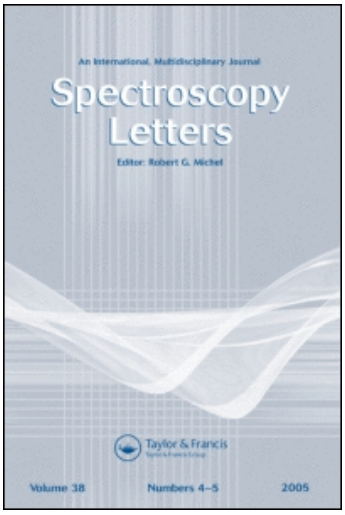

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PHOTOACOUSTIC STUDIES ON VERY THIN POLY(METHYL METHACRYLATE) FILMS PREPARED BY A CASTING-ON-WATER METHOD

photoacoustic spectroscopy, casting-on-water method, ultrathin polymer film,

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ABSTRACT

Photoacoustic (PA) responses from very-thin poly(methyl methacrylate) (PMMA) films were investigated at various lamination conditions. The PA signal increased when the dye-doped films were laminated up to five layers, but tended to saturate beyond five layers. When the blank films were superimposed on the dye-doped film, the signal became smaller. The signal was larger when the dye-doped film was arranged outermost in the laminated film assembly of dye-doped and blank films. The results imply the effect of film vibration on the PA response.

INTRODUCTION

Photothermal spectroscopies have been proven powerful for nondestructive and ultratrace analysis.[1-3] Among them, photoacoustic

spectroscopy (PAS) detects acoustic waves from nonradiative relaxation of photoexcited sample materials. Thus, thermal diffusion from the solid sample to the gas phase plays an important roll for the detection of PAS signal by a microphone.[4,5]

In this study, we have investigated photoacoustic (PA) responses from very-thin polymer films prepared by a casting-on-water method.[6-8] This film is self-standing in spite of ~80 nm thickness, so that various types of multilayered film assemblies can be easily prepared. The PA response from the multilayered film assembly with different orientations and lamination conditions have been compared.

EXPERIMENTAL

Sample dyes, Disperse Red 1(DR1) and 2, 3, 7, 8 ,12, 13, 17, 18-octaethylporphine (OEP) (Aldrich) were recrystallized twice from toluene. Poly(methyl methacrylate) (PMMA) (Yoneyama Regent Co. Ltd., degree of polymerization 6,000) and poly(ethylene glycol)dodecyl ether (PEG) (Tokyo Kasei, number of polyoxyethyrene units: 25) were used as received.

Very thin PMMA films were prepared by a casting-on-water method developed by T. Kajiyama and his coworkers.[9, 10] For example, 0.1 g of PMMA and 7.9 mg of DR1 was dissolved in 1.0 ml of chloroform, and then toluene (1.0 ml) and PEG(0.5 mg) were added to the chloroform solution. About 10 μl of this mixed solution was carefully spread on the water surface filled in a round Teflon dish with the use of a microsyringe. The very thin PMMA film quickly formed on the water surface.[6-8] The film was then transferred into a round frame (6 mm diameter) of a square polyester sheet (10

x 10 mm), and dried in a desiccator. The thickness of the film was estimated to be ~80 nm by the conductivity method. The film is self-standing in the frame.

Figure 1(a) shows a schematic illustration of the PAS system for the measurements of very thin PMMA films. Monochromatic light from a 300W Xenon lamp was chopped and was introduced into a PAS cell by using an optical fiber (ϕ(diameter) = 4 mm). The power was about 0.3 mW at 485 nm. The photoacoustic (PA) signal was picked up by a microphone(Panasonic, WM-36D). The output signal was amplified by a AC preamplifier (Gain: 26.4 dB), and was acquired by a lock-in amplifier (NF, NF-5560).

As shown in Figure 1(b), a PAS cell is made of an aluminum body with holes (ϕ = 5 mm) for passing through the excitation light. The optical fiber was attached to this hole to introduce the excitation light. The square polyester sheet (10 x 10 mm) having a self-standing sample film of (ϕ = 6 mm) (right of Figure 1(b)) was fixed tightly in the cell by silicone rubber sheets. The internal volume of the cell is about 30 mm^3.

RESULTS AND DISCUSSION

Figures 2 and 3 show PA spectra of single-layer PMMA films containing OEP and DR1, respectively, together with absorption spectra of corresponding dyes in chloroform. In both cases, spectral features are essentially identical between PA and absorption spectra. The absorption spectrum of the dye-doped PMMA film could not be obtained due to very low absorbance (~0.02) and large fluctuation (more than 0.01 in absorbance) of baseline. The present PAS system was almost free from baseline fluctuation, and thus it was about two orders of magnitude as sensitive as the absorption spectroscopy.

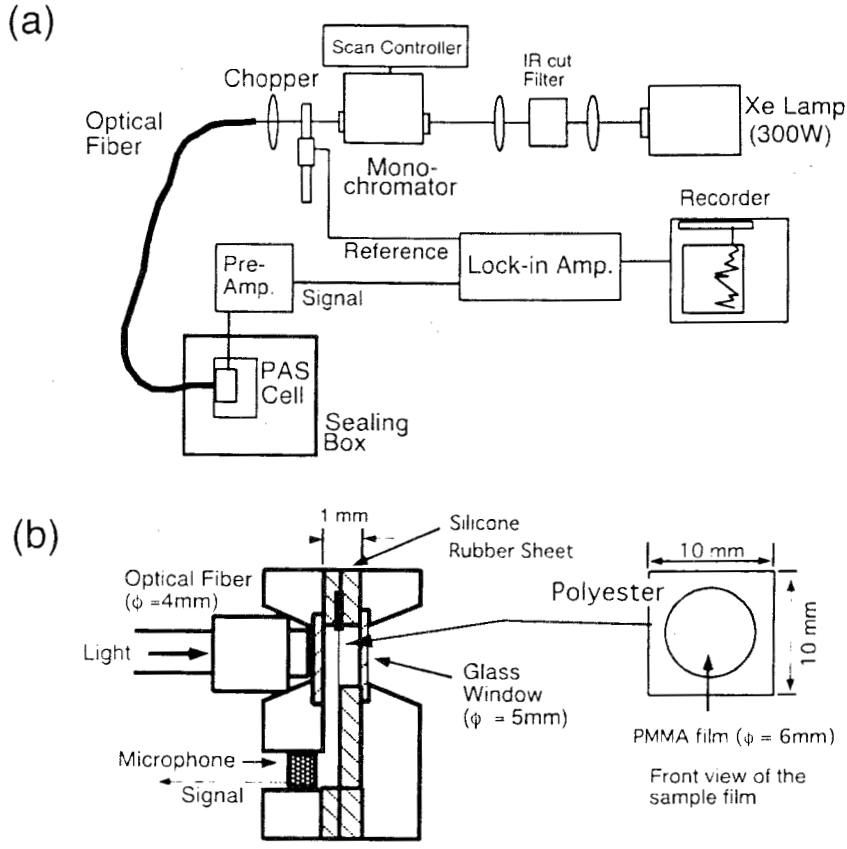

FIG. 1. Schematic illustration of the PAS measurement system (a) and the PAS cell (b).

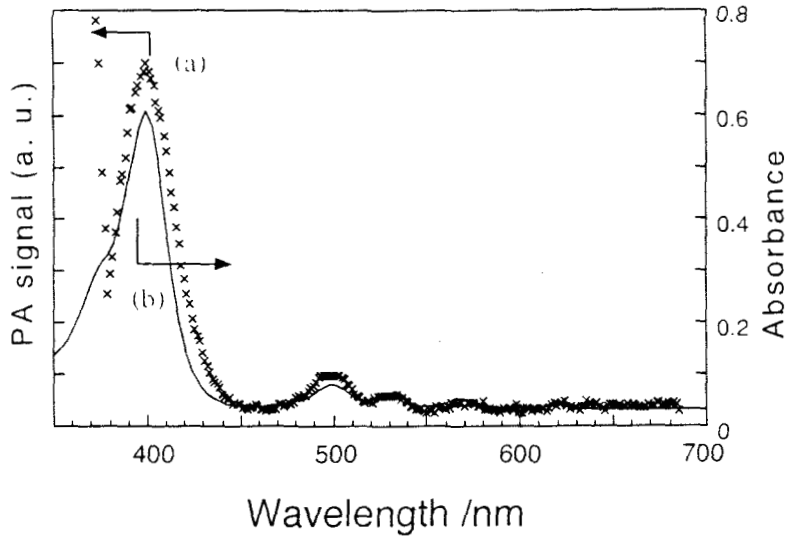

FIG. 2. PA spectrum of a OEP-doped PMMA film (a: x) and absorption spectrum of OEP in chloroform (b: ——).

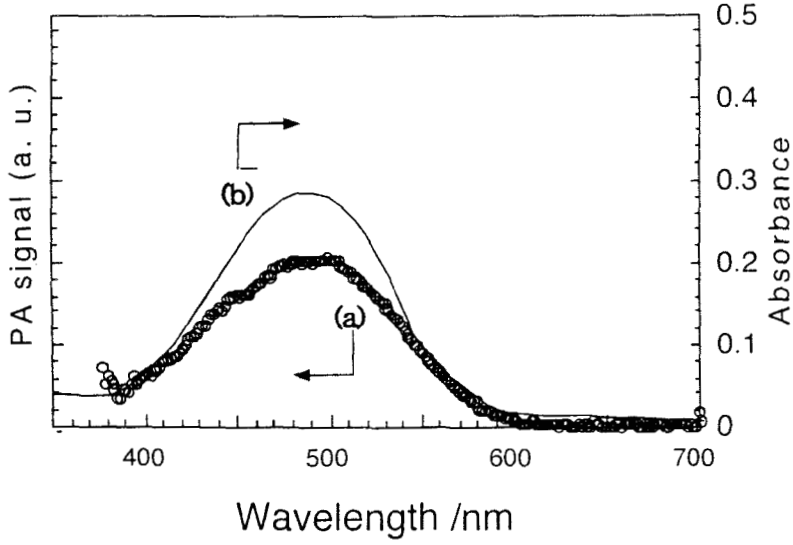

FIG. 3. PA spectrum of a DR1-doped PMMA film (a: ○) and absorption spectrum of DR1 in chloroform (b: ——).

One of the noteworthy characteristics of the present PMMA film is that the film is self-standing in spite of ~80 nm thickness. Thus, some periodic deformation (vibration) of the film induced by photothermal effects is likely to occur. From this viewpoint, the thickness of the sample film was varied by laminating blank films (without dye) on one side of the DR1-doped PMMA film, as shown in the top of Figure 4.

The PA signal from the laminated film assembly was compared by changing the number of blank films. As shown in Figure 4, the PA signal tended to decrease with increasing the number of blank films. Lamination of films must increase heat capacity of the film assembly, so that heat transfer from the film to air in the cell may be reduced. Thus, the effects of film vibration were not clear.

Because the PMMA film is self-standing in the PA cell, the cell space is spatially divided into two sites: the one site is directly connected to a microphone, while the other spatially isolated from the microphone by the film (see Figure1(b)). In order to clarify whether such spatial division of the cell space affects the PA response or not, we have examined the following experiments. As shown in Figure 5(a), DR1- and OEP- doped films were attached on opposite surfaces of a four-layered blank film assembly, making a six-layered film assembly, and PA responses of the film assembly were compared with different orientations as to the surface: the OEP-(A) or the DR1-(B) doped film is facing the excitation light (see Figure 5(a)). Figure 5(b) shows PA spectra of the six-layered film assembly in different orientations (A and B in Figure 5(a)). Two large peaks at around ~400 and ~500 nm clearly correspond to the Soret band of OEP and the absorption peak

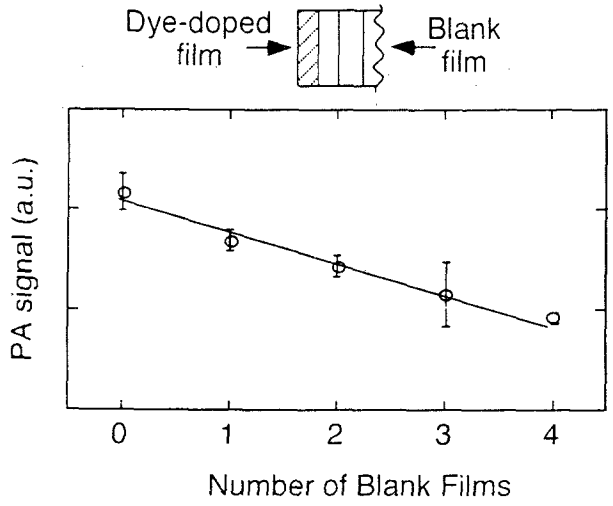

FIG. 4. PA signals when the blank films are laminated on one side of blank films. The laminated film assembly is schematically shown on the top. Excitation wavelength is 490 nm.

of DR1, respectively, and there were no appreciable differences between the two spectra. These results suggest that spatial division does not affect the observed PA signal intensity. Probably the thickness of the six-layered film assembly is at most ~0.6 μm and thus the absorption of light by the dye and PMMA is negligible.

Next, we prepared two kinds of five-layered assemblies as shown by C and D in Figure 6(a); the DR1-doped film was attached on one surface (left in the figure) of a four-layered blank film assembly (C), and the DR1-doped film is sandwiched between two-layered blank film assemblies (D). The PA signal of the above-described two film assemblies were compared at various modulation frequencies (Figure 6(b)). The PA signals at modulation frequencies of 100-

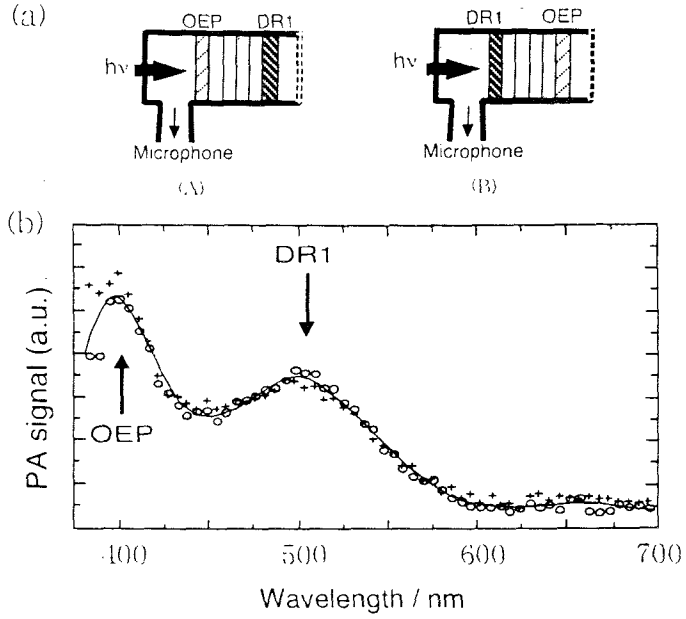

FIG. 5. (a) Configuration of the six-layered film assembly containing OEP- and DR1-doped films at the opposite surfaces as to the light path in the cell: OEP-(A) or DR1-(B) doped film is oriented facing the excitation light.
(b) PA spectra of six-layered film assembly in different film configuration: ○,(A); ×,(B).

400 Hz could not be obtained because of large background noises. Figure 6 clearly shows that the D-film assembly gives smaller PA signals than the C-film assembly in the whole modulation frequencies. In addition, the signal difference between C- and D-film assemblies became larger at higher modulation frequencies. These results also imply that thermal diffusion from the DR1-doped film to the outer air phase is lesser in the D-film assembly. However, the thickness of the five-layered film assembly is estimated to be at

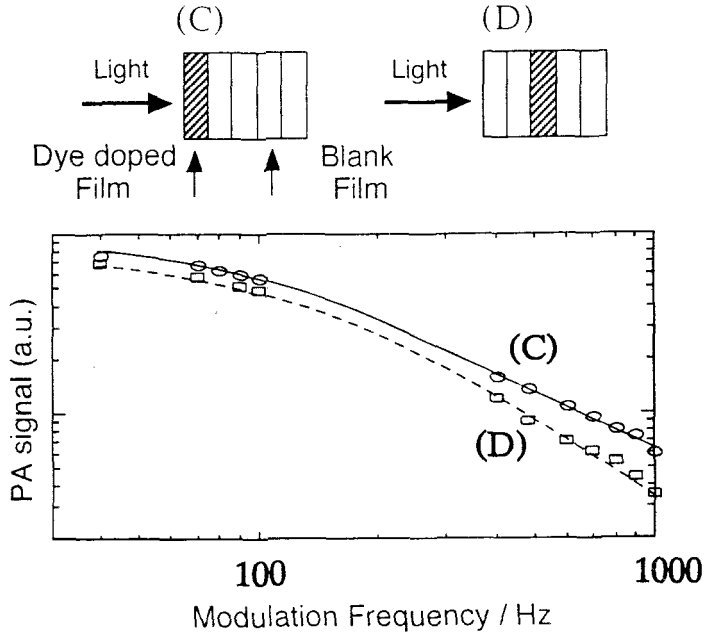

FIG. 6. Comparison of PA signal intensities in two types of laminated film assemblies at various modulation frequency. Two types of five-layered film assemblies are prepared: (C) DR1-doped film is laminated on one side of the four-laminated blank film assembly, and (D) the DR1-doped film is sandwiched between double-layered blank film assemblies.

most ~ 0.5 μm. Thus, the effect of film thickness on thermal diffusion in the films must be negligible. One of the plausible reasons for this signal difference is that the presence of film-film interfaces among the laminated films assembly. In fact, unusual variation appeared on proceeding lamination. This must affect any thermal properties of the film assembly. In the case of C-film assembly, the DR1-doped film is exposed to air, so that thermal diffusion from the film to air occurs directly and effectively as compared with the D-film assembly.

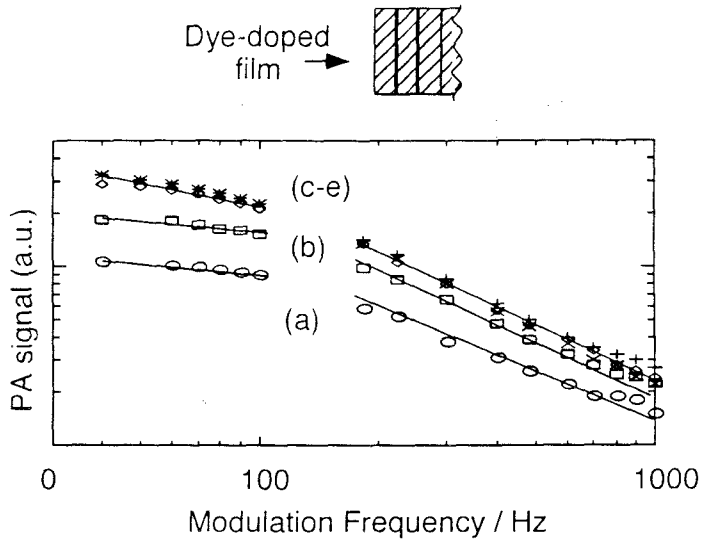

FIG. 7. Comparison of PA signals from multilayered assemblies of DR1-doped films at various modulation frequencies: number of laminated films. 1(○), 2(□), 5(◇), 10(+), 20(×).

Figure 7 shows PA signals of several multilayered assemblies of DR1-doped films at various modulation frequencies. In the whole frequency region, the intensity of PA signal is not proportional to the number of laminated films. The signal increases with the number of films up to five layers, but it tends to saturate beyond five layers. Since the absorbance at the absorption maximum (~490 nm) of 20-layered film assembly is at most ~0.4 and the excitation light is powerful enough to pass through the film assembly, the signal saturation beyond five layers must be ascribed to damping of thermal diffusion in inner-layer films, as in the case of Figure 6.

In conclusion, we have shown that the present PMMA film had efficient thermal diffusion because of its very thinness and self-standing property. Analysis of the time profile of PA signal induced by pulsed laser excitation will offer valuable information about possible vibration of the film.

ACKNOWLEDGMENTS

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