

A thin polystyrene air bubble

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Generation of unsupported thin polystyrene films in the form of air bubbles is reported. These films have the thickness of the order of a wavelength of light. One such film reported here has a thickness of about 300 nm. The thickness of the films is estimated by UV-Vis and FTIR spectroscopic methods. Stability of these films with respect to soap bubbles is also discussed.

POLYMERS have become an essential part of modern science and technology. The last few decades have witnessed a phenomenal growth in the knowledge of polymer-based materials. From simple plastic materials to foams, liquid crystals, photonics, renewable resources, flame retardants, coatings, the application is vast¹. As a natural consequence, efforts are continuously being made to generate newer polymer-based materials.

Understanding the properties of polymers is an important requirement for development of newer materials. Among other forms, regular thick films, Langmuir-Blodgett films, thin polymer films on supported membranes have been used to study properties of polymers and molecules embedded in them. Polymer foams have also been extensively studied. Use of polymer in the form of membranes is an emerging area². Polymer-lipid composite films have opened new avenues for membrane mimetic studies³. Unsupported membranes in the form of bubbles may be of interest to study processes occurring in membranes in the absence of the bulk solvent around or any external support. Challenge involves making sufficiently thin (also stable) membranes to mimic membranes used in other forms. In other communications, generation of thin bubble membranes from ordinary shampoo and detergents have been described^{4,5}.

We describe here, a method for making thin polystyrene films in the form of an air bubble. These bubbles have thickness of the order of a wavelength of visible light, as they appeared to be coloured by interference of light. The bubbles are stable with a continuous flow of air into them and if pressure is maintained higher than the atmospheric pressure. They crunch spontaneously when the air flow is stopped. The UV-Vis and FTIR spectroscopic studies have been used to establish the thickness of the film. The stability of the bubble in the air with respect to soap bubbles is also discussed. Polymers in the form of thin bubbles may be of use in rheology. Also, this may have great practical applications

such as making large quantities of polymer foils by simple air blowing compared to conventional methods. Interesting molecular alignments may be observed if dopants are incorporated in these films. These thin unsupported polymer films may also be useful in optoelectronics.

About 1.0 ml of toluene was added to 1.01 g of polystyrene (Aldrich, USA; MW 280,000) and was left to mix. A viscous mixture was obtained. A film was then made from the mixture, on one end of a glass dropper. Air at high pressure (about 17 psi) was blown through the other side of the dropper and a bubble was formed. High air pressure was maintained to keep the bubble in proper shape. Generally, the bubble was formed in the shape of a tube (kidney beans) with varied thickness at different parts of the bubble (this can be made out from different colours at different places). Sufficient time was allowed to elapse to make the bubble free of toluene. Spectroscopic investigations were carried out by inserting the bubble in the sample compartments of UV-Vis and FTIR spectrophotometers.

When light passes through a uniform thin film interference, fringe patterns are generated depending on the film thickness and the wavelength of light. In the case of a bubble, light passes through two such thin films. Ideally, if the thickness of the two films were same and if the films were held parallel to each other the resulting interference fringe pattern would be same as that of a single film. In this case, the situation is complicated as the bubble can be thought of as two films which are not exactly parallel to each other. In addition, if the thickness of the film across a bubble is not uniform, the interpretation of the interference fringes would become even more difficult. In the case of a polystyrene bubble, the film thickness across the bubble is not uniform and thus the calculation of the film thickness from the interference maxima and minima⁶ would provide only an estimate of the thickness. Figure 1 illustrates the UV-Vis spectra of a polystyrene bubble at three different spots. When a value of 1.5916 is used as the refractive index of polystyrene, the thickness obtained from spectra A, B, C, are < 200 nm, 230 nm and 300 nm respectively. For calculations of thickness, the variation of refractive index with the wavelength of light is not taken into consideration. It is evident from the spectra that there is considerable variation in thickness across a bubble. This variation may be due to the non-uniform air pressure across a tubular bubble at the time of formation. As toluene remains in the film even after the formation of the bubble, the final thickness at any spot may be less than that at the time of formation. When a film is converted into a bubble, high air pressure expands the film and the shape of the bubble depends on the flow of air. When the bubble does not expand further, an opening is generated at the interface between the glass surface and the film to release the air pressure. Continuous

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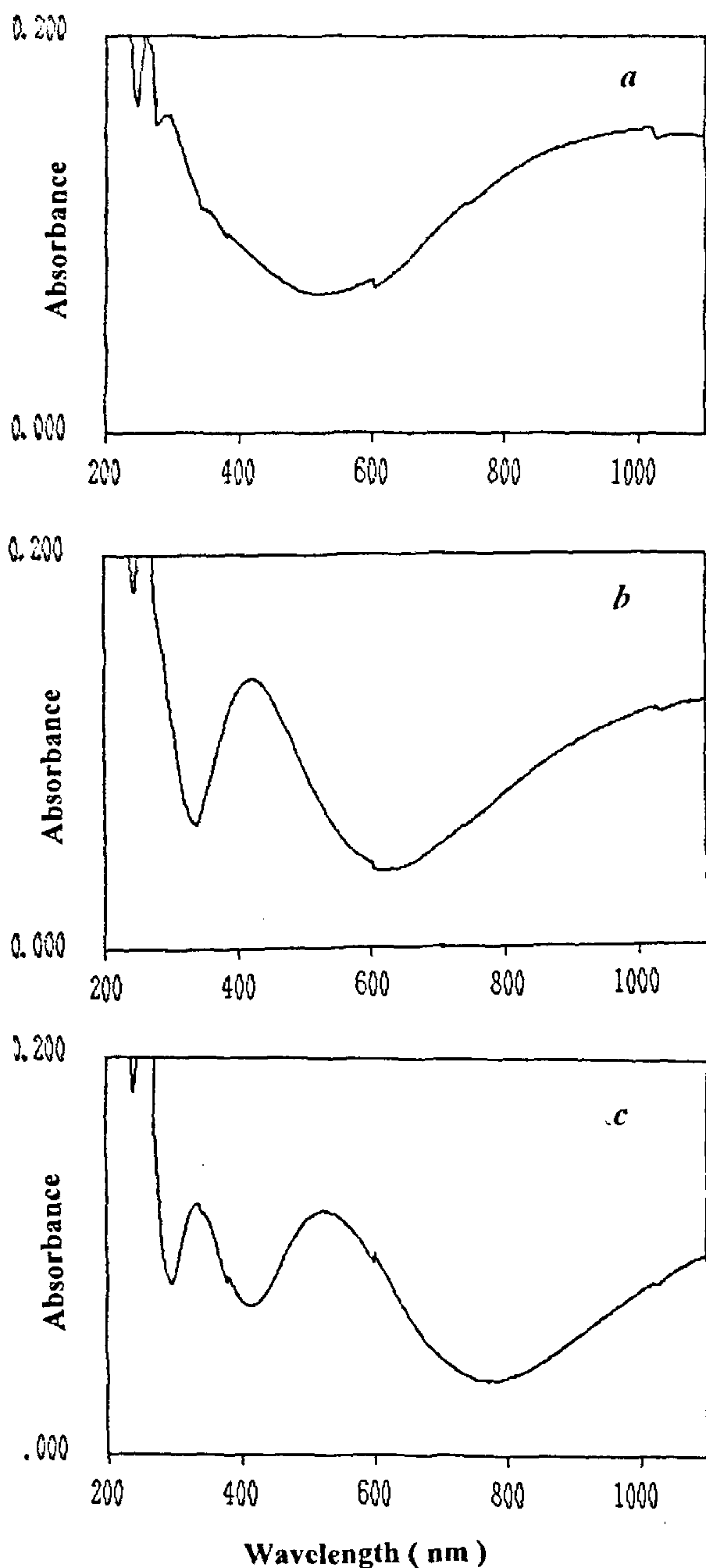


Figure 1. UV-visible spectra of a polystyrene bubble at three different spots. *a*, $d < 200$ nm; *b*, $d \approx 230$ nm; *c*, $d = 300$ nm; d = estimated thickness of the bubble film.

r flow is required to keep the bubble in shape and prevent it from spontaneous crunch.

Vibrational spectroscopy has been used as a powerful tool to obtain structural and bonding information at the level of a chemical bond⁷. The vibration frequencies and

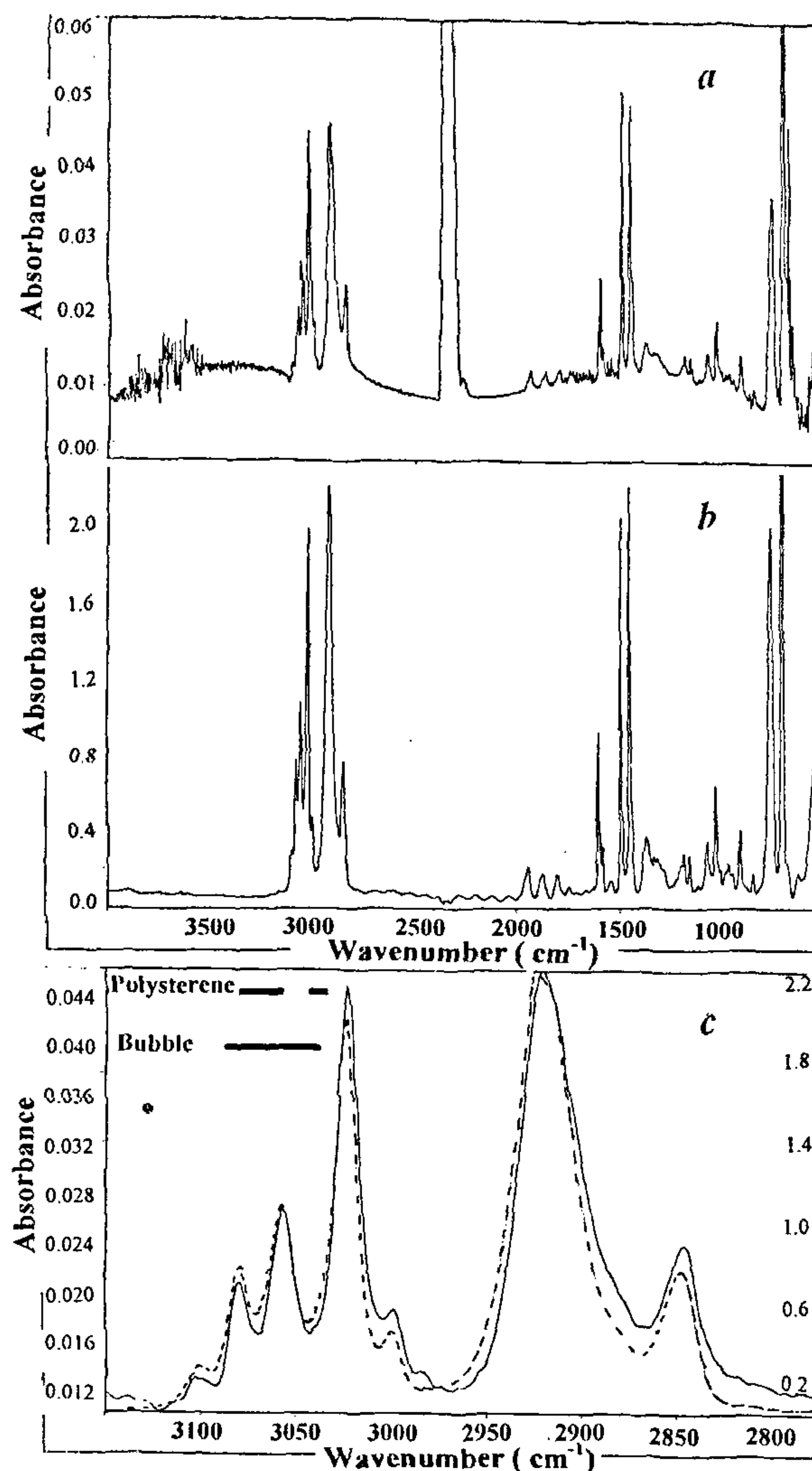


Figure 2. FTIR spectra of the same polystyrene bubble (Figure 1) and that of a 38.1μ polystyrene film. *a*, Polystyrene bubble. The atmospheric CO_2 peaks at 2350 cm^{-1} are off scale; *b*, 38.1μ polystyrene film; *c*, Comparison of the two spectra in the region $3150\text{--}2775 \text{ cm}^{-1}$. The solid line is the bubble and the serrated line is the film spectrum.

absorption intensities are very sensitive to change in environment, bonding, etc. FTIR spectroscopy has been applied to measure the thickness of thin foam films⁸. In the present context, FTIR spectroscopy has been used to learn about the polystyrene bubble in comparison to a film. Also, an estimate can be made about the thickness of the film by comparing the intensities of the vibrational transitions occurring from a film and that from the bubble. The FTIR spectrum of the same bubble as above (used for UV-Vis study) is shown in Figure 2*a*. For comparison, the FTIR spectrum of a 38.1μ polystyrene film (supplied by Nicolet Instrument Co., USA) is

shown in Figure 2*b*. In Figure 2*c* spectra of both the polystyrene film and the bubble are shown with expansion in the region 3150–2775 cm^{-1} . Applying the Lambert–Beer law of absorbance to both the thick film (38.1 μ) as well as the bubble and considering the peaks at 3025, 2920 and 1450 cm^{-1} , an average thickness of 315 nm is obtained for the bubble film.

The general features of the FTIR spectrum of the thin polystyrene bubble is same as that of a thick film. The total number of peaks occurring in the thick film and the thin bubble film are same. Also, the peaks for both the systems occur approximately at the same positions. This is obvious from Figure 2*a*, *b*. This indicates that the general structural features of a thick polystyrene film is retained in a bubble with film thickness of about 300 nm. It may be noted here that the infrared absorption peaks due to a thin polystyrene bubble do not match exactly with those of the thick film. The positions and the intensities of peaks, relative to each other, are not necessarily the same. There may be small differences in the nature of bonding in a thin polystyrene bubble compared to that in a thick film giving rise to differences in the FTIR spectra. Also, there could be structural differences between a thick film and a thin bubble giving rise to different oscillator strengths and vibration frequencies.

The present study demonstrates that it is possible to make thin polystyrene films in the form of air bubbles. They are stabilized by keeping the air pressure inside the bubble higher than that outside. It would be important to dope these bubbles with different molecules and see if the properties of such dopants are different depending on the thickness of the films. Work in this direction is in progress in our laboratory.

Ordinary shampoo or detergent bubbles when encased in a container are fairly stable by themselves⁴. On the other hand, the polystyrene bubbles crunch spontaneously once the air flow is stopped. It may be possible that detergent bubbles are organized in a membrane-like structure and their stability originates from a combination of hydrophobic and hydrophilic interactions leading to a membrane-like organized structure. There is no such force acting in the polystyrene film and the network structure is not stable without any external force acting on it in the form of a support (in this case, the air flow). It is also worth mentioning here that the polystyrene bubble is stable even under high air flow whereas an ordinary soap bubble would not be stable under such conditions. Generation of bubbles with thinner films may reveal interesting features of thin polymer membranes in the air.

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Synthesis and anticancer activity of new derivatives of podophyllotoxin

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Six new 4-alkylamino compounds 6.1–6.4, 7.1–7.3, derived from podophyllotoxin have been synthesized and evaluated for their anticancer activity *in vitro*. All analogues of podophyllotoxin showed inhibitory activity against L1210 and K562 cells. Compounds 6.2, 6.3, 6.4, 7.1, 7.2 are as potent or more potent than VP-16 in their inhibition of L1210 cells. The inhibitory activities of all analogues against K562 cells are less potent than that of VP-16.

ETOPOSIDE (VP-16, 1), which is a semisynthetic glycoside derivative of podophyllotoxin (2), has been used in cancer chemotherapy¹. This compound causes extensive DNA strand breaks from inhibition of the nuclear enzyme DNA topoisomerase II (topo II), which functions in decatenating supercoiled DNA prior to transcription². Changes in the 4 β -O-glucosidic substituent of 1 are of interest for simple structures which may be as potent or more potent than 1 in inhibiting the human DNA topoisomerase II^{3–5}. In our previous studies^{6,7} we found that substitution of the glycoside moiety in 1 by a similar nitrogen-containing group at C-4 β position led to some compounds which have anticancer activity comparable or superior to 1. Considering the useful biological activity in the human body and good water-solubility of amino acids, we introduced amino acid analogues into podophyllotoxin at the C-4 position and synthesized new derivatives of podophyllotoxin, compounds 6.1–6.4, 7.1–7.3. The synthesis route of target compounds is shown in scheme 2.

The 4 β alkylamino acid benzyl ester demethylepipodophyllotoxin (6.1–6.4) were synthesized by direct nucleophilic substitution ($\text{S}_{\text{N}}1$) of appropriate L- α -amino

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