Planar waveguide from PPV derivatives

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Abstract

We report in this paper the result of thin film fabrication of MEH-PPV and MEH-PPB having good optical transparency and low surface roughness suitable for planar waveguide application. The linear optical properties of the polymers were characterized using reflectometry and prism coupling, while the nonlinear optical property was measured by means of optical third harmonic generation (THG). The waveguide attenuation of the polymer films was determined by employing prism coupling set-up equipped with a photodiode array detector. The MEH-PPV waveguide film was shown to have a very low attenuation of 0.5 dB cm^{-1} at 1064 nm yielding an unprecedentedly high figure of merits of 11 at 1 GW/cm^2.

Key words: PPV derivatives, planar waveguide, linear optics, nonlinear optics, waveguide attenuation.

Sari

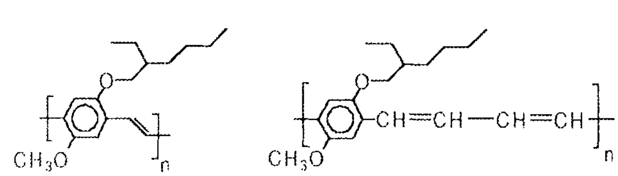
Pandu gelombang Planar dari turunan PPV

Dalam tulisan ini dilaporkan fabrikasi film tipis polimer MEH-PPV dan MEH-PPB yang mempunyai transparansi optik tinggi dan permukaan yang halus sehingga cocok untuk aplikasi pandu gelombang planar. Sifat optik linier dari polimer yang bersangkutan diukur dengan teknik reflektometri dan kopling prisma dan sifat optik nonlinier diukur dengan metoda *third harmonic generation* (THG). Selanjutnya, atenuasi pandu gelombang dari film polimer yang bersangkutan diukur dengan konfigurasi kopling prisma dan detektor *diode array*. Film pandu gelombang yang dihasilkan dalam eksperimen ini memiliki atenuasi rendah sebesar 0.5 dB cm^{-1} pada panjang gelombang 1064 nm dan menghasilkan "figure of merits" (FOM) sebesar 11 pada intensitas 1 GW/cm^2 yang merupakan nilai tertinggi sejauh ini.

Kata kunci: Turunan PPV, pandu gelombang planar, optika linear, optika nonlinear, atenuasi pandu gelombang.

1 Introduction

Conjugated-chain polymers such as polyacetylene (PA), polydiacetylene (PDA), and poly(p-phenylene vinylene) (PPV) have long been recognized as potentially useful nonlinear optical materials due to their large off-resonance cubic susceptibilities [1]. The development of their applications in the form of thin film devices has nevertheless been less than encouraging in spite of advantages offered by their remarkably fast response, relatively simpler and less expensive fabrication technology. The main hurdles to this development are the difficulties in meeting the figures of merit (FOM) for those applications. Foremost among them is the major issue of meeting the low loss requirement in the film, which in turn imposes severe condition on the purity, homogeneity and the surface smoothness of the film. The polymers having the right combination of characteristics for the required FOM have so far eluded researcher's attention. While PPV is recognized for its high cubic nonlinearity [2,3,4,5,6,8], high stability and optical damage threshold [4,9], this material is nevertheless completely insoluble and therefore not amenable to thin film fabrication for producing low loss waveguide. Despite intensive efforts in search of new solutions, those problems remain the major challenges for the realization of polymer based photonics devices.



(a) (b)

Figure 1 Molecular structure of MEH-PPV and MEH-PPB

One of the recently proposed solutions for improving processability of PPV, is the grafting of side chains of methoxy and hexyloxy groups to its main chain [10]. The basic repeat unit of MEH-PPV is monomer of PPV grafted with side chains of methoxy and ethylhexyloxy groups, and that of MEH-PPB is a similar molecule containing two double bonds in its vinyl chain as shown in Fig. 1. These PPV derivatives are known to be soluble in a number of solvents such as chloroform, tetrahydrofuran (THF), 1,4-dioxane, toluene, chlorobenzene, methylene chloride, and 1,1,2,2-tetrachloroethane (TCE) [10]. Regarding the detailed syntheses of MEH-PPV and MEH-PPB, the readers are referred to a previously published report [10]. The high solubility of PPV derivatives offer broader ranges of concentration variation which can in turn be more readily optimized with the other processing parameters using spincoating technique. Taking advantage of this new possibility, we have recently succeeded in producing high quality films of poly(N-vynilcarbazole) by means of spincoating its solution with the suitable choice of solvent as well as processing parameters consisting of polymer concentration, spinning speed and spinning temperature [11]. This technique has now been applied to planar waveguide fabrication of PPV derivatives such as poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene-1,3-butadiene-1,4-diyl] (MEH-PPB) on a substrate of fused silica with the air as the covering layer. The fabricated waveguides and results of their various characterizations will be described in this paper. Its estimated figure of merit will be determined and compared with results obtained in other cases.

2 Experiments

The thin films were prepared from solution of MEH-PPV (M_w = 25,000 (GPC) and T_g = 68°C)) and MEH-PPB (M_w = 20,000 (GPC) and T_g = 86°C) in toluene, which were spincoated on fused silica substrates (35 mm × 25 mm × 1 mm) at room temperature. Toluene was chosen as the solvent for its low hygroscopic property and suitable boiling point. Prior to the spinning process, the polymer solutions were filtered using 0.45 μm microphore filter to ensure their purity and homogeneity. The spincoating process was carried out under a laminar flow box to reduce contamination by dust particles. In addition, an aluminum substrate holder inset was introduced on the spincoater to keep the air dry surrounding the spin coater and thereby avoid the formation of interference ring pattern on the film. The waveguide films were always annealed at about 78°C for 24 hours in vacuum oven to remove residual solvent. In order to determine a suitable condition for MEH-PPV thin film preparation, the polymer weight concentration (c_w) was varied between 3% to 5% while a two-speed mode spincoating process was employed with the first speed kept at constant value (300 rpm) for 3 seconds before shifted to a higher second speed (ω) to be varied in the range of 300 - 4000 rpm. For the determination of suitable processing parameters for MEH-PPB thin film preparation, the weight concentration of the polymer solution (c_w) was varied between 1% to 6% and the second spinning speed varied between 300 - 6000 rpm.

The thickness, d, and surface roughness, R_a, of the films were measured with a Tencor Instrument model α-step 200 profiler at 400 μm scale range. The transmission and reflection spectra were measured by a Perkin-Elmer spectrophotometer model Lambda 9. Refractive indices of polymer films were measured by means of prism coupling technique. TE polarized lights of 633 nm from HeNe laser and 1064 nm from NdYAG laser were used in two separate measurements, where the light was coupled into the waveguide using high index glass prism of LaSFN18. The film was clamped onto the half-cut prism mounted on a precision rotary table and the laser beam was focused and directed onto the perpendicular corner of the coupling prism. The coupling angle was adjusted until a guided mode was launched through the waveguide. The refractive indices were calculated from the coupling angles according to the formula of Ulrich and Torge [14]. Further, a dispersion curve of the refractive index was calculated using Fresnel formula from the transmission and reflection spectra measured by a Perkin-Elmer spectrophotometer model Lambda 9.

The waveguide loss measurement was performed by employing the same prism coupling set-up described above. The losses were measured by the scattered radiation from a streak of the guide which was imaged onto a diode array using a lens [13]. The loss coefficient was determined from semilogarithmic graph showing the detected intensity as a function of the distance traversed by the light along the streak.

Measurement of THG by means of Maker fringe technique was performed by using an actively/passively mode-locked Nd:YAG laser (Quantel model YG 501) with duration of 30 ps and frequency of 10 Hz. The laser beam was focused on the samples which was placed in a vacuum chamber mounted on a rotation table.

3 Results and Discussions

The films of MEH-PPV and MEH-PPB prepared with the chosen parameters of c_w = 5% and ω = 2000 rpm are both transparent with a light orange color and red color respectively. It turned out that our choice of toluene as the solvent has a dominant role in producing the most transparent film with lowest surface roughness. The thickness (d) of these films are quite homogeneous as confirmed by the absence of perceptible interference fringes. The surface quality is quantitatively described by the variation of its surface depth profile or surface roughness (Ra) determined by using the graphical-centerlines technique [14]. The surface smoothness of the films was then characterized by their normalized surface roughness R_a/d which varies between 0.3% and 0.4% among films of the best quality, obtained with those chosen parametrs at room temperature. It is worth noting that the thickness (d) of all films prepared by this technique, and the corresponding spinning speeds (ω), polymer concentrations (c_w) are found to satisfy the relation given by the empirical equation.

Tabel 1 Summary of the linear ($n(\lambda_1)$, $n(\lambda_2)$) and nonlinear ($\chi^{(3)} = |\chi^{(3)}| e^{i\Phi}$) optical data of MEH-PPV (λ_{max} = 477 nm, λ_0 = 570 nm, α_{max} = 1.5 10^5 cm^{-1}) and MEH-PPB (λ_{max} = 490 nm, λ_0 = 600 nm, α_{max} = 2.2 10^5 cm^{-1}). The refractive indices at 633 nm and 1064 nm are obtained from prism coupling experiments, the rest are results from reflectometry measurement.

Polymer	λ_L [nm]	$n(\lambda_L)$	$n(\lambda_L/3)$	$\lvert\chi^{(3)}(-3\omega;\omega,\omega,\omega)\rvert$ [10^{-12}] esu	Φ [°]
MEH-PPV	633	1.7639 ± 0.0002			
	1064	1.6415 ± 0.0012			
	1064	1.667	1.394	18±2	180±20
	1431	1.652	1.594	21±2	105±10
	1710	1.648	1.968	17±1	4±10
MEH-PPB	633	1.9592 ± 0.0015			
	1064	1.7393 ± 0.0012			
	1064	1.748	1.335	22±2	130±5
	1470	1.729	1.634	23±1	90±10
	1800	1.710	2.164	19±2	

$$d_2 = d_1\left(\frac{\omega_2}{\omega_1}\right)^{\alpha}\left(\frac{c_{w2}}{c_{w1}}\right)^{\beta} \qquad (1)$$

with ω_1 = 2000 rpm, c_{w1} = 5 %, α = - 0.50, β = 1.61, and d_1 (ω_1, c_{w1}) = 542 nm for MEH-PPV films, while α = - 0.53, β = 1.49 and d_1 (ω_1, c_{w1}) = 450 nm for MEH-PPB films [15].

The transmission spectra of MEH-PPV and MEH-PPB thin films prepared with the same parameters are shown respectively in Fig. 2.a. The spectra were corrected from the reflection losses of film-substrate and film-air interfaces following the method proposed previously [9]. For the purpose of performing this correction, refractive indices dispersion curves of the PPV derivatives were calculated using Fresnel formula from transmission and reflection spectra measured by a reflection spectroscopy [6]. The result is shown in Fig. 2.b. It is found that in both cases the effect of reflection loss becomes dominant at long wavelength or the tails of the as measured absorption spectra. Without a proper treatment of the data, these spectra would fail to reveal the highly favorable sharp out-off of the absorption effect at the tails. Both spectra in Fig. 2.a display broad absorption maxima with the maximum absorption coefficient α_{max} and corresponding wavelength λ_{max} listed in Table 1. The cut off wavelength, λ_0, which is defined as the intercept between the base line and the tangent to the absorption edge, does not show significant difference between the two spectra. The values of λ_0 as presented in Table 1 clearly indicates the desirable window of transmission (λ > 600 nm) for waveguide applications at long wavelength.

We have included in Fig. 2.b and Table 1 the refractive indices determined by prism coupling method. These figures are the result of computer evaluation from coupling angles and film thickness measured from experiment following the method described previously [12, 13]. These data are needed for the subsequent determination of $\chi^{(3)}$ from the Third Harmonic Generation (THG) experiment to be discussed later.

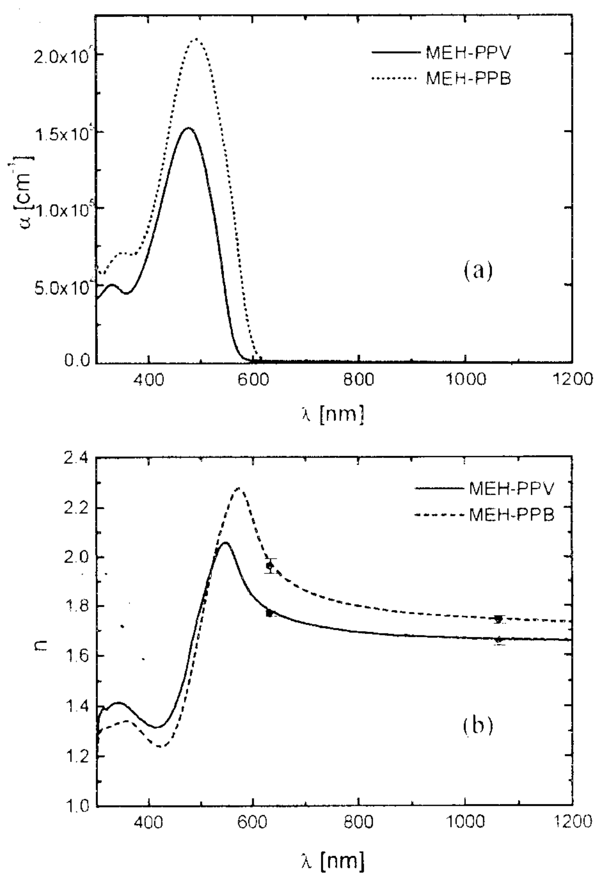


Figure 2 Spectra of the absorption coefficient α and the refractive indices n of MEH-PPV and MEH-PPB films. (a) Spectrum of 51.8 nm-thick film of MEH-PPV (solid line) and spectrum of 58.8 nm thick film of MEH-PPB (dashed line). (b) Dispersion of refractive indices n of MEH-PPV (solid line) and MEH-PPB (dashed line) films. The values represented by full circles in figure (b) were those obtained from prism coupler.

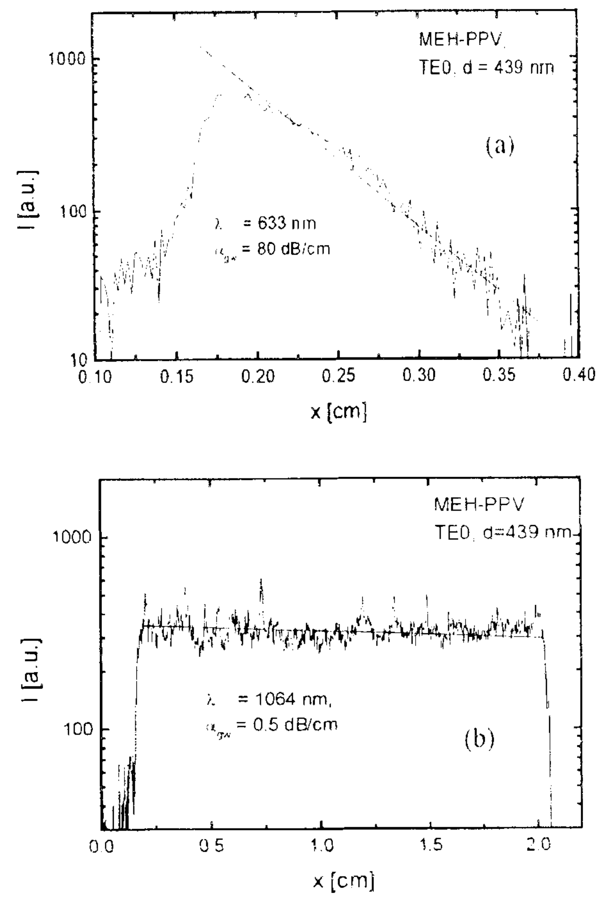


Figure 3 Stray light of 439 nm thick film of MEH-PPV waveguide for TEO mode in semilogarithmic presentation for λ_L = 633 nm (a) and λ_L = 1064 nm (b)

In our experiment, the loss coefficient was measured as the total loss due to absorption as well as scattering. The results are shown in Fig. 3.a and 3.b as stray lights of MEH-PPV waveguide at λ_L = 633 nm and λ_L = 1064 nm, respectively. The distance scale in the figure was calibrated by the number of pixels per centimeter determined by a ruler. A statistical linear fitting was carried out on the logarithmic plots of data displaying the dependence of scattered light intensity on the distance of propagation. The slopes of the resulted lines were then determined to yield the coefficients of loss in question. The results show that the value of α_{gw} depends sensitively on the laser wavelength. i.e. α_{gw} = (80 ± 5) dB/cm at 633 nm and α_{gw} = (0.5±0.1) dB/cm at 1064 nm for the MEH-PPV waveguide. Nevertheless, it is most important to note that the loss at 1064 nm given above is considerably lower than that given by a previous report which cited a value of α_{gw} = (4.4±0.3) dB/cm at λ = 633 nm for MP-PPV [16], α_{gw} = (1.0±0.3) dB/cm at λ = 830 nm for DMOP-PPV [17], α_{gw} = 1.5 dB/cm at λ = 950 nm for DPOP-PPV [18], α_{gw} = (1.0±0.5) dB/cm at λ = 1064 nm for DFV-PDPV [19] and α_{gw} = (79±9) dB/cm at λ = 1064 nm for unsubstituted PPV [9]. This was further corroborated by our visual observation that the laser light could only traverse a full distance of 5 mm in the MEH-PPV waveguide at λ_L = 633 nm, while the entire length of the waveguide was readily traversed by the light at λ_L = 1064 nm. Since the measurements were performed along the same lateral position of the same film, the difference is not supposed to have any contribution from the surface condition of the film. It is interesting to note however, that our measurement yields an absorption coefficient of MEH-PPV at 633 nm of about three times its value at 1064 nm. We are thus led to suggest that in addition to absorption loss, the major contribution to the large difference between α_{gw}'s at those two wavelengths must have come from the difference between the corresponding absorption tails. Compared to MEH-PPV waveguide, a visual inspection of the CCD camera showed that a waveguide made of MEH-PPB film could only transmit guided light for about 2 mm at λ_L = 633 nm, while the light was able to traverse the entire length of the waveguide (about 30 mm) at λ_L = 1064 nm without significant reduction of the intensity. Based on the sensitivity of the eye with an average of about 27 dB, it is estimated that the waveguide loss of MEH-PPB is more than 100 dB/cm at λ_L = 633 nm, while the waveguide appears to perform reasonably good at λ_L = 1064 nm.

For the determination of cubic nonlinear susceptibility of the films, measurement of their THG effects was carried out using Maker fringe technique [6] and analyzed following the method described in a previous report [20] by taking into account the thickness, optical density and refractive indices of films at the fundamental (ω) as well as the third harmonic (3ω) wavelengths. The results of both polymer films are given in Table 1. It is important to note that the estimated values of $\chi^{(3)}$ for these PPV derivatives are of the same order of magnitude as that found for the unsubstituted PPV [6]. This means that the more favorable characteristics of the derivatives can be attained without sacrificing the most essential nonlinear optical properties of the original polymer. We further note that $|\chi^{(3)}|$ of MEH-PBB is only slightly larger than that of MEH-PPV, while the conjugation length L of MEH-PBB is about 4/3 of that of MEH-PPV. This is obviously at variance with the 1-D scaling law expressed by $\chi^{(3)}$~L^6 [7].

For NLO and integrated optics applications, the figures of merit (FOM) commonly adopted for material evaluation are the W-FOM and T-FOM expressed by the following combination of parameters [20].

$$W = \frac{n_2 I}{2\alpha_0 \lambda} \qquad (2)$$

$$T = \frac{2\alpha_2 \lambda}{n_2} \qquad (3)$$

where I is the laser intensity, λ the laser wavelength, α_0 the linear absorption coefficient, α_2 the nonlinear absorption coefficient and n_2 the nonlinear refractive index. While all other parameters are given directly from

Tabel 2 Figures of merit for optical waveguides of PPV (λ_0: polymer absorption edge, λ_L: laser wavelength, α_{gw}: measured loss coefficient of guided wave)

Material	λ_0 [nm]	λ_L [nm]	$\|n_2\|$ [cm^2/W] / method	α_{gw} [cm^{-1}]	W at 1 GW/cm^2	Ref.
MEH-PPV	570	1064	2.4 10^{-13} / THG 1710 nm	0.1	11	this work
P4-BCMU	585	1064	4.6 10^{-13} / THG		1	[24]
PPV	521	1064	9 10^{-14} / m-line	9	0.1	[10]
		1064	3.0 10^{-13} / THG		0.15	[24]
		925	5 10^{-12} / m-line	9	3	[10]
CNE-PPV	514	1064	7.6 10^{-14} / THG		4	[24]
DA-PPV	502	1064	3.0 10^{-14} / THG		0.1	[24]
DPOP-PPV	447	1064	2.1 10^{-14} / THG		0.7	[24]
		950	1 10^{-14} / interferometer	0.4	1	[19]

the experimental results, the value of n_2 was estimated from the cubic nonlinear susceptibility ($\chi^{(3)}$) according to well known expression [22]

$$n_2(\omega) = \frac{3}{4}\frac{1}{n_0^2 c\varepsilon_0} Re\left[\chi^{(3)}(-\varpi;\varpi,-\omega,\omega)\right] \tag{4}$$

where n_0 is its linear refractive index and ε_0 is the permittivity of free space. This nonlinear refractive index plays an essential role in nonlinear optical application and it features strongly in the FOM's for nonlinear waveguide. As mentioned earlier, the cubic nonlinearity values of the polymer derivatives are in the same order of magnitude of the value of PPV. The FOM of MEH-PPV waveguide was determined for laser wavelength of 1064 nm and laser intensity of 1 GW/cm^2, using the figures given in Table 1, namely $\alpha_0 = \alpha_{gw} = 0.1$ cm^{-1}, $\chi^{(3)} = 1.8 \times 10^{-11}$ esu and the approximation $\chi^{(3)}(-\omega;\omega,-\omega,\omega) \approx \chi^{(3)}{}_0(3\omega;\omega,\omega,\omega)$. The result of applying equation (2) yields a W-FOM of 11 from these data. This value is significantly higher than those reported previously on PPV based Polymer [9] and larger than that of polydiacetylene P4-BCMU [23] as shown in Table 2. Unfortunately, The T-FOM can not be determined here as the two-photon absorption measurement was not carried out in this experiment. Nevertheless this result alone clearly suggests that MEH-PPV is a promising material for nonlinear optics device applications.

4 Conclusions

We have demonstrated in this experiment that a suitable choice of parameters for spincoating process has resulted in good quality MEH-PPV and MEH-PPB films, with the associated planar waveguides displaying favorable characteristics for nonlinear optical device applications. It was shown that the enhanced selubility of PPV derivatives has made possible the spincoating of homogeneous film of smooth surface and uniform thickness, while sustaining the large cubic susceptibility of PPV. It was also found that for both MEH-PPV and MEH-PPB films, the cubic susceptibility $\chi^{(3)}$ normalized by the corresponding linear coefficient absorption α does not follow the scaling law of 1-D conjugated polymers. Most important of all, the low waveguide loss demonstrated by the MEH-PPV film waveguide has resulted in an enhancement of its FOM to a value significantly higher than P4-BCMU, implying the promising application of these polymers for photonic devices.

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