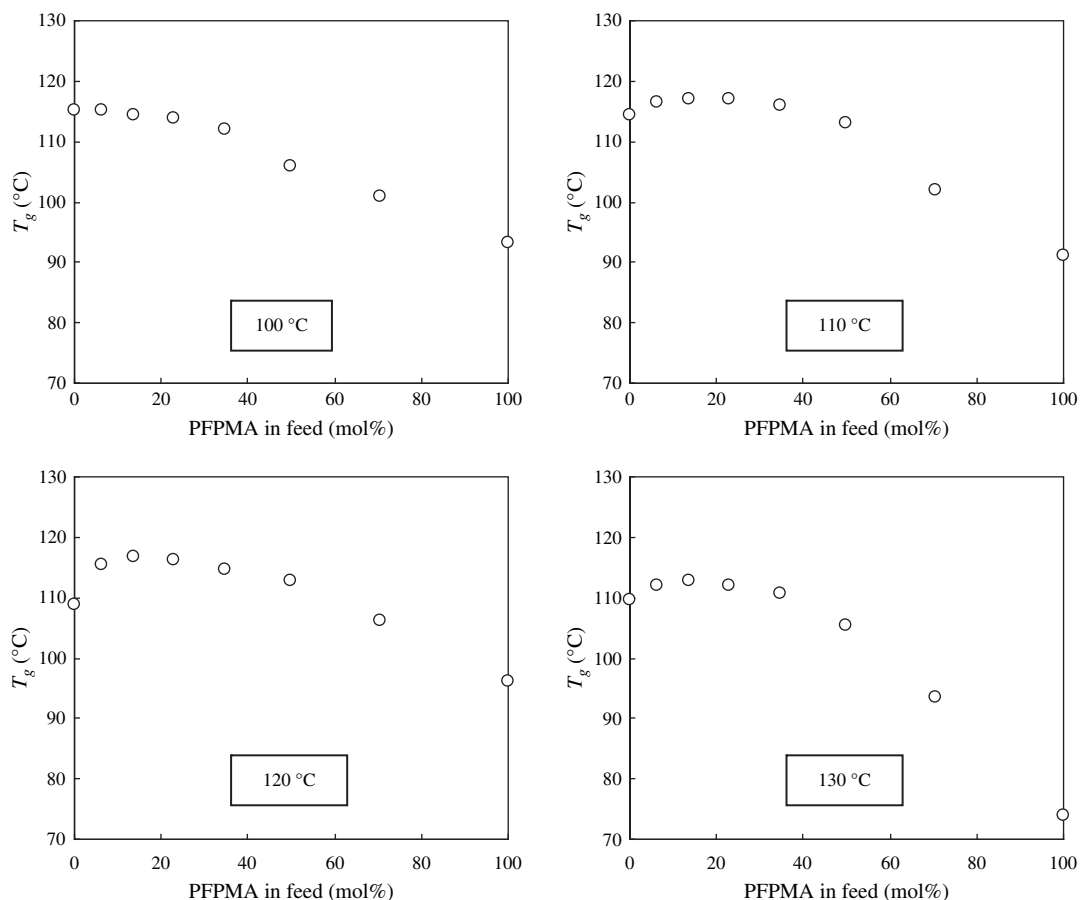| DBPO	nLM	Temperature	Time
0.01 mol%	0.125 mol%	100–130 °C	48 h

Fig. 2. Composition dependence of glass transition temperature for MMA-*co*-PFPMA bulks polymerized at 100–130 °C for 48 h.

2.4. Characterization techniques

T_g measurements were performed on a differential scanning calorimeter (DSC-60, Shimadzu Co.). All polymer samples were heated under an air atmosphere from room temperature to 150 °C, then cooled to 0 °C and reheated to 150 °C at a scanning rate of 10 °C/min. T_g was measured during the second heating scan as the midpoint of the heat capacity transition between the upper and lower points of deviation from the extrapolated liquid and glass lines. The weight percent of the remaining monomer in the polymer bulk was measured by gas chromatography (GC-2010, Shimadzu Co.) as follows. The polymer bulk was dissolved in a small amount of chloroform; methanol was then added to precipitate the polymer. The monomer concentration in the supernatant was determined from the corresponding peak area of the gas chromatograph. TG analyses were carried out under air using a thermogravimetry and differential thermal analysis instrument (TG/DTA-6200, SII Nano Technology Inc.) at a scanning
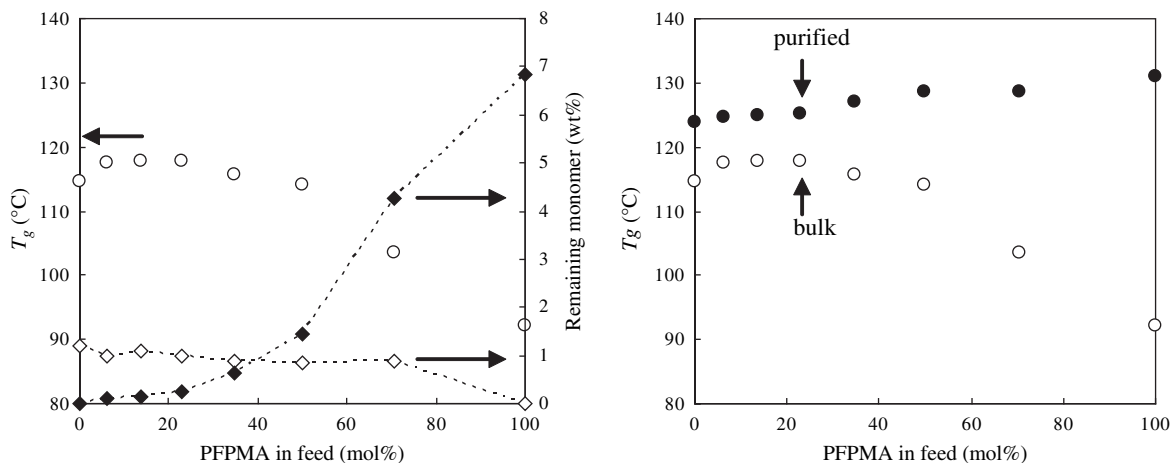

Fig. 3. (Left) T_g plots of MMA-*co*-PFPMA bulks polymerized at 110 °C for 48 h (○) and the amount of remaining MMA (◇) and PFPMA (◆) monomer in the bulks against the PFPMA content in the monomer feed. (Right) Comparison of T_g between bulks (○) and purified copolymers (●).
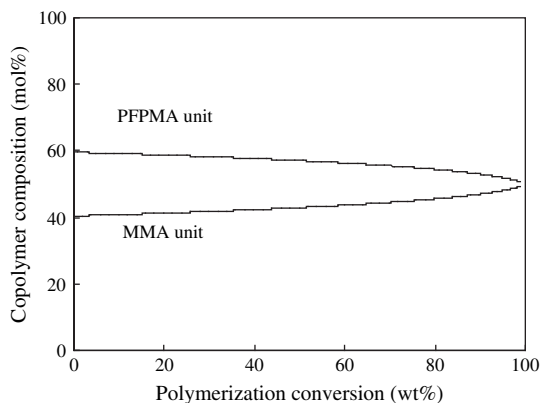
Fig. 4. Change in accumulated copolymer composition with polymerization conversion when the MMA and PFPMA contents in the monomer feed are 50 mol%.

Fig. 6. Change of 5% weight loss temperatures for MMA-co-PFPMA bulk and purified polymers against PFPMA in the monomer feed.

rate of 10 °C/min from room temperature to 450 °C. The weight-average molecular weight (M_w) of the polymers was estimated by gel permeation chromatography (GPC-LC20AD, Shimadzu Co.) using THF as the eluent at a flow rate of 0.6 mL/min. The molecular weight calibration curve was obtained using polystyrene standards. The density of the polymer bulk was measured through the water displacement method. The refractive indices were measured using a prism coupling method (Model 2010, Metricon Co.). The probe wavelengths in the prism were 409.2, 650.3, 833.7, and 1546 nm. Transmittance of the polymer bulk was measured with a spectrophotometer (U-2800A, Hitachi Ltd.) at a scanning rate of 100 nm/min. The end faces of the polymer rods were polished and the sample lengths were 3.0 cm. Water absorptions of the polymer bulk were measured as follows. Polymer bulks were prepared to have the exact same volume (ϕ12 × 10 mm); these samples were then immersed in pure water at 75 °C, and the time series variation of their weights was measured.

The attenuation spectra of GI POFs were measured through the cut-back method. A tungsten lamp (AQ-4303B, Ando Electric Co, Ltd) and spectrum analyzer (AQ-6315R, Ando Electric Co, Ltd) were used as the light source and detector, respectively. The −3 dB bandwidth of the GI POF was evaluated through the time domain method. For the light source, a laser diode with a 650-nm wavelength was adopted. An input pulse generated by the pulse generator was inserted into the GI POF through a single mode silica optical fiber (SMF) with core diameter of 5 μm. The refractive index profile of the core region was estimated through the near field pattern (NFP) method. A laser diode with a 650-nm wavelength and a SI POF with a core diameter of 400 μm were utilized as the light
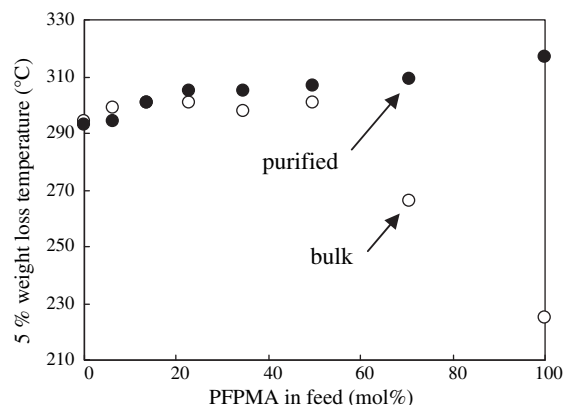
source and probe fiber, respectively. The NFP was measured using a charge-coupled device (CCD) camera set (LEPAS-11, Hamamatsu Photonics K.K. Co, Ltd).

3. Results and discussion

3.1. Thermal properties of MMA-co-PFPMA

The relationship between the T_g of the MMA-co-PFPMA bulk and PFPMA content in the monomer feed was examined. A previous study clarified that poly(PFPMA) has a low ceiling temperature and the polymerization temperature strongly affects the conversion—i.e., the T_g of the bulk [11]. Thus, the copolymerizations were carried out at 100, 110, 120, and 130 °C, and all copolymer bulks were analyzed. The preparation conditions and results are presented in Table 1 and Fig. 2, respectively. The numbers in Fig. 2 denote the polymerization temperature.

T_gs for copolymers can generally be described by the Gordon–Taylor equation [13] and changes linearly with the weight fractions of the monomer content. For this copolymeric system, however, it was interesting to observe that the T_g plots exhibited positive deviations at all polymerization temperatures. While the abscissa axes of Fig. 2 are the molar fraction of PFPMA in the monomer feed, the results are similar even if it is converted to the weight fraction. T_g for PMMA is in the range of 109–114 °C and the influence of the polymerization temperature is small. On the other hand, for poly(PFPMA), T_g is 91–96 °C when the polymerization temperature is 100–120 °C, but it drastically decreases to 74 °C when polymerized
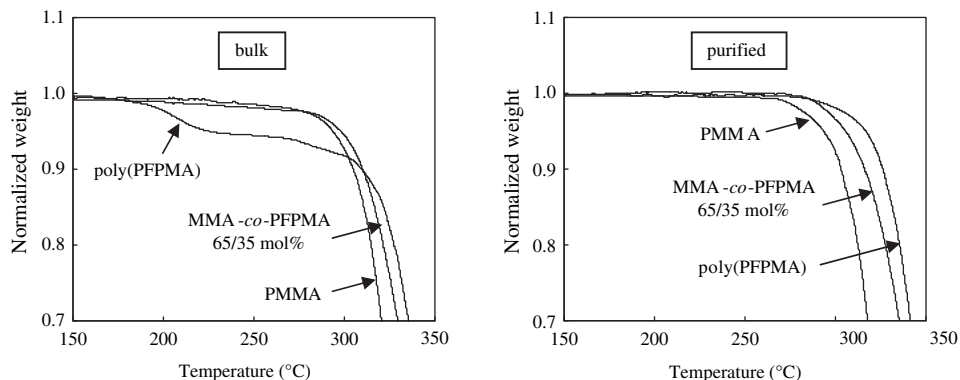

Fig. 5. Thermogravimetric curves of PMMA, MMA-co-PFPMA (65/35 mol%), and poly(PFPMA) measured under air at a scanning rate of 10 °C/min. Left and right figures show bulk and purified polymers, respectively.
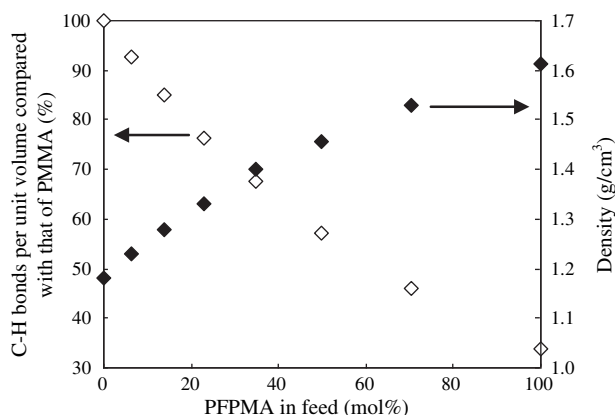
Fig. 7. Density and percentage of C–H bonds per unit volume compared with that for PMMA of copolymer bulks against the PFPMA content in the monomer feed.

Fig. 8. Transmittance spectra of PMMA, MMA-*co*-PFPMA (65/35 mol%), and poly(PFPMA) bulks. The optical path was 3.0 cm.

at 130 °C. To discuss the results shown in Fig. 2 in detail, the amount of remaining monomers in the bulks polymerized at 110 °C—which provided the highest T_g—was determined. Additionally, T_g for the purified polymers obtained by precipitating the same bulks was also analyzed. Although there seemed to be no big difference in T_g for the polymerization temperatures of 110 °C and 120 °C, the bulks polymerized at 120–130 °C tended to have some voids caused by the volume contraction. Thus, the polymerization temperature was fixed to 110 °C in this study. The result is shown in Fig. 3.

The amount of remaining MMA in all bulks except for poly(PFPMA) was about 1 wt% and was nearly independent on the monomer feed composition, while the remaining PFPMA underwent many changes. While approximately 7 wt% of unreacted PFPMA remained in the poly(PFPMA) bulk, the amount of PFPMA drastically decreased after copolymerizing with MMA. This may be derived from the monomer reactivity ratios. Fig. 4 shows the change in copolymer composition with the polymerization conversion calculated by the Mayo–Lewis equation. Here, r_{12} and r_{21} (M_1: MMA, M_2: PFPMA) are 0.56 and 1.30, respectively [12], and the initial monomer content in the feed is 50/50 mol%. The details of the theory and calculated procedure are described elsewhere [1,14].

Given ideal polymerization, PFPMA polymerizes preferentially; the polymer consisted of 60 mol% PFPMA units in the initial stage. As a result, the PFPMA conversion was improved with the presence of MMA. On the other hand, Fig. 3 (right) indicates that the T_g of purified copolymer with no remaining monomers linearly increased as the PFPMA content in the monomer feed increased due to the high T_g of poly(PFPMA). Fig. 3 shows that the T_g of the copolymer bulk increased with increasing PFPMA content when the bulk had a small amount of remaining monomers, while it decreased when the bulk has a lot of remaining monomers due to the plasticization effect. This is why the T_g plots for the copolymer bulks exhibited positive deviations. The most important point about these experiments is that the copolymer bulks had higher T_g than PMMA when the PFPMA content in the monomer feed was 0–50 mol%.

Table 2
Refractive indices of PMMA, MMA-*co*-PFPMA (65/35 mol%), poly(PFPMA) bulks.[a,b]

MMA (mol%)	PFPMA (mol%)	Refractive index			
		409.2 (nm)	650.3 (nm)	833.7 (nm)	1546 (nm)
100	0	1.5054	1.4886	1.4851	1.4794
65	35	1.5005	1.4807	1.4760	1.4699
0	100	1.5076	1.4838	1.4786	1.4717

[a] The polymerization reactions were performed at 110 °C for 48 h with DBPO (0.01 mol%) and nLM (0.125 mol%).
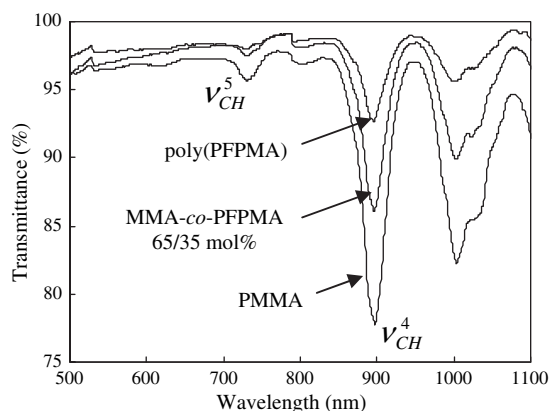[b] Monomer conversions were 93–99 wt%.

Thermogravimetric curves of the bulk and purified polymers and the 5% weight loss temperature of these samples are shown in Figs. 5 and 6, respectively.

For purified polymers, the thermogravimetric curves are shifted to higher temperature with increasing PFPMA content since the 5% weight loss temperature of poly(PFPMA) was as high as 317 °C. On the other hand, the weight of poly(PFPMA) bulk began to decrease at 190 °C due to the vaporization of the remaining 7 wt% of the monomer. However, the curve of the copolymer bulk was almost the same as the purified one due to the small amount of remaining monomers in the bulk. Fig. 6 indicates that the copolymer bulks had higher decomposition temperatures than PMMA when the PFPMA content in the monomer feed was lower than approximately 50 mol%.

3.2. Optical properties of MMA-co-PFPMA

In this section, the optical properties of the copolymer bulk obtained in Section 3.1 are discussed. The preparation conditions were the same as shown in Table 1, and the polymerization temperature was 110 °C. Since the wavelengths of the high-speed light source (670–680 nm) were located in the tail of the 5th overtone of C–H stretching vibrational absorption, reduction of the C–H bonds per unit volume of polymers is the most effective way of lowering the attenuation. The number of C–H bonds per unit volume n can be estimated by the density of the bulk and is calculated from Eq. (1) for this copolymeric system.
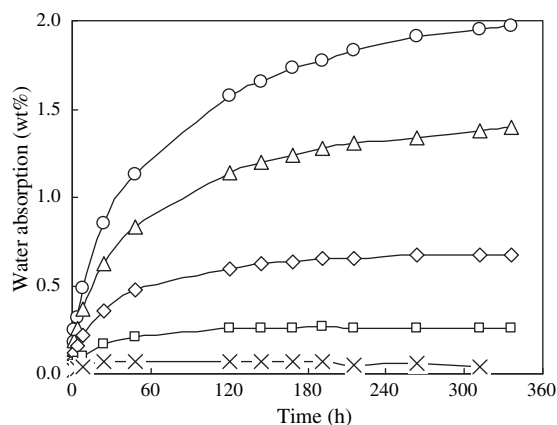

Fig. 9. Time series variation of water absorption measured with water at 75 °C. The sample volumes were φ10 × 10 mm. The PFPMA contents in the monomer feed were 0 (○), 6 (△), 23 (◇), 50 (□), and 100 (×) mol%.
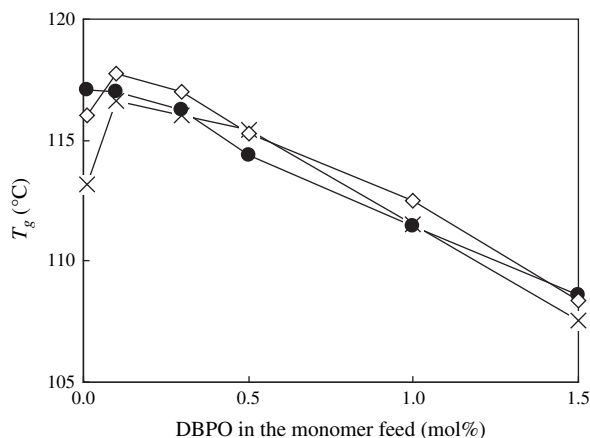
Fig. 10. Relationship between the amount of DBPO and T_g of the copolymer bulks. The PFPMA contents in the monomer feed were 23 (●), 35 (◇), and 50 (×) mol%.

$$n = \left(\frac{8w_1}{m_1} + \frac{5w_2}{m_2}\right)dN_A \qquad (1)$$

where d is the density of the bulk, w_1 and w_2 are weight fractions of MMA and PFPMA, m_1 and m_2 are molecular weights of MMA and PFPMA, and N_A is Avogadro's number. Fig. 7 shows the data from the density measurement of copolymer bulks and the percentages of C–H bonds per unit volume compared to PMMA.

While the number of C–H bonds per PFPMA monomer unit is five, which is smaller than that for MMA by only three, the amount per unit volume of poly(PFPMA) is as small as 34% of that for PMMA due to the bulky structure. Accordingly, the percentage of C–H bonds per unit volume of the copolymer decreased as the PFPMA content in the monomer feed increased. The transmittance of the copolymer bulk with a PFPMA content of 35 mol% was measured and compared with those for PMMA and poly(PFPMA). To evaluate the data precisely, the measured transmittance (X) was corrected as below to take the light reflections at the end faces of the bulks into account.

$$T = X/(1 - R)^2 \qquad (2)$$

where T is the actual transmittance and R is the reflectance ratio. When the light enters the surface vertically, the reflectance ratio can be described by the following expression.

$$R = [(n_1 - n_2)/(n_1 + n_2)]^2 \qquad (3)$$

where n_1 and n_2 are the refractive indices of polymer bulk and air, respectively. The refractive indices of the bulks were measured by the prism coupling method, and the data are summarized in Table 2. n_1 for each wavelength was calculated by the Sellmeier equation, and n_2 was approximated as 1.0003. The revised transmittance spectra are shown in Fig. 8.

The strong peaks at 720 and 900 nm correspond to the 5th and 4th overtones of C–H vibration, respectively [15]. The copolymer had 68% C–H bonds per unit volume compared to PMMA, as shown in Fig. 7; this resulted in the smaller C–H absorption intensity for the transmittance spectrum. Moreover, a conspicuous increment in the scattering loss, which is one of the specific characteristics of copolymers, was not observed. In general, when both monomer reactivity ratios are not equal to unity, large heterogeneous structures of refractive index are formed and the copolymers tend to have extremely high scattering losses. However, since PMMA and poly(PFPMA) have almost identical refractive indices, as shown in Table 2, the increment in scattering loss is negligible and the effect on reducing C–H absorption is enhanced in this copolymeric system. The copolymer bulk was clarified as having a higher transmittance at broad wavelengths than PMMA.

To keep using the copolymeric fiber as a transmission medium for home networks, low attenuation should be maintained for a long time. The most serious cause of attenuation degradation is water absorption. For the wavelength region of 670–680 nm, the 4th O–H stretching vibration and O–H bending vibration combine. Kaino reported that the attenuation of a POF based on PMMA considerably increased in a humid environment [16]. The water absorption of the polymer bulks was measured by immersing the samples in water at 75 °C and is shown in Fig. 9.

The saturated water absorption of poly(PFPMA) is as small as 0.04 wt% and is 1/50 of the absorption for PMMA. This is due to fluorine and the smaller amount of carbonyl groups per unit volume, which tend to produce hydrogen bonds with water molecules. The saturated water absorptions of the copolymers with PFPMA contents of 6, 23, and 50 mol% were 1.4, 0.68, and 0.25 wt%, respectively. Based on these results, GI POFs based on the copolymer can be expected to have good humid stability.

3.3. Effect of the amount of initiator on T_g of copolymer bulks and its optimization

We prepared MMA-*co*-PFPMA in the same manner as shown in Table 1 and investigated the thermal and optical properties. Next, the optimum preparation condition that provides the highest T_g is discussed by focusing on the amount of initiator. As shown in Fig. 2, we confirmed that the copolymer has the highest T_g at 117 °C when
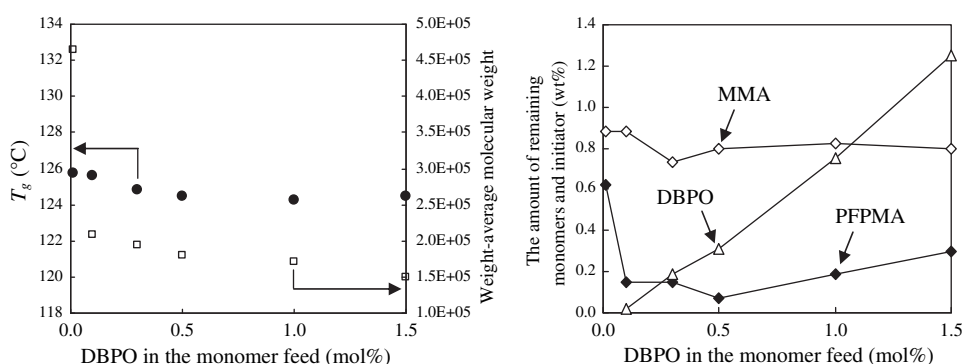

Fig. 11. (Left) Relationship between the amount of DBPO in the monomer feed, T_g of purified polymers, and weight-average molecular weight. (Right) Amount of remaining monomers and DBPO in the copolymer bulks against the amount of DBPO in the monomer feed. The PFPMA content in the monomer feed was 35 mol%.
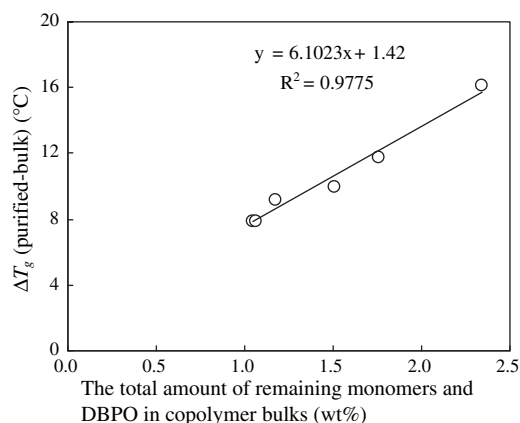
Fig. 12. Relationship between the total amount of remaining monomers and DBPO in copolymer bulks and ΔT_g (purified – bulk). The PFPMA content in the monomer feed was 35 mol%.

Table 3
Optimum preparation conditions for copolymer bulks.

MMA	PFPMA	DBPO	nLM	Temperature	Time
65 mol%	35 mol%	0.1 mol%	0.125 mol%	110 °C	48 h

the PFPMA content and amount of DBPO are 23 and 0.01 mol%, respectively. From the data, the maximum T_g should be obtained when the PFPMA content is at 23–50 mol% by increasing the amount of added DBPO. Fig. 10 shows the T_g plots of the copolymer bulks with PFPMA contents of 23, 35, and 50 mol% versus the amount of added DBPO.

The copolymer bulk was found to have the highest T_g of 118 °C when the PFPMA content and amount of added DBPO were 35 and 0.1 mol%, respectively. Interestingly, increasing the DBPO to more than 0.1 mol% lowered the T_g of the bulks. We can surmise two possible factors for this phenomenon: either T_g of the polymer decreased with the reduction in molecular weight, or by the presence of low-molecular weight compounds which plasticized the bulk. The T_g of purified copolymer with a PFPMA content of 35 mol%, the weight-average molecular weight, and the amount of unreacted monomers and DBPO were measured.

The molecular weight decreased from 460,000 to 150,000 as the amount of added DBPO was increased from 0.01 to 1.5 mol%, while the T_g of the purified copolymers were almost the same. On the other hand, while the amount of remaining MMA was 0.8–0.9 wt%

in all cases, the remaining PFPMA decreased from 0.6 to 0.07 wt% when the added DBPO increased from 0.01 to 0.1 mol%. In addition, the amount of unreacted DBPO increased against the amount of added DBPO in the feed. Fig. 12 shows the relationship between the ΔT_g (purified – bulk) and the total amount of remaining components in the bulk.

The approximated line by the least-square method goes through near the zero point; this means that the plasticization effect from the remaining monomers and unreacted DBPO decreased the T_g of the copolymer bulks. Therefore, the copolymer bulk had the highest T_g when the amount of added DBPO was 0.1 mol% and produced the fewest remaining components, as shown in Fig. 11 (right). The optimum preparation conditions for T_g are summarized in Table 3. In the following investigation, the copolymer bulks prepared with these conditions were utilized.

3.4. Preparation and characterization of core and cladding polymers

As a dopant that forms a parabolic refractive index profile in the core region of the GI POF, DPS was selected. DPS is a common dopant for GI POFs based on PMMA and shows a good compatibility with MMA-*co*-PFPMA. Copolymer bulks with several amounts of DPS were prepared under the conditions shown in Table 3, and the T_g and refractive index were measured. For comparison, the same experiments were carried out with PMMA. The results are shown in Fig. 13.

Note that the refractive index of the copolymer was slightly lower than that for PMMA. The data summarized in Table 2 indicate that the copolymer had a lower refractive index than both PMMA and poly(PFPMA). This is because the copolymer had a larger free volume since the MMA and PFPMA sizes are quite different. Thus, the copolymer with DPS had a lower T_g than PMMA by approximately 15 °C when they had the same refractive index.

An important parameter that indicates the appropriate amount of dopant is the numerical aperture (*NA*), which is expressed as follows:

$$NA = \sqrt{n_1 - n_2} \tag{4}$$

where n_1 and n_2 are the refractive indices of the core middle and cladding layer, respectively. To confine the light into the core region, a *NA* of over 0.2 is desired. In other words, the necessary amount of dopant depends on the kind of cladding material. For instance, if we use a copolymer with the same composition as the core, the refractive index of the core must be over 1.4971 to obtain a *NA* of 0.2 from the following equation:
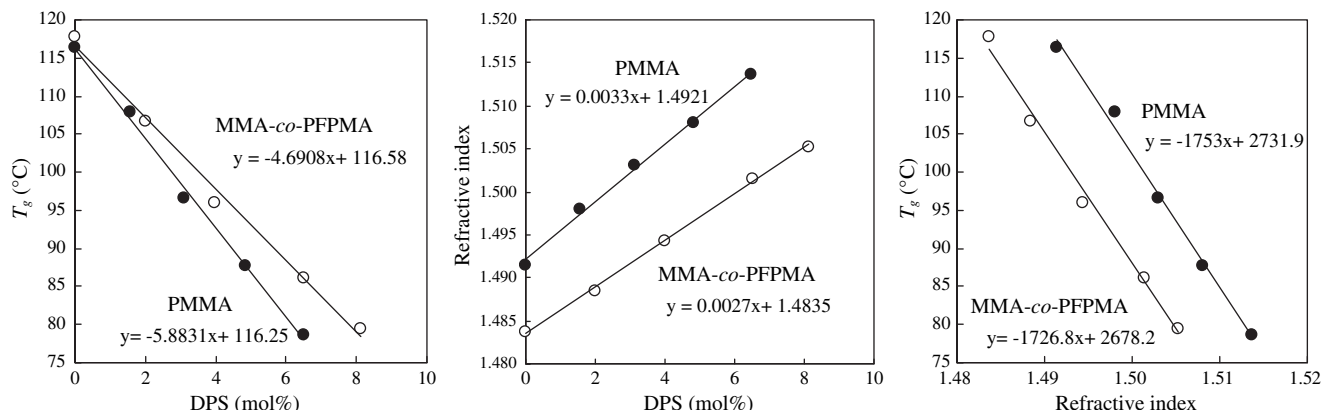

Fig. 13. Relationship between the amount of doped DPS, T_g, and refractive index of MMA-*co*-PFPMA (65/35 mol%) and PMMA bulks.
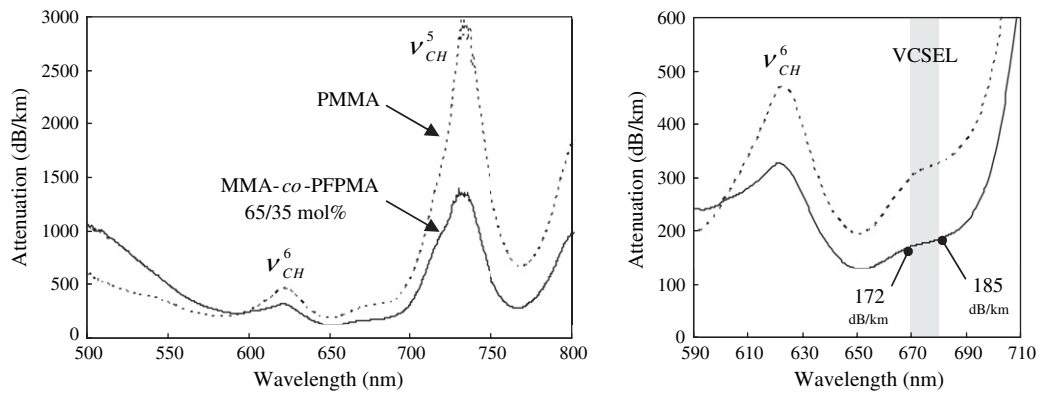
Fig. 14. Attenuation spectra of GI POFs based on MMA-*co*-PFPMA (65/35 mol%) (solid line) and PMMA (broken line).

$$n_1 = \sqrt{NA^2 + n_2^2} = \sqrt{0.2^2 + 1.4837^2} = 1.4971 \qquad (5)$$

where 1.4837 is the refractive index of the copolymer with a PFPMA content of 35 mol%. When the refractive index of the copolymer core is 1.4971, the T_g is calculated as 93 °C from Eq. (6), which satisfies the required value of home networks (>90 °C).

$$T_g = -1726.8 \times 1.4971 + 2678.2 = 93 \qquad (6)$$

However, the mechanical properties of this copolymer are somewhat inferior to PMMA, and thus the copolymer cladding system is not suitable. On the other hand, when using PMMA as the cladding material, the necessary refractive index of the core is calculated as 1.5048, which results in a low T_g of 80 °C.

Therefore, to reduce the refractive index of the cladding, a copolymer of MMA and 2,2,2-trifluoroethyl methacrylate (TFEMA) was investigated as the cladding material. Although the T_g of poly(TFEMA) is as low as 70 °C, the refractive index is also as small as 1.4182 [7]. The relationship between the T_g, refractive index, and TFEMA content in the monomer feed has already been reported [17]. When the TFEMA content is 20 mol%, a copolymer with a low refractive index of approximately 1.47 that maintains a T_g of over 100 °C can be obtained. Moreover, GI POFs with the copolymer cladding have been shown to have good humid stability since the saturated water absorption of the copolymer is much lower than that of PMMA [17]. Based on the theory of light propagation, a small part of the propagating light goes through the cladding layer. Thus, the cladding material must also have high transparency. The percentage of C–H bonds per unit volume of poly(TFEMA) is 64% of that for PMMA, and the copolymer has smaller absorption losses [7]. In addition, the scattering loss of the copolymer is small enough because both monomer reactivity ratios are close to unity [18]. When MMA is M_1 and TFEMA is M_2, the

reactivity ratios are $r_{12} = 0.83$ and $r_{21} = 0.86$. PMMA and poly(TFEMA) have quite different refractive indices, and the mechanism for reducing the heterogeneity of the refractive indices is completely different from MMA-*co*-PFPMA. In this study, cladding with 20 mol% TFEMA was used. The T_g and refractive index were 100 °C and 1.4703, respectively. To maintain the T_g of the core over 90 °C, the amount of added DPS must be less than 5.7 mol%, according to the approximated equation in Fig. 13 (left). Thus, MMA-*co*-PFPMA (65/35 mol%) with 5 mol% DPS was prepared as the core. T_g was 92 °C and the NA was 0.28.

3.5. Preparation and transmission properties of GI POF

A preform with a GI profile was prepared by the rod-in-tube method, and a GI POF that was 100 m in length was successfully obtained by heat drawing. The attenuation spectrum of the GI POF is shown in Fig. 14. The broken line is a spectrum of a GI POF based on PMMA for comparison. The attenuation spectra were measured by the cut-back method.

The emission wavelength (670–680 nm) of VCSEL is located in between the 5th and 6th overtones of C–H stretching vibrational absorptions. While the attenuation at wavelengths of 670–680 nm for the PMMA-based GI POF was as high as 295–323 dB/km due to the strong C–H absorption losses, the copolymeric GI POF had much smaller peaks and the attenuations were 172–185 dB/km, which satisfies the required attenuation for the proposed optical home network systems. Currently, the scale of heterogeneity and corresponding scattering loss of the copolymer are being investigated in detail and the results will be reported elsewhere.

The −3 dB bandwidth of the GI POF—measured by launching via SMF with a core of 5 μm—was as high as 1.34 GHz. The length of the test fiber was 50 m, which is expected to be the maximum laying distance in a house, and the launching method was almost identical to the exciting condition supposed in practical use. The high bandwidth ensures that there is enough capacity to transmit data at a high-speed rate of gigabits per second. This is attributed to the GI profile in the core region. Fig. 15 represents the NFP image and light intensity profile of the GI POF, which directly relate to the refractive index profile in the core region. The DPS added in the core diffused into the cladding layer and formed the quadratic profile, leading to high-speed data transmission.

4. Conclusion

As a novel base material for GI POF to be used in gigabit in-home communications, MMA and PFPMA copolymers were prepared, and its thermal and optical properties were characterized. When the PFPMA content in the monomer feed was lower than 50 mol%, both
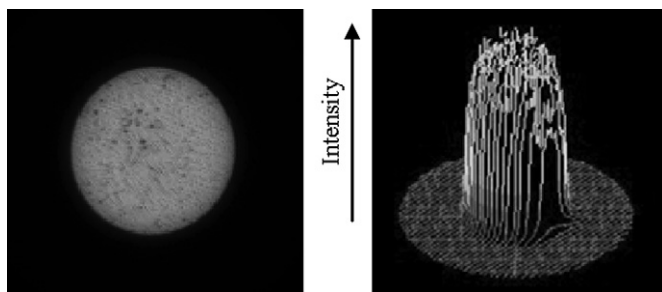

Fig. 15. Observed NFP image (left) and intensity profile (right) for the GI POF based on MMA-*co*-PFPMA (65/35 mol%) through 50 m and launched via a SI POF with a core diameter of 400 μm.

the T_g and decomposition temperature were shown to be higher than for PMMA. Copolymers with few C–H bonds per unit volume exhibited a higher transmittance than PMMA without the increase in scattering loss associated with general copolymerizations. The optimum preparation conditions were investigated, and the highest T_g of 118 °C was obtained when the PFPMA content and amount of added initiator (DBPO) were 35 and 0.1 mol%, respectively.

A low-loss and high-bandwidth GI POF based on the copolymer with an attenuation of 172–185 dB/km at wavelengths of 670–680 nm was successfully obtained. Both the core and cladding layer were designed to have good humid stability, and the minimum T_g was controlled to be over 90 °C, ensuring long-term usage in a house environment. A notable feature is that all materials used for the GI POF are commercially available, and no complicated synthesis, purification, or polymerization technique is necessary. A detailed procedure for preparing the GI POF continuously through the co-extrusion process and optimizing the refractive index profile is in progress. We believe that the GI POF can be a leading medium for home networks in the near future.

Acknowledgements

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