Characteristics of Dual Amplified Spontaneous Emission from MEH-PPV Solutions

G. Sreelekha\textsuperscript{a,b,*}, G. Vidyac, K. Geethab, R. Josephc, S. Prathap\textsuperscript{d}, P. Radhakrishnan\textsuperscript{a,b}, C.P.G. Vallabhan\textsuperscript{b}, and V.P.N. Nampooria\textsuperscript{b}

\textsuperscript{a}International School of Photonics,
\textsuperscript{b}Centre of Excellence in Lasers and Optoelectronic Sciences,
\textsuperscript{c}Department of Polymer Science and Rubber Technology,
\textsuperscript{d}Department of Applied Chemistry,
Cochin University of Science and Technology, Cochin-22, Kerala, India

Corresponding author:
\textsuperscript{*}Corresponding Author: sreelekasatheesh@gmail.com

ABSTRACT— We report the observations of dual wavelength amplified spontaneous emission from the solutions of a conjugated polymer poly [2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) in Tetrahydrofuran and 1, 2 Dichlorobenzene. We have prepared MEH-PPV using a modified procedure and purified several times in each step, the material offers low molecular weight, low polydispersity index and high thermal stability, which are some of the most important requirements for the fabrication of photoluminescent devices. The variation in the features of amplified spontaneous emission with increasing polymer concentration is presented. For intermediate polymer concentrations, narrow emissions were observed for the 0-0 and 0-1 vibronic peaks which were not reported in solutions to the best of our knowledge. The ASE characteristics sensitively depend on concentration as well as pump power. The gain studies show that MEH-PPV is a potential laser media. By varying the concentration of the solution and pump power we can use either of the two different wavelength bands for lasing applications.

KEYWORDS: dual amplified spontaneous emission, laser gain, laser material, photoluminescence.

I. INTRODUCTION
Conjugated polymers are attracting great interest because of their unique electronic and optical properties. The initial objectives in the investigation of conjugated polymers were focused on the study of their electric and transport properties. When the organic chemistry was improved, conjugated polymeric materials with quantum yields comparable to that of laser dyes are now available. Consequently, they can be used as gain media for lasers [1]-[4] and optical amplifiers [5] that are tuneable throughout the visible spectrum.

The photo luminescent characteristics of conjugated polymers can be modified by varying the effective conjugation length, i.e., the average number of chemical repeat units in the undisturbed sequence of the polymer. Such a tuning parameter to modify the energy gap is generally, besides the band gap tuning by composition, not available for classical inorganic semiconductor materials with fixed types of atoms and set of lattice parameters. In this sense, conjugated polymers are very versatile and constitute a novel class of organic laser materials. The absorption and fluorescence spectra are well separated, so that the re-absorption of emitted light is weak.

The laser action of a semi conducting polymer poly (2-methoxy, 5-(2’-ethylhexyloxy)-p-phenylenevinylene (MEH-PPV) in the liquid state, operating in the yellow/red wavelength region, was achieved for the first time in 1992.
The reported lasing performance of this polymer dissolved in xylene was comparable to that of the most efficient laser dye, Rhodamine 6G [6]. In this paper we discuss the Amplified Spontaneous Emission (ASE) phenomenon in MEH-PPV dissolved in Tetrahydrofuran (THF) and 1, 2 Dichlorobenzene, and especially the dual wavelength emission features observed in the same. The MEH-PPV was purified by continuous extraction with hexane and THF using soxhlet extraction method and re-precipitated in methanol.

II. EXPERIMENTAL PROCEDURE

A. Material

All reagents were commercially available and used as received unless otherwise stated. Tetrahydrofuran (THF) was freshly distilled over sodium before it was used. All reactions were carried out under nitrogen atmosphere.

The monomer used for preparation of MEH-PPV, 1, 4-bis (bromo methyl)-2-[2’ethylhexyloxy]-5-methoxy benzene was synthesized according to a procedure reported by Wudl et al. [7]. A mixture of 4-methoxy phenol (0.04mol) and sodium methoxide (0.07mol) in methanol was refluxed for 1h. After cooling to room temperature, 2-ethyl hexyl bromide (8mL, 0.04mol) was added drop-wise and further refluxed for 24h until the brownish solution turned light yellow. Methanol had been removed under reduced pressure. The remaining mixture was combined with dichloromethane, washed several times with NaOH followed by brine solution and dried over MgSO₄. After removing the solvent clear liquid product was obtained (yield=54%). A 0.01mol of 2-[2’-ethylhexyloxy]-5-methoxy benzene] was dissolved in 30mL glacial acetic acid and para-formaldehyde (0.06mol) was added. The resulting solution was cooled down to 0°C and 7mL (30-33%) HBr in glacial acetic acid was added drop-wise to the above solution upon stirring. After the reaction mixture was heated to 75°C and stirred for an additional 4h. The reaction mixture was then cooled, concentrated and stored in a refrigerator overnight. A pale white precipitate was obtained which was dissolved in a minimum amount of dichloromethane and washed with NaHCO₃ solution. The organic layer was separated and dried over MgSO₄. The dried precipitate was further dissolved in acetone and re-precipitated in methanol. The yield obtained was 94%. The Polymerization of MEH-PPV was carried out by Gilch route from their monomer. To improve the quality of the compound in each step, we have done purifications several times. The material was purified by continuous extraction with hexane and THF. The low molecular weight fractions (oligomers) were dissolved in hexane and collected separately. High molecular weight fractions were dissolved in THF. The THF soluble fraction was used for further analysis. After extraction, the dissolved polymer was re-precipitated in methanol. The precipitate was collected by filtration and then dried in vacuum. The color of the MEH-PPV has changed from dark red-orange to fluorescent red-orange after purification.

B. Chemical Characterization

MEH-PPV was characterized by elemental analysis. The molecular weight of MEH-PPV was determined by GPC measurement in toluene with polystyrene as the standard (Waters 2414, Netherlands). The thermal stability of the polymer was determined using TGA-Q50 TA instruments at a heating rate of 100°C/min in nitrogen atmosphere. The 1H spectrum of the polymer was recorded at 400MHz using in CDCl₃, containing a small amount of TMS as the internal standard (Brucker NMR Spectrophotometer). The FT-IR spectrum of the sample was recorded using Brucker spectrophotometer.

C. Experimental Setup

The absorption and fluorescence spectra were recorded using UV-VIS spectrophotometer (Jasco V-570) and Cary Eclipse Spectrofluorimeter respectively. The amplified spontaneous emission was studied in MEH-PPV dissolved in Dichlorobenzene and THF. Solutions of various concentrations ranging from 0.18mg/ml to 9mg/ml were studied. The
ASE studies of the solution are conducted by taking the sample solution in a quartz cuvette of 1 cm x 1 cm x 3 cm dimensions. The emission spectra were recorded by exciting the sample with 532 nm radiation at which the sample has good absorption. The pump beam was obtained from a Q-switched frequency doubled Nd-YAG laser which gives pulses of 10 ns duration at 532 nm and at a repetition rate of 10 Hz. A cylindrical lens was used to focus the pump beam in the shape of a stripe on the sample. The pump beam was absorbed by the front layer of the sample and it created a stripe like excited gain medium. A vertical slit was incorporated in the path of the beam between the cylindrical lens and the sample so as to vary the stripe length on the sample. In the present case it was adjusted to a pump beam width of 4 mm and 8 mm. The output was collected from the edge of the front surface of the cuvette using an optical fiber in a direction normal to the pump beam. The emission spectra were recorded with Acton monochromator attached with a CCD camera. The emitted beam from the edge of the cuvette was so strong and highly directional that we could collect it even without any focusing and also at a distance of 2.5 cm from the cuvette.

III. RESULTS AND DISCUSSIONS

A. Chemical Characterization Studies

The 1H NMR spectrum and FT-IR spectrum of MEH-PPV synthesized by the present method is shown as Figs. 1(a) and 1(b).

The 1H NMR shows peak at 7.49 and 7.11 ppm corresponding to aromatic protons and vinylene protons, respectively. The peaks for all other protons appeared below 4.00 ppm. In the FT-IR spectrum absorptions at 2920, 2852, 1460, 1380 cm\(^{-1}\) are assigned to the CH\(_2\) and CH\(_3\) groups of side chains. The 3050 and 964 cm\(^{-1}\) bands are due to the olifinic C-H stretching and trans-substituted olifinic C-H bending, respectively.

The gel permeation chromatogram of the polymer is shown in Fig. 2.

The molecular weight of MEH-PPV is 46777 g/mol and a polydispersity index 1.38. The low polydispersity value of the MEH-PPV suggests that the molecular weight distribution of the polymer was uniform. The thermogram for the MEH-PPV sample is shown in Fig. 3.
B. Photo Physical Studies

Absorption and fluorescence spectra of MEH-PPV dissolved in Dichlorobenzene and THF at low concentration were recorded (Fig. 4).

Amplified spontaneous emission was observed when pumped with a pulsed Nd-YAG laser at 532nm. The pump power was varied using a variable neutral density filter. The dependence of the emission intensity and spectral line width of the emission, on pump intensity and the excitation length of the pump beam was studied in detail. When the sample was excited using a beam in the form of stripe, it forms a cylindrically shaped active gain medium. The fluorescence emitted by the chromophore at one end is strongly amplified by the active medium and it emits a highly directional output beam [10].

We observed that, at very low concentration, (0.18mg/ml), the spectrum shows 4 bands around 560nm, 597nm, 635nm and 673nm, of which the one at 560nm is prominent (Fig. 5(a)).

The overlap was very small so that self absorption will be low. When dissolved in THF absorption peak was at 495nm while the emission spectrum showed a peak at 550nm and a shoulder around 590nm. When dichlorobenzene was used as solvent, absorption peak was at 500nm and emission at 567nm and a shoulder is found to exist around 604nm. There was a blue shift in the absorption and emission spectrum when both cases were compared. The shift can be explained by considering that the conjugation length of the polymer changes in different solvents [8]. Thus a shorter average conjugation length for MEH-PPV in THF compared to Dichlorobenzene is the reason for blue shifted absorption and emission spectra [9].
From the analysis of the band position these four bands can be realized as the vibronic bands (0-0), (0-1), (0-2) and (0-3) respectively [11]. On increasing the concentration, the (0-0) and (0-1) bands were well developed to separate narrow peaks. For the intermediate concentrations in our measurement range, we observed amplified spontaneous emission at both (0-0) and (0-1) bands (see Figs. 5(a) and 5(b)) unlike in the previous report where ASE was observed only for one band in solution form [12].

Sample showed dual wavelength lasing up to an optimum concentration above which the shorter wavelength emission is suppressed. This is due to the effect of concentration quenching more on short wavelength in comparison with that of the higher wavelength emission [13]. The overlap of absorption and PL spectrum may also affect the shorter wavelength at high concentration. This explains the observation of longer wavelength emission for higher concentration and the absence of the shorter wavelength emission. There is an energy transfer between longer wavelength and shorter wavelength depending upon various parameters like pump power, concentration of the solution and stripe length. Hence in order to obtain dual wavelength lasing one has to optimize these parameters. We can use the (0-0) and (0-1) bands for lasing applications by varying the concentration and pump power.

By proper choice of these parameters one can also obtain single wavelength emission. For e.g. at 0.5mg/ml concentration with 7mJ/pulse pump power and 8nm stripe length, the shorter wavelength emission dominates over the longer wavelength, while at 0.75mg/ml concentration, with a pump power 5mJ/pulse and stripe length 8nm the longer wavelength emission was predominant over the shorter wavelength. For a higher concentration of 9mg/ml, the shorter wavelength band was found to be completely suppressed and longer wavelength band was emerged as a narrow band of high intensity.

Both peaks have the same polarization state with degree of polarization 0.7, which is measured as

$$\frac{I_{\text{max}} - I_{\text{min}}}{I_{\text{max}} + I_{\text{min}}}$$

Figs. 6(a) and 6(b) show FWHM of emission spectrum of MEHPPV in THF and the ratio of vibronic peaks at pump power energy of 5mJ/pulse. At lower concentration P1 is higher than P2 and FWHM was found to decrease with increasing concentration. However, above certain concentration P2 becomes prominent over P1 and at higher concentration P1 disappears completely.

![Fig. 6: (a) FWHM of ASE peaks 1 and 2 at different concentrations and (b) Relative peak intensity (P1/P2) with respect to concentration](image-url)

The FWHM reduces up to the concentration of 3mg/ml with a lowest value as 5.2nm. At higher concentrations the FWHM shows slight enhancement as a result of gain saturation.
Even though ASE was not prominent in dichlorobenzene the similar phenomenon was found in this solution. Our studies also show that the line width of emission in the case of MEH-PPV in solvent dichlorobenzene was larger than that in the case of solvent THF. Dichlorobenzene is of aromatic while THF is nonaromatic. In the case of aromatic solvent, aggregation of solute will be more in comparison with nonaromatic solvent like THF. The fluorescence emission of aggregates is also nearly in the same position as that of monomer which will lead to enhancement in the line width. Hence the larger line width of emission observed in case of dichlorobenzene can be attributed to the aggregate formation. Previous reports have concluded that aggregates do not emit ASE, perhaps because aggregates show longer decay time and therefore smaller transition probability [14, 15]. These observations show that aggregates reduce the PL efficiency [16].

We also studied the dependence of fluorescence intensity at 600nm as well as the FWHM with increasing pump power. As clearly seen from Fig. 7(a), fluorescence intensity is found to enhance abruptly above threshold pump power.

The presence of threshold is an indication of signal amplification. Moreover, FWHM decreases with increasing pump power. (Fig. 7(b)).

At a fixed pump power and concentration, the fluorescence intensity and FWHM depend on stripe length as expected. For e.g., at a concentration of 0.75mg/ml, the FWHM was 1.5nm at a power of 3mJ/pulse and a stripe length of 8mm, we got lasing. At 2.25mg/ml concentration, the lasing was present at 4mm and 8mm stripe length with the same power. The FWHM obtained were 3.1nm and 2.7nm respectively. For every cases (various concentration and stripe length), the FWHM was decreased with respect to power first and then increased. The line separation with respect to concentration was observed to be almost the same which is shown in Table 1.

| Table 1: Variation of FWHM and Fluorescence Intensity with Respect to Concentration |
|----------------------------------|--------------------------------|----------------|----------------|
| Concentration (mg/ml) | Peak 1 (560nm) FWHM | Intensity | Peak 2 (598nm) FWHM | Intensity |
| 0.18                | 27.7                          | 1133 | 789                      |
| 0.5                 | 14.2                          | 49326 | 33.5                      | 39995   |
| 0.75                | 10.4                          | 202400 | 5.4                        | 616100 |
| 1.5                 | 378400                        | 5.4   | 3439200                  |
| 3                   | 42100                         | 5.2  | 1205400                  |
| 6                   | 6.9                           | 1590200 |                          |
| 9                   | 9.3                           | 652600 |                          |

Gain was calculated using the standard definition of laser gain as given by Shank [17]. The gain of ASE was found to be maximum of 13.2/cm at 580nm, for a concentration of 9mg/ml and energy of 3mJ/pulse. This value is comparable with those of efficient laser dyes like Rhodamine 6G. The gain spectrum is shown in Fig. 8.
The solution does not get denatured at pump power level used in the present experiment.

Previous investigations on MEH-PPV in solution form have reported ASE only at 600nm [12, 18]. ASE emission in solution is due to the single chain polymers. At lower concentrations it is associated with the (0-0) first vibronic transition from the polymer chain. The (0-0) band is a characteristic of interchain exciton. As the concentration is increased, the distance between the MEH-PPV chains decrease and aggregation between conjugation segments in different chains occur. The (0-1) band is related to the excitons in the aggregated state [13]. The (0-1) band is farther from the absorption edge compared to (0-0) band and hence self absorption is less in the longer wavelength band [19]. Although ASE is present at both the bands at lower concentrations, the effect of self absorption is increased with concentration and hence the emission is dominant at (0-1) band.

In thin film form, however, it is reported [12] to have dual emission at 600nm and 640nm in contrast to our observation at 560 and 597nm in solution. The photo physical properties of MEH-PPV solution and films are different. In film, the shift is because of the stronger interaction of the MEH-PPV dipoles with its surroundings in the highly polarisable environment [20].

Another difference is in polydispersity index of the material prepared. The polydispersity index of MEH-PPV was reported as greater than 1.5 [12], [21]-[25] in previous papers. But we have obtained the value as low as 1.38. This may be because of the purifications we have done several times in each step.

**IV. CONCLUSION**

The present study shows that MEH-PPV synthesized by the modified synthetic route has narrow molecular weight distribution and good thermal stability. We have studied the concentration dependence on the evolution of dual amplified spontaneous emission from MEH-PPV solution in solvents such as THF and 1, 2 dichlorobenzene. We also observed an energy transfer between the 0-0 and 0-1 vibronic peaks which finally resulted in the emergence of an intense peak corresponding to the 0-1 band and a complete suppression of the 0-0 band at very high concentrations. The amplified spontaneous emission characteristics sensitively depend on both the concentration and pump power. The gain studies show that MEH-PPV is a potential laser media. We can use either of the two different wavelength bands for lasing applications.

**ACKNOWLEDGMENT**

The authors wish to acknowledge University Grants Commission, New Delhi for the financial assistance through CELOS project.

**REFERENCES**


G. Sreelekha is a post graduate in Applied Electronics from Bharathiar University, Coimbatore. Currently she is doing research at International School of Photonics under CELOS project. She did her B.Sc. Electronics at College of Applied Sciences, IHRDE, Peermade. She has 7 years of teaching and 5 years of research experiences. Her area of research is polymer photonics.

G. Vidya is doing research at Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology. She did her B.Sc Chemistry, at B.C.M College, Kottayam and M.Sc Polymer Science, at M.G. University, Kottayam. Her area of interest is in the field of conducting polymers.

Dr. K. Geetha had been working as research associate at CELOS, CUSAT. She received her degrees from MG University and PG from CUSAT. Now, she is working as assistant professor at Sreekrishna College, Guruvayoor. Her area of interest is Polymer photonics.

She has more than 10 publications in internationally reputed journals.

Dr. Rani Joseph is a post graduate in Chemistry from Kerala University. She did her Bachelor of Technology and PhD in Polymer Technology from Cochin University of Science and Technology. She was the head of the Department during 2003-2006. She is currently working as Professor in the Department of Polymer Science and Rubber Technology Cochin University of Science and Technology. She has 35 years of post graduate teaching and research experiences. She has published more than 200 research papers in internationally reputed journals. She has presented more than 100 invited lectures /contributory papers in National and International Conferences. 25 students have taken PhD under her supervision. At present 10 students are working under her supervision. She has contributed chapters to RAPRA handbooks like Rubber Bonding, Polymer Foams, etc. Her research areas are Nanocomposites, Polymer blends, Polymers for optical recording, Photorefractive and photoconducting polymers, Electrically conducting polymers, Fiber reinforced composites, etc.

Prof. S. Prathapan is Associate professor at Department of Applied Chemistry, CUSAT. He received graduate degree from Kerala University, PG from CUSAT and Ph.D. from Indian Institute of Technology, Kanpur. He had postdoctoral fellowship from Rockefeller University and Carnegie Mellon University and he has visiting assignments at North Carolina State university, University of Connecticut, Carnegie Mellon University. He has more than 35 research publications in international journals. His interesting areas of research are Synthetic and Mechanistic Organic Chemistry, Conducting Polymers, Porphyrin Chemistry and Photochemistry.
Prof. C.P. Girijavallabhan received PhD degrees from Kerala University in 1971 and did postdoctoral research at Southampton University, United Kingdom. He was also a visiting professor at Fraunhofer Institute, Freiberg, Germany. Currently he is Emeritus Professor at ISP and CELOS. He is the founder director of International School of Photonics. His research interests include lasers, laser matter interactions, optoelectronics, molecular physics and solid state physics. He is the member of the governing council of the Nuclear Science Center (NSC), President of Photonics Society of India and a fellow of the Optical Society of India. He was the Vice President of the Indian Laser Association. He has published more than 200 research papers in international journals.

Dr. V.P.N. Nampoori is the Professor of Photonics in International School of Photonics, Cochin University of Science and Technology. He took his PhD in Physics in the field of Molecular Spectroscopy. At present he is working in topics related to Lasers, Photonics and Nonlinear Dynamics. Dr. Nampoori is one of the members of the core team to establish a well developed Laser and Photonics Laboratory in CUSAT. Now, this is one of the leading laboratories in Lasers and Photonics in India. He also designed the course structure for Integrated MSc Photonics Course as a part of the Center of Excellence in Lasers and Optoelectronic Sciences. Dr. Nampoori has published more than 300 research papers and guided about 15 PhDs in lasers, laser spectroscopy and fiber optics. Significant contributions of Dr Nampoori are in the area of Fiber optic Sensors, Nonlinear Optics and Photonic materials. Recently his group has developed a fiber optic amplifier which works in the visible range of the light spectrum. Dr. Nampoori is also interested in the field of Science Education through e-learning platform, popularization of science by writing popular articles in Malayalam and English periodicals.