Spectroscopic study of Styryl films doped PMMA prepared dip coating method

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Abstract: In this work, sample of laser dye:styryl (9M) havebeen prepared in solid films by dip coating method. Coating materials consist of styryl (9M) and polymer as a host (polymethelmethacrylate, PMMA) percentage 30% and 70% respectively and the dye have 10^{-2} [M] concentration. The prepared filmsthickness has been controlled by adjusting the withdraw speed of system. Thefluorescence of samples in solid phases have been studied under high-excitation conditions to induce fluorescence, in this work a laser 532 nm of 50 mW has been used. In addition to this, other topicssuch as spectroscopic properties have been studied including lifetime, quantum yield and absorption coefficient. From the experimental results. Any shift have not been appeared with the increase of the thickness in samples i.e. it remains approximately fixed.

Keywords: Dye laser, polymer, dip coating, fluorescence, thickness

Date of Submission: 05-08-2017

Date of acceptance: 13-08-2017

I. Introduction

Dye doped polymers havelarge field of applications in the fields of modern photonic technology apart from its use as an alternative to solid state laser media [1, 2]. Laser dyes are large organic molecules. The color emitted by the laser dyes depend upon the surrounding medium i.e. the medium in which they are dissolved [3, 4]. However, there are many oflaser dyes that can be used to span continuously the emission spectrum from the near ultraviolet to the near infrared.Laser dyes are also used todope solid-state matrices, such as poly(methyl methacrylate) (PMMA) to provide gain media for solid state dye lasers. [5] Dip-coating is a simple techniques used to fabricate of blends films by dipping the substrates samples in the selected solution to get homogeneous selected films. It is a low cost and waste-free process method used to prepare thin layers from chemical solutions that is easy to scale up and offers a good control on thickness. The dip-coating process involves immersing a substrate into a desired coating liquid or liquid-like jelly for enough time, to ensure that the substrate is completely wetted, and the withdrawing the substrate from the solution bath. After the solvent has evaporated, a uniform solid filmis deposited upon the surface of the substrate [6, 7]. The mechanism of dip coating summarized as follows shown in Fig (1): When the slide dipped into the coating bath, if the speed is not too great, most of the gas originally in contact with the substrate is displaced by the coating liquid at the bath surface. The submicroscopic region where that happens is called the dynamic wetting line. At higher speeds, submicroscopic bubbles of the gas may be entrained at the coated surface [8, 9].

With rising speed the amount of entrained gas increases until it becomes intolerable. This is the air entrainment limit on coating speed, a fluid mechanical phenomenon. [10].



Figure (1) Stages of dip coating processes

In fast withdrawal speeds quickly move the substrate from the solution bath and hence, the solvent evaporation at the liquid surface is minimized [11].

Several forces are involved in the film deposition. The major forces are viscous drag, gravitational force, capillary force (resultant force of surface tension), and inertia force.

A dip-coating analysis was first presented by Landau and Levich (1942) [12]. This analysis has subsequently been reviewed widely (e.g. Deryagin and Levi, 1959) [13]. The model derivation was based purely on the hydrodynamics of a Newtonian fluid flow.

By using the classical equations, a matching condition for the film entrainment and the static meniscus regions can be identified and used to obtain an expression for the film thickness as shown in Equation [16][17]:

$$X = 0.944 \frac{(\eta \, u_0)^{2/3}}{\sigma^{1/6} (\rho \, g \,)^{1/2}} \tag{1}$$

where X is the limiting film thickness, u_o is the withdrawal speed, η is the solution viscosity, ρ is the solution density, σ is the solution surface tension. The withdrawal speed is the most common parameter used to control the film thickness. There have been a large number of researchers studying the film thickness dependency on the withdrawal speed. [18].

II. Experimental

2.1 Fabrication of Dye – Doped Polymer thin Films Processes

Dye doped polymer films were fabricated by dip coating technique. The solution of the polymer is prepared by dissolving the required amount of polymer. A required amount of dye solution was added to polymer solution.

Glass substrate (size 2.5 cm x 7.5cm) under normal laboratory conditions (dark room, 35 C^{0}). The process flow diagram of the thin film preparation is shown in Fig (3-2).



Fig. (2): Process flow diagram of the thin film preparation.

2-2 Thickness measurements by Weight method

The simplest method for film thickness determination based on the mass difference. The filmthickness can be calculated from the mass of the coating if the density and the area on which the material is deposited is known. The thickness is calculated using the following equation:

 $x = \frac{\Delta W}{2.\rho.A} \qquad (2)$

Where x is the film thickness, m is the mass of the coating, A is the area tested and ρ is the deposited material density.



Fig (3): Absorption for styryl thin films with different withdraw speed (a) 0.5 (b) 5 (c) 10 (d) 15 and (e) 20 cm/min



Fig (4): Absorption for styryl thin films with different withdraw speed (a) 0.5 (b) 5 (c) 10 (d) 15 and (e) 20 cm/min

III. Results and Discussions

Films thickness is an important variable in devices fabrications. Fig. (5)Shows the effect of withdraw speed on film thickness. Figure (5) shows that the films thickness increases from 3200 to 9270 nm with increasing withdraws speed from 0.5 to 20 cm/min. The orientation of the mesoscopic structure is vertical and is obviously due to gravity.

In case of very low withdrawal speeds, i.e. in the capillarity regime, the solvent evaporation becomes faster than the movement of the drying line leading to a continuous feeding of the upper part of the meniscus by the solution through capillary rise. By assuming that the evaporation rate is constant and applying the mass conservation law. This is nearly the same result in reference. This nearly the same result in Ref[9].

On theother hand however, films may also be obtained if the "capillarity regime" isapplied, where very low withdrawal speeds are used. Here solvent evaporationbecomes faster than the movement of the drying line leading to a continuousfeeding of the upper part of the meniscus and finally also to thicker films.



Fig. 5 Thickness variation with withdraw speed

IV. Conclusions

Thickness of the membrane increase with increasing of withdraw speed of system, the best rate of PMMA to obtain a homogenies film was (20g) for (10 ml), as well as the greater the thickness of the membrane the greater the intensity of absorption and fluorine.

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BahaT.Chiad. "Spectroscopic study of Styryl films doped PMMA prepared dip coating method." IOSR Journal of Applied Physics (IOSR-JAP), vol. 9, no. 5, 2017, pp. 14–17.

DOI: 10.9790/4861-0905021417