Spin-Coating of Polystyrene Thin Films as an Advanced Undergraduate Experiment

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Spin-coating (casting) is a commonly used technique to apply thin films on two-dimensional surfaces of wafers. The technique has important technological applications in the fabrication of microcircuits and microreactors, magnetic disks, flat screen displays, antireflection coatings, compact discs (CD, DVD), television tubes, and nanomaterials *(1–5).* Coating polymer films on a wafer is a popular way of studying the optoelectronic properties of a polymer. In addition, doped polymer films are used both for scientific studies of dopants and technological applications.

We describe a method of thin polymer film casting on glass slides. Polystyrene and commercially-available expanded polystyrene foam packaging material are used. The polymers are dissolved in toluene and then drops of the solution are spread on a spinning glass slide. UV–vis absorption spectrum of the film, occurring as a result of the interference of light, is used to calculate the thickness of the films. The following equations are used for the calculation of thickness *(6–7),*

$$\nu = \frac{\dfrac{n(\lambda_1)}{\lambda_1} - \dfrac{n(\lambda_2)}{\lambda_2}}{N_{\text{cyc}}} \qquad (1)$$

$$d = \frac{1}{2\nu} \qquad (2)$$

where $n(\lambda_1)$ and $n(\lambda_2)$ are the refractive indices of the film at wavelengths λ_1 and λ_2, N_{cyc} is the number of cycles in the interference fringes between λ_1 and λ_2, and d is the thickness of the film. By applying eqs 1 and 2 to the experimentally observed maxima and minima, the thickness of the film can be obtained. For simplicity, the refractive index of the film is assumed to be wavelength independent. In more rigorous treatments, the wavelength-dependent refractive indices can be calculated from appropriate equations and may be used. A value of 1.6 for the refractive index of polystyrene as well as expanded polystyrene foam is used here. Ordinary glass slides absorb light strongly below about 330 nm; hence, the measurement in the experiments was limited to wavelengths between 330 nm and 1100 nm.

FTIR spectra of the films on glass slides are also used to determine the polymer film thickness. As glass absorbs strongly below 2000 cm^{-1}, the film vibrational characteristics occurring below 2000 cm^{-1} cannot be identified. The C−H stretching vibrations of polystyrene and expanded polystyrene foam occur in the region between 2700 cm^{-1} and 3200 cm^{-1} and can be recorded with the present sample. The Beer–Lambert law is applied to calculate the thickness of each film from its FTIR spectrum with respect to a reference 38.1-µm-thick polystyrene film. The calculated film thicknesses using both methods are compared. The thicknesses of the coated films are plotted as a function of the concentrations of the starting solutions to check the applicability of the well-known power law *(2, 3).*

Dye-incorporated polymer films have potential applications in the electronics industry, such as making sensors and display systems. A dye, [para-red; 1-(4-nitrophenylazo)-2-naphthol, molecular weight 293.28] synthesized by students in an earlier laboratory experiment, is mixed with the polymer solution. The solution is deposited on a glass slide to form a thin film. A blue-colored, permanent-marker-pen ink (commercially available) is also incorporated into the polymer film and is deposited on a glass slide. The present dyes were chosen for easy detection using a UV–vis spectrophotometer. The dyes in the film are identified from their visible spectra.

The experiments reported in this article can be performed by advanced undergraduate students with knowledge of spectroscopy.

Experimental Procedure

The experimental arrangement is fairly simple. An ordinary, commercially available cooling fan (a "CPU Cooler") was modified to accommodate approximately 1-in. × 1-in. glass slides that could rotate above the fan at the speed of the fan. The "CPU Cooler" was glued to a 4-in. × 4-in. wooden plate so that the fan would not move while rotating. The cover of a microscope-slip-container box was glued onto the rotating side of the fan. The sample compartment of the experimental setup is shown in Figure 1. Polystyrene beads and expanded polystyrene foam packaging materials

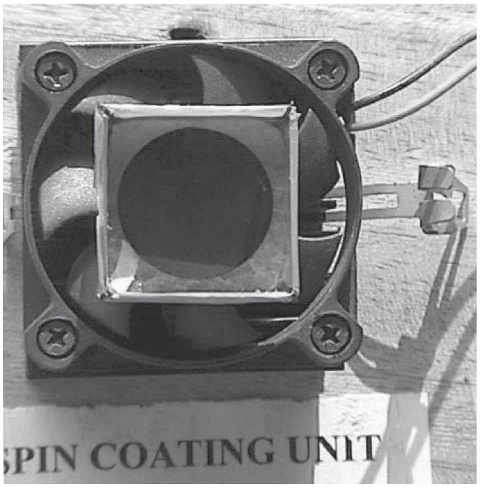

Figure 1. A view of the experimental setup for spin-coating of thin films.

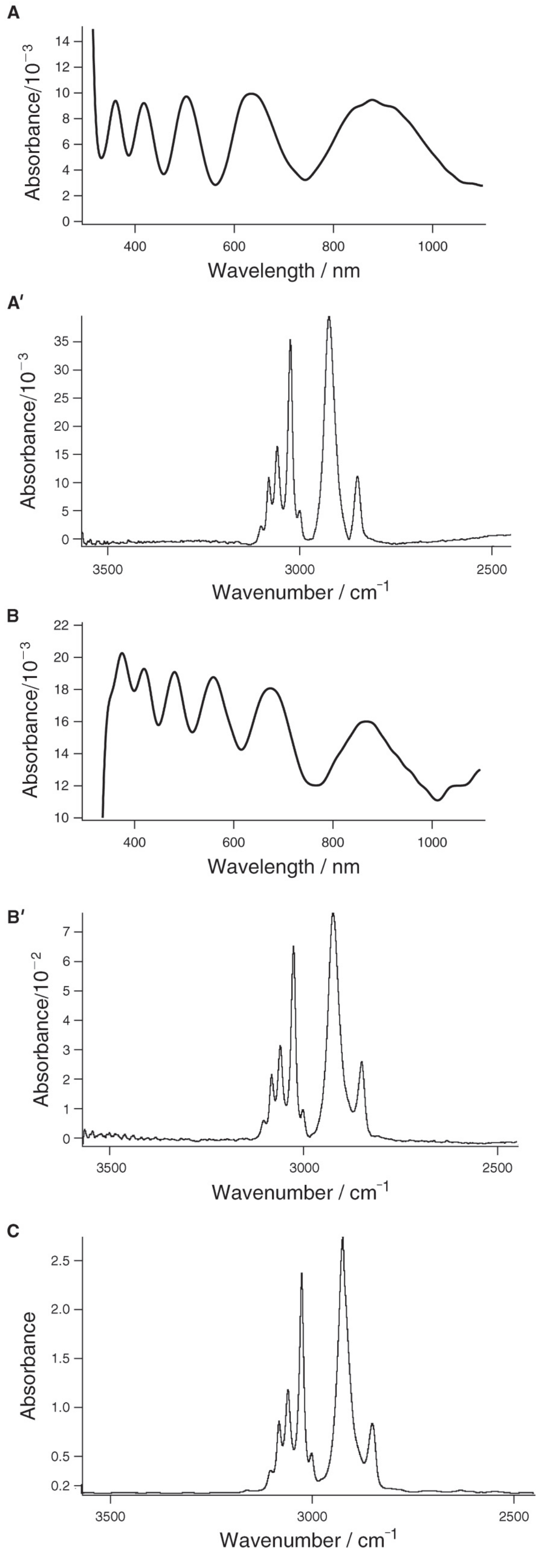

Figure 2. (A) Typical UV–vis and (A′) FTIR spectra of a spin-coated polystyrene film; (B) Typical UV–vis and (B′) FTIR spectra of a spin-coated expanded polystyrene foam film; (C) FTIR spectrum of a reference 38.1-μm-thick polystyrene film.

were dissolved in toluene to make solutions with varying polymer concentrations. Microscope slides were cut into roughly 1-in. × 1-in. sizes. One slide was placed inside the sample holder. The fan was then turned on to the highest speed (input voltage: 12 V, dc power) with an approximate revolution per minute (rpm) value of 2400. The rpm was measured using a tachometer (Electronic Automation Private Ltd.; DT2001-B). Measured amounts of polymer solutions were dropped at the center of the rotating slide. Several samples were prepared from single or multiple drops of the polystyrene and the expanded polystyrene foam solutions. The slides were then air-dried overnight to remove excess toluene; they could also be vacuum dried in a desiccator. UV–vis and FTIR spectra of the slides were taken by placing the slides vertically inside the sample compartment of the appropriate spectrophotometer. A Hitachi U-2001 UV–vis spectrophotometer was used to record UV–vis spectra and a Nicolet Impact 410 FTIR spectrophotometer was used to record IR spectra. For the UV–vis study a wavelength scan speed of 800 nm/min was used. Each IR spectrum was an average of 128 scans.

For depositing thin films of polymer doped with dyes, a para-red dye, which was synthesized in an earlier laboratory experiment, was used. The appropriate amount of either the dye (para-red, 5.0×10^{-3} g) or the permanent ink (Luxor, 40 μL) was added to 2 mL of the previously prepared polystyrene in toluene solutions.

Hazards

Caution should be taken when handling the glass slides and while dropping liquid on the rotating slides. Toluene is highly flammable, harmful or fatal if swallowed, causes irritation, can damage the lungs and irritate the respiratory tract, and is a cancer and birth defect hazard. The setup must be kept inside or near a hood. A barrier must be kept in front of the setup to avoid flying glass hitting the student in case the system fails (this has not happened in our labs). Para-red dye is an ingestion hazard: it causes cyanosis due to methemoglobinemia and it causes bacterial mutation. There is no known inhalation hazard or skin contact hazard associated with para-red dye.

Results and Discussion

The UV–vis spectra of polystyrene and expanded polystyrene foam films and their corresponding FTIR spectra respectively are shown in Figure 2, A, A′, B, and B′. Figure 2A corresponds to serial number 2 of polystyrene in Table 2 and Figure 2B corresponds to serial number 5 of expanded polystyrene foam in Table 1. The FTIR spectrum of a reference 38.1-μm-thick polystyrene film is shown in Figure 2C. Using eqs 1 and 2, the thickness of each film is calculated from its UV–vis spectrum. The calculated thicknesses of the polystyrene and expanded polystyrene foam films at various concentrations of the starting materials are presented in Tables 1 and 2. Using the Beer–Lambert law, the thicknesses of the same films were calculated from their FTIR spectra and are also presented in Tables 1 and 2. Included in the table are the thickness data for films with different starting concentrations of the polymers. It is evident from the data that both methods give results that are in reasonable agreement with

Table 1. Thickness of the Expanded Polystyrene Foam Films at Various Initial Solution Concentrations, as Calculated from UV–Vis and FTIR Methods

Series No.	Volume of Solution Added /µL	Concentration/ (gm/100mL)	Calculated Thickness /nm	
			UV–Vis Method	FTIR Method
1	50	1.95	125	127
2	50	3.09	275	271
3	50	4.33	430	423
4	50	6.16	668	531
5	50	8.63	1021	1118
6	50	9.83	1176	1152

Table 2. Thickness of the Polystyrene Films at Various Initial Solution Concentrations, as Calculated from UV–Vis and FTIR Methods

Series No.	Volume of Solution Added /µL	Concentration/ (gm/100mL)	Calculated Thickness /nm	
			UV–Vis Method	FTIR Method
1	50	4.66	502	478
2	50	6.12	751	640
3	50	7.16	1210	1284
4	50	9.18	1437	1283
5	50	11.67	2060	1934
6	50	12.91	3015	3225

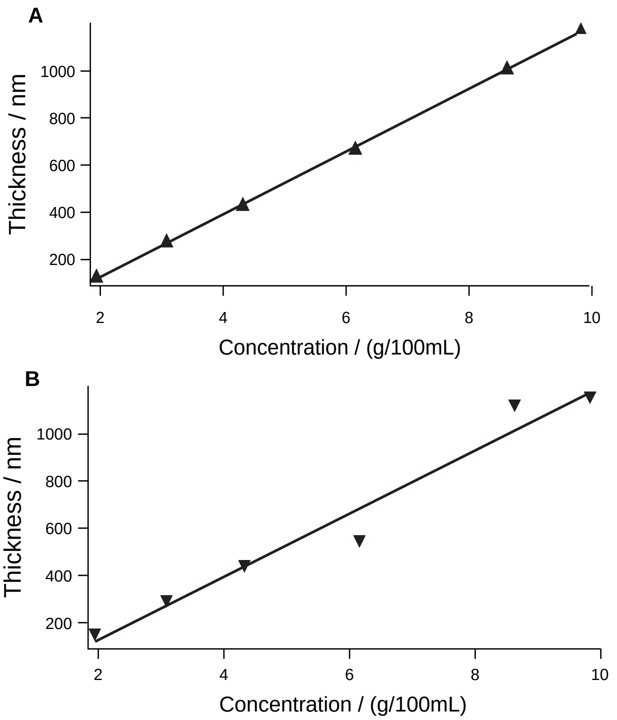

Figure 3. Plot of thickness of expanded polystyrene foam film versus initial concentration of solution, as obtained from (A) UV–vis spectra and from (B) FTIR spectra.

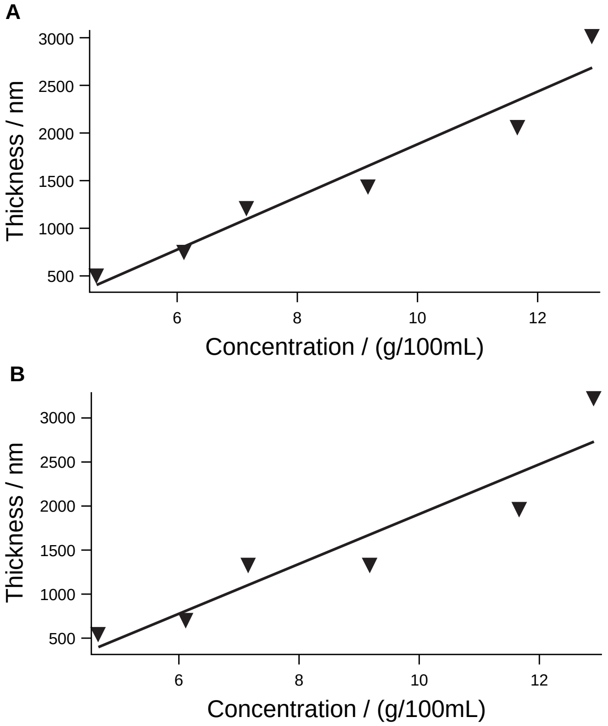

Figure 4. Plot of thickness of polystyrene film versus initial concentration of solution, as obtained from (A) UV–vis spectra and from (B) FTIR spectra.

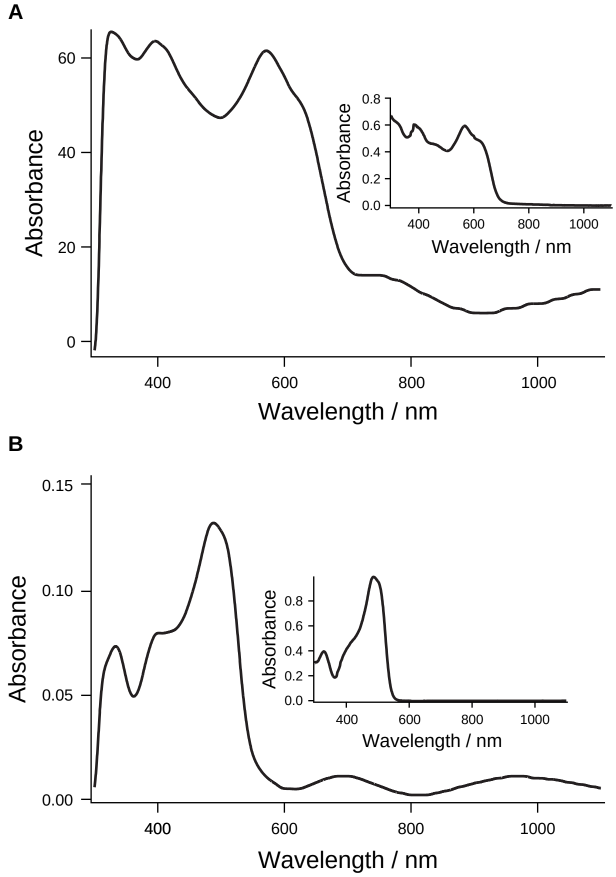

Figure 5. UV–vis absorption spectra of doped (A) blue permanent marker pen ink in a film and (B) para–red dye in another film. Insets are the corresponding absorption spectra of dyes in toluene.

each other. In addition, plots of the thickness of coated films as a function of concentration of the polymer in the initial solution result in a nearly linear relationship as shown in Figures 3 and 4.

This relationship follows the empirical expression for the thickness *(2),*

$$d = \frac{K\eta^{\gamma}C^{\beta}}{\omega^{\alpha}} \tag{3}$$

where d is the thickness of the film, K is an overall calibration constant, C is the polymer concentration in grams per 100 mL solution, η is the intrinsic viscosity, ω is the number of rotations per minute (rpm), and α, β, and γ are the exponent factors. The exponent factors are determined experimentally and can be used to predict the final thickness of the film. It has been reported that eq 3 can be as simple as *(3)*

$$d = \frac{K\eta C}{\omega^{1/2}} \tag{4}$$

In our experiments ω was constant and the equation can be further simplified by assuming η is constant (even though it may not be the case in absolute sense) over the concentration range we have used. Thus, the thickness of the film depends only on the concentration of the polymer solution. Plotting the resultant thickness of the film versus the concentrations of the solution, the relationship was found to be linear (Figures 3A and 3B and Figures 4A and 4B).

The visible spectra of coated films doped with para-red dye and permanent-marker-pen ink on glass slides are shown in Figure 5. The visible spectrum of each dye doped in the film is very similar to that of the dyes dissolved in toluene. The method demonstrates the ability to incorporate dye molecules into thin organic films that are coated onto glass slides. The primary condition for making dye-coated thin films is that both the dye and the polymer material be soluble in the same solvent.

Conclusion

We demonstrated the viability of an undergraduate experiment to make thin polymer films coated on glass slides using a simple cooling fan as the “spinning wheel”. The film thicknesses measured by the UV–vis interferometric method and the FTIR method using the Beer–Lambert law of absorbance yielded nearly similar results. The thickness of the film as a function of the concentration of the initial solution showed a nearly linear relationship in all cases. Further, the incorporation of dyes into the film demonstrated the possibility of dopant incorporation in films.

Acknowledgment

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$^{\text{W}}$Supplemental Material

Instructions for the students and notes for the instructor are available in this issue of *JCE Online*.

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