NOTES

A Boat-Casting Technique for the Preparation of Very Thin Plastic Films Suitable for Optical Studies

Synopsis

A meniscus coating technique utilizing a Teflon "boat" for dispensing a viscous solution of a polymer in a volatile solvent upon a suitable substrate provides very thin plastic films (>*ca.* 0.5 μm) which are usually of acceptable optical quality for spectrophotometric measurements.

We have been interested for some time in the study of photochemical processes in polymer films that have a high content of aromatic groups. Such films are very highly absorbing in the near- and middle-ultraviolet regions and virtually opaque in most of the far-ultraviolet region at film thicknesses that can be practically achieved by conventional methods. In order to be able to utilize optical monitoring techniques in studying photochemical changes in polymeric films, we required very thin films of suitable optical quality. Such films were also required for related luminescence studies utilizing plastic samples. For example, in order to monitor the middle-ultraviolet absorption bands of bisphenol-A polycarbonate films, a thickness of approximately 1–2 μm was requisite.

Conventional film-forming techniques (press molding, "doctorblade" casting, slow solvent evaporation from standing methylene chloride solutions of the resin) did not provide sufficient film area of uniform (thin) thickness and smooth surface for a series of photochemical studies. (Dip-coating techniques were not attempted.) Modifying the "Teflon boat" method of meniscus-coating long strips of material[1] did provide such films. The modification is sufficiently novel and potentially useful to warrant a brief description. There are certain limitations, however, which should be appreciated before the method is invoked for any particular application.

In contrast to the doctor-blade technique, wherein a shearing effect between the blade and the viscous solution is utilized to provide a uniform solution coating upon the substrate, the "boat technique" involves the drawing of a flowing solution at a constant rate across the substrate. Thus the solution viscosity, draw rate, fill level, pore size, solvent evaporation rate, and height above the surface as depicted in Figure 1 will control the coating thickness and constancy thereof upon the substrate. Equations for determining the coating thickness in a vertical configuration as a function of such parameters reportedly have been worked out.[2] For the horizontal configuration, however, it has been a matter of trial and error in order to produce films of desired characteristics.

We utilize the constant-speed drive arm of a Rodder-Streaker* apparatus to draw a small Teflon boat containing a few milliliters of solution across a series of quartz plates. In this fashion, 1 in. strips of 1–2-μm-thick polycarbonate film could be cast upon several 1.5-in.-wide quartz plates laid end to end. Depending upon the set of particular conditions mentioned above, these films provided up to $^2/_3 \times 12$ in. of virtually smooth

* This unit was designed for impregnating preparative thin-layer chromatogram plates with a concentrated, narrow streak of solution delivered via a constantly traversing syringe. It is available from Rodder Instrument, Los Altos, California.

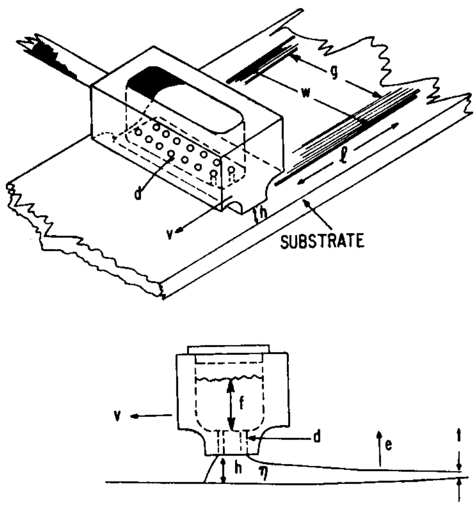

Fig. 1. Details of the "Teflon boat" arrangement for casting very thin plastic films from solution. The number of pores and the diameter *d* thereof may range from 10–30 and 0.005–0.025 in., respectively, depending upon the solution viscosity η, the height *h* of the boat above the substrate, and the traversal rate *v*. Edge effects do occur as shown in the drawing, and the final width *g* of film of desired thickness *t* is usually >50% of the overall width *w*. The thickness *t* of the center strip of width *g* will be uniform along a length *l*, depending upon a certain effective average fill level *f* of solution in the boat. Methylene chloride (a solvent with a very high evaporation rate, *e*) solutions of polycarbonate resins (ca. 5%) can be used to make films ranging from 1.0–4.0 μm by appropriate choices for *d* and *v*.

surface area with a thickness tolerance of ±0.1 μm.† When random sections in the center of these films were examined spectroscopically, virtually coincidental absorbances of about 1.5 ±0.02 units were obtained for the polycarbonate absorption maximum at 272 nm. The quartz slides were of convenient dimensions for manipulation in the sample chambers of conventional spectrometers or in our ultraviolet irradiation apparatus. However, *very careful* manipulation of these films while pulling them from the quartz plate using ordinary adhesive tape allowed us to utilize these very thin films unsupported upon frames, without destroying their acceptability for optical studies.

Thin polycarbonate films of suitable optical characteristics have been made this way from methylene chloride solutions of commercially available powdered resins which, if cast using a doctor-blade technique or by slow solvent evaporation, yielded thick films with evident crystallinity. Very thin, acceptable poly(methyl methacrylate) films have also been prepared by this technique.

The obvious limitations to this technique are twofold. First, as with any technique utilizing viscous solutions, there may be a "machine direction," i.e., orientation with respect to the drawing direction, and the problem of eliminating residual solvent, if essential as in our studies, is encountered. Second, the practical limitations such as size of the boat, platen area, etc., are rather obvious. It may, however, prove a useful method for the preparation of films for studies of chemical/photophysical phenomena in plastic matrics wherein regions of high absorbance are of distinct interest.

† Cross-sectional tracings of the thickness of the films were obtained with a Tallysurf instrument. I thank R. S. Owens and W. R. Reed for their assistance in making these measurements.

References

1. C. S. Herrick, U.S. Pat. 3,201,275 (Aug. 17, 1965).
2. C. S. Herrick, private communication.

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