Raman spectra of polymethyl methacrylate optical fibres excited by a 532 nm diode pumped solid state laser

K J Thomas[1,3]**, M Sheeba**[1]**, V P N Nampoori**[1]**, C P G Vallabhan**[2] **and P Radhakrishnan**[1]

[1] International School of Photonics, Cochin University of Science and Technology, Cochin 682022, Kerala, India
[2] Centre of Excellence in Lasers and Optoelectronic Sciences, Cochin University of Science and Technology, Cochin 682022, Kerala, India

E-mail: thomasjony@gmail.com

Abstract

Polymethyl methacrylate (PMMA) optical fibres are fabricated by a preform drawing process. The Raman spectra of PMMA fibres are recorded using a diode pumped solid state laser emitting at 532 nm and a CCD-spectrograph in the 400–3800 cm^{-1} range. The variation of the Raman intensity with the length of the optical fibre is studied. Investigations are carried out on the variation of FWHM of the Raman peak at 2957 cm^{-1} with the length of the optical fibre and pump power. The differential scattering cross section and gain coefficient of the Raman peak at 2957 cm^{-1} in PMMA are calculated in relation to that of toluene.

Keywords: polymer optical fibre, Raman spectrum, scattering cross section, gain coefficient

1. Introduction

In the last decade polymer optical fibres (POF) and devices are found to be widely used in short distance communications and optical integrated circuits. They are more flexible and less brittle than glass, and are cost-effective in comparison with silica fibres. The applications of polymer optical fibres include data communication in local area networks, illuminated displays, optical interconnects between electronic components, optical amplifiers and lasers in the visible region, fibre optic components such as splitters, filters, optical switches and sensors [1–4]. Recent technologies have very much succeeded in decreasing the loss in PMMA optical fibres [5, 6] and in the development of POF amplifiers and lasers [7–10]. But very little work has been done in the area of Raman scattering in PMMA optical fibres. Stimulated Raman scattering in a polymer fibre has been developed into a Raman amplifier and fibre Raman laser [12–15].

In this paper, the fabrication of PMMA fibres and their Raman spectra excited by 532 nm radiation from a CW diode pumped solid state laser are presented. The variation of spectra with different pump powers and fibre lengths has been studied. The differential scattering cross section and gain coefficient of the Raman peak at 2957 cm^{-1} in PMMA are also calculated.

2. Fabrication of polymer optical fibre

Methyl methacrylate (MMA) is a suitable candidate for the fabrication of polymer preforms since it has good optical quality and is compatible with most of the organic dopants [1, 2, 4, 16]. Usually the commercially available MMA (Alfa Aesar, UK 99%) contains inhibitors such as hydroquinon. These inhibitors are removed by washing MMA with 5% NaOH solution and drying over anhydrous $CaCl_2$. The monomer is again purified by distillation under vacuum conditions. An initiator (0.01 mol/l benzoyl peroxide) and a chain transfer agent (0.06 mol/l n-butyl mercaptan) are added to MMA and stirred well. The mixture is then polymerized in a glass tube at 70 °C for 72 h and at 90 °C for 12 h. The polymerized preform is heat drawn into fibres of the required diameters by controlling the feed rate of the preform and drawing rate of the fibre.

[3] Author to whom any correspondence should be addressed.
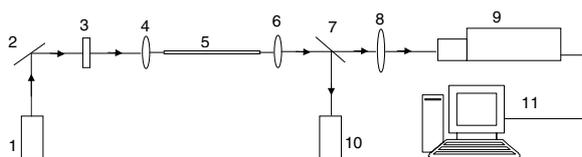
Figure 1. Schematic representation of the experimental set-up for measuring Raman spectrum. (1) DPSS (532 nm, cw, 50 mW); (2), (7) dichroic mirror (532 nm); (3) ND filter; (4), (6), (8) lenses; (5) PMMA POF; (9) monochromator with CCD; (10) beam dump; (11) computer for data acquisition.

3. Experimental arrangement

The experimental set-up for recording the Raman spectrum of PMMA fibre is given in figure 1. The PMMA fibre is pumped by 532 nm CW DPSS (Suwtech Laser DPGL-2050F) at 50 mW. A 532 nm dichroic mirror is placed before focusing the laser into the fibre, to select the 532 nm pump. A variable neutral density (ND) filter is placed after the dichroic mirror to change the pump power. The transmitted light through the fibre is coupled to the monochromator by two convex lenses of matching f-numbers for maximum signal collection. Another 532 nm dichroic mirror is placed in between the lenses to separate out the pump from Raman signals. Raman signals are recorded by the monochromator–CCD (Acton Research SpectraPro-500i, 500 mm focal length, 0.05 nm resolution) system. Raman spectra are recorded at different pump powers and for different lengths of the PMMA fibre. All experiments are performed at room temperature (22 °C).

For measuring the differential scattering cross section, the fibre is replaced by a PMMA cube of 1 cm side. The cube is prepared from a section of the PMMA preform which was used for fibre fabrication and all the sides are polished well. When pumped with 50 mW CW radiation, the scattered Raman signals are collected at 90° to avoid the pump signals and are recorded by the monochromator–CCD system. Then the toluene solution is taken in a 1 cm × 1 cm × 5 cm cuvette and its Raman signals are recorded under the same experimental conditions.

4. Results and discussion

4.1. Raman spectrum in PMMA POF

Figure 2 shows the Raman spectrum of the PMMA polymer fibre of length 50 cm and diameter 310 μm. Most of the Raman bands are identified with those in the spectrum available in the literature [12–15]. Raman bands near the pump wavelength (532 nm) are obtained with less intensity in the given spectrum due to the presence of a dichroic mirror placed in front of the spectrograph to reduce the transmitted pump intensity. Out of the observed Raman bands, the one at 2957 cm^{-1} is the most prominent which is due to the C–H stretching vibration [12, 14]. The other observed bands are at 602, 853, 925, 999, 1081, 1264, 1460, 1648, 1736, 2848, 3001 and 3454 cm^{-1}. The band at 1648 cm^{-1} is attributed to the combination band arising out of ν(C=C) and
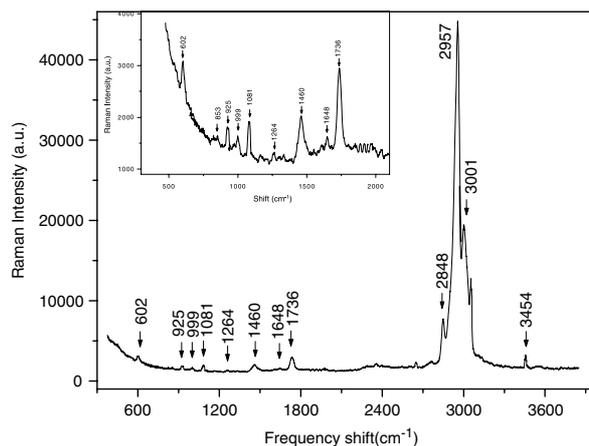
Figure 2. Raman spectrum of the PMMA POF pumped by 532 nm DPSS laser (50 mW). Inset shows the enhanced spectral region 500–2000 cm^{-1}.

Table 1. Observed Raman bands in PMMA POF and their assignments.

Raman band (cm^{-1})	Assignments
602[a]	ν(C–COO), ν_s(C–C–O)
853[a]	ν(CH$_2$)
925[b]	ν(CH$_2$)
999[a]	O–CH$_3$ rock
1081[a]	ν(C–C) skeletal mode
1264[a]	ν(C–O), ν(C–COO)
1460[a]	δ_a(C–H) of α-CH$_3$, δ_a(C–H) of O–CH$_3$
1648	Combination band involving ν(C=C) and ν(C–COO)
1736[a]	ν(C=O) of (C–COO)
2848[a]	Combination band involving O–CH$_3$
2957[a]	ν_s(C–H) of O–CH$_3$ with ν_s(C–H) of α-CH$_3$ and ν_a(CH$_2$)
3001[b]	ν_a(C–H) of O–CH$_3$, ν_a(C–H) of α-CH$_3$
3454	$(2\nu_2)$ Overtone of 1730 cm^{-1}

[a] Assignments match with [12, 14].
[b] Assignments match with [14] only.

ν(C–COO) modes and the band at 3454 cm^{-1} is attributed to the first overtone involving (C=O) of C–COO. The above two Raman bands are observed for the first time in PMMA POF. Assignments of other Raman bands are shown in table 1. The observed Raman spectrum agrees fairly well with those available in the literature [12, 14].

4.2. Variation of relative Raman intensity with fibre length

The variation of relative intensity ratio of Raman bands at 2957 and 3001 cm^{-1} with fibre length is shown in figure 3. The diameter of the fibre taken is 220 μm and is excited by 50 mW, 532 nm DPSS. Initial length of the fibre is 200 cm and it is decreased step by step. For each length of the fibre, the Raman spectrum is recorded and the relative intensity ratio is evaluated. The evaluation of the ratio of intensities will remove the effects due to the experimental artefacts if any. For longer lengths of the fibre, the relative intensity is observed to be less and the ratio increases as the fibre length is decreased. For
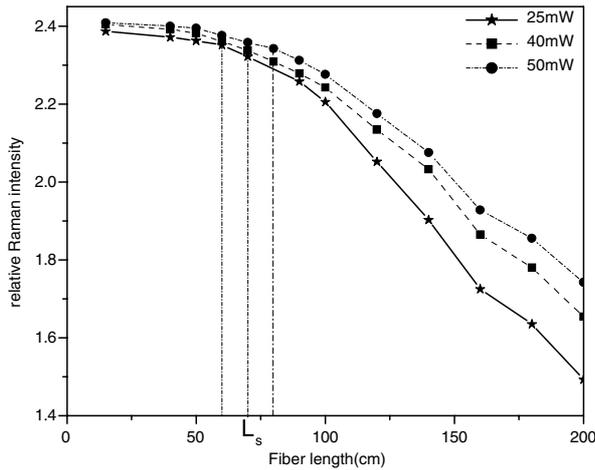
Figure 3. Variation of relative intensity ratio of Raman bands at 2957 and 3001 cm^{-1} with fibre length.

a length of fibre up to critical length L_s, the ratio remains constant and decreases afterwards. The intensity (I_R) of Raman signals is proportional to the transmitted pump intensity (I_{Pt}) and the length (L) of the fibre. The transmitted pump intensity is given by [11]

$$I_{Pt} = I_{Pi} \exp(-\alpha L) \approx I_{Pi}(1 - \alpha L) \qquad (1)$$

where I_{Pi} is the input pump intensity and α is the fibre attenuation coefficient. Hence the Raman intensity is given by

$$I_R \propto L I_{Pi}(1 - \alpha L). \qquad (2)$$

For constant input pump intensity,

$$I_R \propto (L - \alpha L^2). \qquad (3)$$

For fibre length $L < L_s$, the contribution of the second term in (2) can be neglected and hence Raman intensity is found to depend on input pump intensity. Within this length of fibre, the decrease in Raman signal strength due to pump depletion is compensated by the Raman gain and hence the Raman intensity remains constant. In other words, Raman signals are strong enough to compensate for the loss due to the attenuation within the critical length L_s. For the fibre length $L > L_s$, the second term in (3) become prominent and hence Raman intensity starts decreasing as the fibre length increases. This nature of the curve is well explained by (3). Even though the increased length of fibre is expected to enhance Raman scattering, the higher value of attenuation coefficient, α, decreases the transmitted pump intensity considerably and hence the Raman intensity. Therefore, for the optimum detection of Raman signals, the fibre length should be less than or equal to L_s for a particular fibre diameter. By analysing figure 3 it is clear that L_s increases with the pump intensity (60 cm for 25 mW, ∼74 cm for 40 mW and ∼80 cm for 50 mW). At longer lengths of the fibre, a tendency is seen to increase the Raman intensity. This problem requires special attention and needs to be taken up separately and will be reported elsewhere.

4.3. Variation of FWHM of Raman band at 2957 cm^{-1}

The band at 2957 cm^{-1} is the most intense Stokes band in the Raman spectrum of PMMA POF and demands further investigations if this sample has to be considered for Raman amplification. So the study of the variation of the FWHM of this peak with parameters like fibre length, pump power, etc, assumes importance. The influence of pump power on the FWHM of the Raman peak is analysed by varying the input power from 1 to 65 mW on a fibre of length 40 cm and diameter 170 μm. The measured values of FWHM are found to be a constant at 42.44 cm^{-1} for all the pump powers. The effect of the interaction length on the FWHM is studied by varying the fibre length from 15 to 200 cm at a constant input power of 50 mW. Even in this case FWHM values remain a constant at 42.44 cm^{-1}. Thus it is clear from these observations that the FWHM of the Raman band at 2957 cm^{-1} is independent of the pump power and the length of the fibre in the regime of spontaneous Raman scattering.

4.4. Calculation of gain coefficient

The relationship between the intensity I, of Rayleigh and Raman scattered radiation from N numbers of molecules and the irradiance F of incident radiation has the general form [13, 17]

$$N\frac{d\sigma}{d\Omega} = \frac{I}{F} \qquad (4)$$

where $\frac{d\sigma}{d\Omega}$ is the differential scattering cross section per molecule. For PMMA, the differential scattering cross section can be calculated by comparing it with that of toluene.

For different experiments, pump wavelength may be different and the above equation for cross section should be corrected by considering the ν^4 dependence. The frequency related cross section is given by [13]

$$N\frac{d\sigma}{d\Omega} = \frac{k' h c^4 \nu_s^4}{8\pi^2 (\nu_p - \nu_s) \left\{ 1 - \exp\left[-h (\nu_p - \nu_s) / kT \right] \right\}} \qquad (5)$$

where ν_s and ν_p are the Stokes and pump frequencies, k' is a constant for the given material, h is the Planck constant, k is the Boltzmann constant and T is the absolute temperature.

Comparing with the absolute scattering cross section of toluene at 1002 cm^{-1} excited by 694.3 nm pump and taking into account the difference of Stokes wavelengths at different pump frequencies and using the experimental results from figure 4, the differential scattering cross section of PMMA at 2957 cm^{-1} pumped by 532 nm is calculated as 1.968 × 10^{-8} cm^{-1} sr^{-1}, which is found to be almost twice the previously reported [13] value of 9.9 × 10^{-9} cm^{-1} sr^{-1}. The high differential scattering cross section leads to higher gain for the medium. The higher value obtained is attributed to the changes in the optical characteristics of the material brought about by the method of preparation of the polymer. Moreover, the thermal treatment and the nature of the initiator for the polymerization would have brought about the changes in the observed results.

The gain coefficient is an important parameter for an amplifier. The importance of gain coefficient is that

3
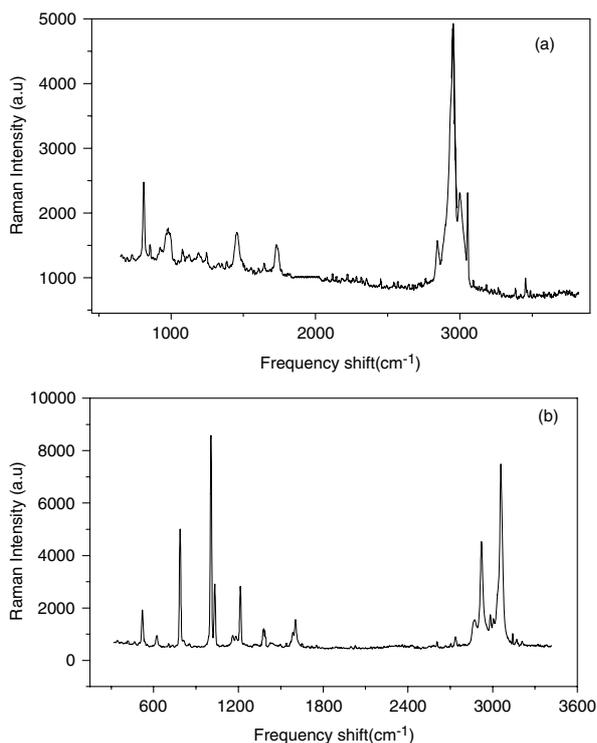
Figure 4. The Raman spectra of (a) PMMA cube and (b) toluene.

it determines the threshold power for stimulated Raman scattering in POF along with parameters like length of fibre, attenuation, effective area of fibre, etc. The relation between the gain coefficient and differential cross section is given by [13]

$$g = N \frac{d\sigma}{d\Omega} \frac{c^2 \left[1 - \exp \left(-h \left(\nu_p - \nu_s \right) / kT \right) \right]}{3h\nu_s^3 n_s \Delta\nu_N} \quad (6)$$

where g is the gain coefficient, $\Delta\nu_N$ is the FWHM intensity, n_s is the refractive index of the material and c is the velocity of light in vacuum. Using (6) the peak Raman gain coefficient at 2957 cm^{-1} (631 nm) is calculated as 3.742×10^{-10} cm W^{-1} with $\Delta\nu_N = 2 \times 10^{12}$ Hz when excited with 532 nm laser radiation. The refractive index of PMMA is taken as 1.49 [4]. The obtained gain coefficient value is greater than the previously reported value (4.64×10^{-11} cm W^{-1}) [13]. The higher the gain coefficient, the less is the required power to get stimulated Raman scattering [13]. Compared with silica fibres [18], polymer fibres have a higher value of scattering cross section and can easily achieve higher Raman amplification. But the main disadvantage of the polymer fibres is their higher attenuation. At present, PMMA POF has attenuation in the range of 60–100 dB km^{-1}. By decreasing the loss considerably, polymer fibre amplifiers can be developed with shorter length of fibre.

5. Conclusion

We have reported the Raman spectra of PMMA POF excited with 532 nm radiation from a CW DPSS laser and Raman

bands are assigned. Two Raman bands at 1648 cm^{-1} and 3453 cm^{-1} corresponding to the combination band involving ν(C=C) and ν(C–COO), and the ($2\nu_2$) overtone vibration of 1730 cm^{-1} are observed respectively in the PMMA polymer optical fibre for the first time to the best of our knowledge. The variation of relative Raman intensity with different lengths of fibre has been studied and a critical length is observed for the optimum detection of Raman signals from PMMA fibre. The variation of FWHM of the Raman peak at 2957 cm^{-1} with fibre length and pump power has been analysed and is found to remain a constant. The differential scattering cross section of PMMA is calculated as 1.968×10^{-8} cm^{-1} sr^{-1} in relation to that of toluene and the gain coefficient of the Raman peak at 631 nm has also been evaluated as 3.742×10^{-10} cm W^{-1}. The observed high value of the differential scattering cross section leads to a higher Raman gain and its suitability as a Raman amplifier medium.

References

[1] Kuzyk M G 2007 *Polymer Fibre Optics: Materials, Physics and Applications* (London: Taylor and Francis)
[2] Nalwa H S 2004 *Polymer Optical Fibers* (Stevenson Ranch, California: American Scientific Publishers)
[3] Bhuiyan M M I, Haga Y and Esashi M 2005 Design and characteristics of large displacement optical fibre switch *IEEE J. Quantum Electron.* **41** 242–9
[4] Rajesh M, Sheeba M, Geetha K, Vallabhan C P G, Radhakrishnan P and Nampoori V P N 2007 Fabrication and Characterization of dye-doped polymer optical fibre as a light amplifier *Appl. Opt.* **46** 106–12
[5] Kaino T, Jinguji K and Nara S 1982 Low loss poly-(methyl methacrylate-d5) core optical fibres *Appl. Phys. Lett.* **41** 802–4
[6] Ziemann O, Poisel H and Vinogradov J 2006 Potential of high speed, short distance optical data communication on large diameter optical fibers *Electronics System Integration Technology Conf.* vol 1 pp 409–14
[7] Karimi M, Granpayeh N and Morraveg Farshi M K 2004 Analysis and design of a dye-doped polymer optical fibre amplifier *Appl. Phys.* B **78** 387–96
[8] Liang H, Zheng Z, Li Z, Xu J, Chen B, Zhao H, Zhang Q and Ming H 2004 Fabrication and amplification of rhodamine B-doped step-index polymer optical fibre *J. Appl. Polym. Sci.* **93** 681–5
[9] Kuriki K, Nishihara K, Nishizawa S, Tagaya Y, Okamoto A and Koike Y 2001 Fabrication and optical properties of neodymium-, praseodymium-and erbium-chelates-doped plastic optical fibres *IEEE Electron. Lett.* **37** 415–17
[10] Kuriki K, Koike Y and Okamoto Y 2002 Plastic optical fibre lasers and amplifiers containing lanthanide complexes *Chem. Rev.* **102** 2347–56
[11] Agrawal G P 2002 *Fibre Optic Communication Systems* 3rd edn (New York: Wiley–Interscience) p 55
[12] Willis H A, Zichy V J I and Hendra P J 1969 The laser-Raman and infra-red spectra of polymethyl methacrylate *Polymer* **10** 737–46

J. Opt. A: Pure Appl. Opt. **10** (2008) 055303

K J Thomas *et al*

[13] Xu X 2001 Stimulated Raman spectrum threshold in polymethyl methacrylate optical fibers *Opt. Commun.* **199** 89–93

[14] Xu X, Ming H, Zhang Q and Zhang Y 2002 Properties of Raman spectra and laser induced birefringence in polymethyl methacrylate optical fibres *J. Opt. A: Pure Appl. Opt.* **4** 237–42

[15] Pallikari F, Chondrokoukis G, Rebelakis M and Kotsalas Y 2001 Raman spectroscopy: a technique for estimating extent of polymerization in PMMA *Mater. Res. Innovat.* **4** 89–92

[16] Garvey W *et al* 1996 Single-mode nonlinear-optical polymer fibers *J. Opt. Soc. Am.* B **13** 2017–23

[17] Albert L D 2002 *The Raman Effect: A Unified Treatment of the Theory of Raman Scattering* (New York: Wiley) pp 95–6

[18] Stolen R H and Ippen E P 1973 Raman gain in glass optical waveguides *Appl. Phys. Lett.* **22** 276–8