Preparation of Thin Polymer Films

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Synopsis

Refined techniques and a simple apparatus for producing thin (300–1300 A.) polymer films on glass slides from appropriate polymer solutions are described. A film thickness reproducibility of ±25A. can be achieved without difficulty. The polymers investigated included Formvar 15/19E, Parlodion, VYDR blend B-7, and Cyanocel. Data are presented which show the effect on film thickness of a drain period for the glass slide just above the polymer solution, the residence time of the glass slide in the polymer solution, the nature of the solvent, the concentration of the polymer solution, the temperature, and the nature of the polymer. The results show that the reproducibility of polymer film thickness and the uniformity of the films is higher as the thickness of the film decreases (below about 1000 A.). Film casting conditions which favor a rapid departure of the solvent from the polymer film (such as elevated temperature, dilute solutions, and solvents of high volatility) yielded a high reproducibility in film thickness and an excellent film uniformity.

INTRODUCTION

Techniques employed for the preparation of thin polymer films and membranes have been described in a previous paper.[1] The authors indicated, however, that it was very difficult to obtain films of reproducible thickness.

The film-forming techniques previously described[1] have now been sufficiently refined so that thin (300–1300 A.) films and membranes of a given thickness uniformity can be repeatedly produced.

This paper describes techniques and a simple apparatus for producing thin films of uniform thickness from appropriate polymer solutions. Data are presented which show the effect of some of the fundamental variables in film formation from polymer solution, such as temperature, polymer concentration, and the nature of the polymer and the solvent.

EXPERIMENTAL

Materials

The film-forming polymers investigated in this study included Formvar 15/95E (polyvinyl formal, Shawinigan Resins Corporation), Parlodion (purified pyroxylin, Mallinckrodt), VYDR, blend B-7 (a high molecular weight vinyl chloride–acetate resin containing approximately 96% vinyl chloride and 4% vinyl acetate, Bakelite), and Cyanocel (a highly cyanoethylated cellulose, American Cyanamid).

The following solvents used in this study were all of reagent grade or better: dichloromethane (Matheson Coleman and Bell, DX 835), 1,2-dichloroethane (M.C.B., DX 800), 1,1,2,2-tetrachloroethane (M.C.B., TX 160), acetone (M.C.B., AX 125), 2-butanone (M.C.B., BX 1670), 2-pentanone (Eastman, P 1928), cyclohexanone (M.C.B., CX 2335), tetrahydrofuran (Eastman, 5308), methyl alcohol (M.C.B., MX 475), ethyl alcohol (Commercial Solvents, Gold Schield, absolute), diethyl ether (M.C.B., EX 190), nitromethane (M.C.B., NX 613), isoamyl acetate (Eastman, 298), acetonitrile (M.C.B., AX 148), acrylonitrile (M.C.B., AX 350), mesityl oxide (M.C.B., MX 415), N,N-dimethylformamide (Eastman, S 5870), p-dioxane (M.C.B., DX 2090).

Methods

Preparation of Polymer Solutions. All of the polymer solutions were freshly prepared just before they were used for film formation. The polymer was dissolved by overnight magnetic stirring of the polymer–solvent mixture with Teflon-covered magnets in closed, amber-colored bottles, at room temperature.

Preparation of Glass Slide Film Supports. Careful preparation of the glass slides used as supports for film casting is very important. The procedure previously described[1] is given below along with some essential modifications.

(1) New plate-glass strips, $5^1/_2$ in. long, $1^1/_2$ in. wide, and about $^3/_{16}$ in. thick, with polished edges, are used as supports for films.

(2) Surfaces of the glass slides must be absolutely clean. With the fingers, all surfaces of the glass are vigorously scrubbed with a moist paste of a wetting-agent, such as Alconox. (Cleaners containing abrasives will, over a period of time, produce extensive scratching of the glass surfaces.)

(3) The glass is rinsed with large volumes of tap water, all surfaces being rubbed with the fingers to remove any film of wetting agent that may remain.

(4) The glass is wiped dry with a clean, absorbent, lint-free cloth.

(5) The surfaces of the glass strip are now "conditioned" by immersing the glass (with a suitable string sling) under a hydrocarbon solvent, such as 2-butanone or 2-pentanone, contained in a large test tube, for 30 min.

The last step in the procedure evolved as the result of many attempts to produce a uniform surface condition on the glass slides prior to dipping them in the polymer solution. The hydrocarbon treatment (*a*) seems to allow time for the dissipation of any static charge produced by rubbing the glass dry with a cloth and (*b*) produces a reasonably constant and reproducible moisture condition on the glass surface. The hydrocarbon used for conditioning the glass in this investigation was 2-pentanone. Fresh solvent was employed at frequent intervals.

Casting of Films. The appropriate polymer solution was placed in a large Pyrex test tube (500 mm. long, 65 mm. O.D.) to a depth of about 145 mm. Approximately 350 ml. of solution was used. The test tube was

then immersed in water contained in a large (12,000 ml.) narrow-neck, silvered Dewar. To maintain constant temperature during film formation, the Dewar was provided with a stirrer, a heater, and a copper tubing coil. Hot or cold water, as needed, was circulated through the copper coil with a Haake constant temperature circulator. The temperature was measured with a thermometer calibrated by the National Bureau of Standards. In all film-forming experiments the bath temperature was controlled to ±0.05°C.

The glass slides were dipped into the polymer solution mechanically. The shaft of a Hurst 4-rpm synchronous motor was held in the chuck of a $^1/_4$-in. hand drill and both were firmly supported in a horizontal position about 15 in. above the Dewar of the film-forming apparatus. A short length of rubber tubing was placed on the shaft of the drill just behind the chuck in such a manner that a narrow groove was produced between the tubing and the chuck. Heavy thread was wound (or unwound) around this groove when the 4-rpm motor was activated to raise and/or lower the glass slide in or out of the polymer solution. The arrangement just described produced a constant raising (and lowering) rate of the glass in and out of the test tube of 0.14 in./sec.

In the preparation of a film, the glass slide was cleaned and conditioned in 2-pentanone for 30 min. (as previously described). During this time, the polymer solution was brought to temperature equilibrium. The glass slide was then removed from the 2-pentanone and was allowed to dry in the air for several minutes. The slide was then fitted with a string sling which allowed it to hang in an exactly vertical position just above the test tube containing the polymer solution. The slide was then mechanically lowered into the polymer solution until about $4^1/_2$ in. of the glass was immersed. The glass was allowed to equilibrate for exactly 20 min. in the polymer solution. (This equilibrium period was found to be essential for reproducible results.) During this equilibrium period, stirring of the water bath was terminated to minimize turbulence in the polymer solution. This precaution contributed to film uniformity. At the end of the 20-min. equilibration period in the polymer solution, the glass was withdrawn, and the polymer film was allowed to dry for 15–90 sec. (depending on the evaporation rate of the solvent) in air at room temperature.

The entire dipping procedure was carried out under a hood that was operated continuously. This provided a relatively constant air movement (about 25 ft/min) across the top of the test tube containing the polymer solution and was a significant controlling factor in the evaporation rate of the solvent from the glass.

Recovery of Polymer Films and Thickness Determination. A large glass jar ($8^1/_2$ in. diameter, $5^3/_8$ in. deep) was filled to the brim with distilled water. After scoring of the edges of the glass slide with a needle, the polymer films were floated off the glass slides on to the surface of the water. Frequently, a quick dip of the glass into the water followed by withdrawal and a subsequent slow dip from the horizontal to about a 45 degree angle

with the surface of the water produced the best results. The entire exterior of the jar was painted black to allow the operator to locate the films with ease.

The thickness of the polymer films was determined by the optical method developed by Blodgett[2] which involves matching of colors (through polarized light) of the polymer on chrome-plated metal strips with colors on standard barium stearate thickness gauges. The thickness gauges employed in this study were prepared in our laboratories by methods described in a recent publication.[1] The chrome-plated brass strips ($5^3/_8$ in. long, $1^3/_{16}$ in. wide, $^1/_{32}$ in. thick) were carefully cleaned and dried. They were then immersed under the water on which the film was floating and raised at about a 45 degree angle under the polymer film. (The polymer films cling to the chrome surface without adhesive.) Hot air from an air blower was used to dry the polymer film and the thickness was determined by color comparison.

The range of the barium stearate thickness gauge used in this study was 732–1318 A. The thickness of films thinner than 732 A. was determined by picking up two to four layers of film on top of each other on the chrome strip. Each layer was carefully dried before the next was added. A large number of observations of multilayer film systems (in the 732–1318 A. range) indicated that the total thickness was a completely additive function of the number of layers involved.

RESULTS

The thickness data reported in this investigation are average thicknesses for a length of film approximately 4 in. × $1^3/_{16}$ in. In general, film thickness reproducibility and uniformity decreased with an increase in film thickness. However, all of the thickness results reported in this study were reproducible to ±25 A.

For a given polymer, the major variables affecting film thickness were (a) a drain period for the glass slide just above the polymer solution; (b) the residence time of the glass slide in the polymer solution; (c) the nature of the solvent; (d) the concentration of the polymer solution; (e) the temperature; (f) the nature of the polymer. The effect of these variables on film thickness is shown by the data presented in Tables I–VI. All solvent boiling points are literature values from a standard reference.[3]

The data of Table I show that, with a rapidly evaporating solvent, such as dichloromethane, a drain period has no effect on the overall film thickness or the film uniformity. However, as the boiling point of the solvent increases, a drainage period decreases the overall thickness of the film and the film uniformity. These latter effects are enhanced by an increase in drain time.

Although it is not obvious from the data of Table I, when a film is allowed to drain in the presence of a relatively high-boiling solvent, such as 2-pentanone or mesityl oxide, the thickest portion of the film is found at the top of the glass (i.e., the portion of the glass removed first from the membrane solution). With no drain period, the thickest portion of the film is always at the bottom of the glass.

TABLE I
Effect of a Drain Period on Film Thickness

Temp., °C.	Solute	Solvent	Solvent b.p., °C.	Solute/ solvent, g./ml.	Film thickness without drain, A.[a]	Drain time, min.	Film thickness with drain, A.[a]
20 0	Formvar	Dichloromethane	39.9	15/800	781–878 (97)	5	781–878 (97)
20.0	Formvar	Dichloromethane	39.9	18/800	1122–1220 (98)	5	1122–1220 (98)
20.0	Formvar	Dichloroethane	83.6	15/800	1025–1220 (195)	5	781–1074 (293)
20.0	Formvar	Dichloroethane	83.6	15/800	1025–1220 (195)	15	732–1074 (342)
20.0	Parlodion	2-Pentanone	101.7	14/800	976–1220 (244)	15	586–1025 (439)
30.0	Parlodion	Mesityl oxide	128.7	12/800	1025–1220 (195)	15	586–1074 (488)

[a] The value in parenthesis is film uniformity. This is defined as the thickness difference (in Angstroms) between the thick and thin ends of the film.

TABLE II
Effect of Residence Time of the Glass Slide in the Polymer Solution
on Film Thickness

Temp., °C.	Solute	Solvent	Solvent b.p., °C.	Solute/ solvent, g./ml.	Residence time in polymer solution, min.	Film thickness, A.[a]
20.0	Formvar	Dichloromethane	39.9	15/800	20	781–878 (97)
20.0	Formvar	Dichloromethane	39.9	15/800	60	830–927 (97)
20.0	Formvar	Dichloromethane	39.9	18/800	20	1122–1220 (98)
20.0	Formvar	Dichloromethane	39.9	18/800	60	1220–1318 (98)
20.0	Parlodion	2-Pentanone	101.7	8/800	20	342–391 (49)
20.0	Parlodion	2-Pentanone	101.7	8/800	60	366–391 (25)
20.0	Parlodion	Mesityl oxide	128.7	8/800	20	512–634 (122)
20.0	Parlodion	Mesityl oxide	128.7	8/800	60	561–634 (73)

[a] Film uniformity (see Table I).

The data of Table II show that film thickness increases with residence time of the glass slide in the polymer solution. This effect is decreased by a decrease in polymer concentration. However, for higher-boiling solvents (2-pentanone and mesityl oxide) at a given polymer concentration, the film thickness and the film uniformity increase with residence time in the polymer solution. For these same solutions (2-pentanone and mesityl oxide),

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TABLE III

Effect of Solvent Boiling Point on Film Thickness

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Solute	Temp., °C.	Solvent[a]	Solvent b.p., °C.	Film thickness, A.[b]
Formvar	20.0	Dichloromethane	39.9	512–561 (49)
	20.0	Dichloroethane	83.6	732–830 (98)
	20.0	p-Dioxane	101.5	1074–1171 (97)
Parlodion	20.0	Acetone	56.5	512–586 (74)
	20.0	Methyl Alcohol	64.6	976–1220 (244)
	20.0	Tetrahydrofuran	64–66	781–878 (97)
	20.0	Ethyl alcohol[c]	78.5	1171–1318 (147)
	20.0	Acrylonitrile	78–79	878–1025 (147)
	20.0	2-Butanone	79.6	610–732 (122)
	20.0	Acetonitrile	82	586–659 (73)
	20.0	Nitromethane	101	927–1171 (244)
	20.0	2-Pentanone	101.7	732–878 (146)
	20.0	Mesityl oxide	128.7	>1318
	20.0	Isoamyl acetate	142.5	>1318
	20.0	Cyclohexanone	156.7	>1318
	30.0	Acetonitrile	82	537–610 (73)
	30.0	Nitromethane	101	732–878 (146)
	30.0	Mesityl oxide	128.7	1025–1220 (195)
	30.0	Dimethylformamide	153.0	512–610 (98)

[a] The solute/solvent ratio for all of the above solutions was 12 g./800 ml.

[b] Film uniformity (see Table I).

[c] A mixture of 12 g. Parlodion in 400 ml. ethyl alcohol plus 400 ml. diethyl ether yielded (at 20.0°C.) a film of 1074–1220 A. thickness.

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TABLE IV

Lack of Correlation of Solvent Viscosity and Dipole
Moment with Thickness of Parlodion Films

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Temp., °C.	Solvent	Solute/ solvent, g./ml.	Solvent b.p., °C.	Solvent dipole moment, Debye units	Solvent viscosity, cpoise	Film thickness, A.
20.0	Acrylonitrile	12/800	78–79	3.88[a]	0.34 (25°C.)[a]	878–1025
20.0	Acetonitrile	12/800	82	3.37[b]	0.325 (30°C.)[b]	586–659

[a] American Cyanamid Co. data.[4]

[b] Data of Weissberger et al.[5]

at a given residence time, the film thickness increases with boiling point, whereas the film uniformity decreases with an increase in boiling point. It is interesting to note that the film uniformity of Formvar films is not changed by the residence time of the glass slide in the polymer solution.

The somewhat limited data presented in Table III for Formvar films shows a correlation between solvent boiling point and film thickness. How-

TABLE V
Effect of Polymer Concentration on Film Thickness

Solute	Solvent	Solvent b.p., °C.	Film thickness at given solute/solvent ratio, A.[a,b]			
			8 g./800 ml.	10 g./800 ml.	12 g./800 ml.	14 g./800 ml.
Formvar	Dichloromethane	39.9	276–293 (17)	358–407 (49)	512–561 (49)	610–659 (49)
Parlodion	Acetone	56.5	294–342 (48)	464–532 (68)	512–586 (74)	732–830 (98)
	Nitromethane	101	390–464 (74)	586–781 (195)	927–1171 (244)	1220– >1318
	2-Pentanone	101.7	342–391 (49)	537–610 (73)	732–878 (146)	976–1220 (244)
	Mesityl oxide	128.7	512–634 (121)	830–1025 (195)	>1318	>1318

[a] All films were prepared at 20.0°C.
[b] Film uniformity (see Table I).

TABLE VI
Effect of Temperature on Parlodion Film Thickness

Solvent	Solvent b.p., °C.	Solvent/ solute, g./ml.	Film thickness at given temperature, A.[a]			
			20°C.	30°C.	40°C.	50°C.
Acetonitrile	82	12/800	586–659 (73)	537–610 (73)	512–561 (49)	464–512 (48)
2-Pentanone	101.7	14/800	976–1220 (244)	927–1074 (147)	781–878 (97)	732–781 (49)
Mesityl oxide	128.7	12/800	>1318	1025–1220 (195)	1025–1171 (146)	878–1025 (147)
Isoamyl acetate	142.5	8/800	561–658 (97)	464–537 (73)	439–488 (49)	366–414 (48)
Dimethylform- amide	152	12/800	—	512–610 (98)	488–561 (73)	464–488 (24)

[a] Film uniformity (see Table I).

ever, the data for Parlodion indicate no overall correlation of film thickness with boiling point. Other factors, such as the viscosity of the membrane solution[6] and the specific solvent interaction of nitrocellulose in the solution process[7] are additional controlling factors in the thickness results reported here.

The data of Table IV show for two solvents whose boiling points and viscosities are in the same range (acrylonitrile and acetonitrile) that there is no easily discernible pattern relating solvent viscosity and/or dipole moment to film thickness.

The film thickness results of Tables III and IV show that a number of solvent and solution properties are related in some manner (not yet explainable) to film thickness. The rather high thickness values observed for Par-

lodion films from the relatively low-boiling solvents, methyl and ethyl alcohol (see Table III), point to the possibility of a unique film structure for a given solvent that may relate to particular solvent capabilities, such as hydrogen bonding.

From the data of Table V, the following observations may be made. (1) Film thickness increases with the concentration of the polymer solution. Similar results have been reported by Schaefer and Harker[8] for Formvar solutions in dioxane. (2) For a given polymer concentration, the lowest-boiling point solvents produce the thinnest and most uniform films; the highest-boiling point solvents produce the thickest and least uniform films. (3) An increase of 50% in polymer concentration (8 g./800 ml. to 12 g./800 ml.) approximately doubles the film thickness.

The following observations can be made from the data of Table VI. (1) As the temperature increases, film thickness decreases and film uniformity increases. (2) As the temperature increases, films prepared from low boiling point solvents achieve film uniformity more rapidly than films from high boiling solvents (with the exception of dimethylformamide). (3) As the temperature increases, a higher-boiling point solvent, such as isoamyl acetate, can yield a film uniformity equal to that of a lower-boiling solvent, such as acetonitrile, if the polymer concentration in the higher boiling solvent is reduced.

The somewhat abnormal film thickness data for Parlodion in dimethylformamide solution cannot be explained at the present time. With a concentration of 12 g. Parlodion in 800 ml. of dimethylformamide, a clear solution was produced at room temperature. However, attempts to form films at 20.0°C. yielded only disconnected fragments of polymer on the surface of the water. At 30.0°C. and above, clear, strong films were easily produced. When the concentration was increased to 36 g. Parlodion in 800 ml. of dimethylformamide, a clear solution was again produced at room tempera-

TABLE VII
Effect of the Nature of the Polymer on Film Thickness

Polymer	Solvent	Solute/ solvent, g./ml.	Temp., °C.	Film thickness, A.
Parlodion	Nitromethane	8/800	20.0	390–464
Cyanocel	Nitromethane	8/800	20.0	732–830
Parlodion	Cyclohexanone (400 ml.) + 2-butanone (400 ml.)	8/800	50.0	309–358
Cyanocel	Cyclohexanone (400 ml.) + 2-butanone (400 ml.)	8/800	50.0	781–830
VYDR	Cyclohexanone (400 ml.) + 2-butanone (400 ml.)	8/800	50.0	342–358
Formvar[a]				

[a] 8 g. Formvar in 400 ml. cyclohexanone plus 400 ml. 2-butanone would dissolve completely only when heated to at least 50.0°C. However, although films were produced from this solution on the glass strips, all attempts to float them off were unsuccessful.

ture. When film formation was attempted at 30.0°C., only cloudy, disconnected polymer fragments could be recovered. At 50.0°C., however (with this more concentrated solution), strong, clear films were produced. These results indicate that some additional interaction between Parlodion and dimethylformamide, beyond that required for a clear solution, is necessary for successful film formation.

It is interesting to note the similarity in thickness of Parlodion and VYDR films prepared from the same solvent system at the same concentration and temperature. However, Cyanocel films prepared under the same conditions are approximately twice as thick as the VYDR and Parlodion films.

A private communication from the American Cyanamid Company indicated the approximate molecular weight of Cyanocel to be 92,000–122,000. Data presented by Noller[9] permit the calculation of an approximate molecular weight of Parlodion of 126,000–151,000. The film thickness data reported in Table VII would seem to indicate that molecular weight is not a significant factor in explaining the thickness of the Cyanocel films.

Cyanocel is a highly cyanoethylated cellulose. It is probable that the substitution of cyanoethyl groups ($-CH_2CH_2CN$) for the three hydroxyl groups on each glucosidic unit of cellulose (the actual degree of substitution is in the range of 2.6 to 2.8) would produce a steric effect that would tend to produce a less compact film structure.

CONCLUSIONS

Under the conditions of film formation described in this report, the reproducibility of the film thickness and the uniformity of the films was higher as the thickness of the film decreased (below about 1000 A.). Conditions which favor a rapid departure of solvent from the polymer film, such as (1) elevated temperature, (2) dilute solutions, and (3) relatively volatile solvents, yielded a high reproducibility in film thickness and a high film uniformity.

Future structure studies of these thin polymer films should aid in a better understanding of some of the thickness variables which have been observed in this investigation.

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Résumé

On décrit des techniques raffinées et un appareillage simple pour la production, sur des lamelles de verre, de minces (300–1300 A.) films de polymère, à partir de solutions polymériques appropriées. On a pu reproduire sans aucune difficulté des épaisseurs de film de ± 25 A. Les polymères étudiés comprenaient le Formvar 15/19E, le Parlodion, le mélange VYDR/B-7 et le Cyanocel. On présente des résultats qui montrent l'influence sur l'épaisseur du film : de la période de glissement de la lamelle de verre juste au-dessus de la solution de polymère, du temps de séjour de la lamelle dans la solution de polymère, de la nature du solvant, de la concentration de la solution de polymère, de la température, et de la nature du polymère. Les résultats montrent que la reproductibilité de l'épaisseur du film de polymère et l'uniformité des films est plus élevée lorsque l'épaisseur du film décroît (en deçà de 1000 A.). Lors de la formation du film, les conditions, qui favorisent une évaporation rapide du solvant (tel que température élevée, solutions diluées et solvants très volatils), donnent une reproductibilité élevée de l'épaisseur de film et une excellente uniformité du film.

Zusammenfassung

Verbesserte Verfahren und ein einfacher Apparat zur Erzeugung dünner (300–1300 A.) Polymerfilme auf Objektträgern aus geeigneten Polymerlösungen werden beschrieben. Eine Reproduzierbarkeit der Filmdicke von ± 25 A. kann ohne Schwierigkeit erreicht werden. Als Polymere wurden Formvar 15/19E, Parlodion, VYDR-Mischung B-7 und Cyanocel untersucht. Ergebnisse betreffend den Einfluss der Abtropfdauer des Objektträgers unmittelbar oberhalb der Polymerlösung, der Verweilzeit des Objektträgers in der Polymerlösung, der Natur des Lösungsmittels, der Konzentration der Polymerlösung, der Temperatur und der Natur des Polymeren auf die Filmdicke werden vorgelegt. Die Ergebnisse zeigen, dass die Reproduzierbarkeit der Filmdicke und Filmeinheitlichkeit mit abnehmender Filmdicke (unterhalb etwa 1000 A.) besser wird. Giessbedingungen für den Film, welche eine rasche Entfernung des Lösungsmittels aus dem Polymerfilm begünstigen (wie erhöhte Temperatur, verdünnte Lösungen und Lösungsmittel hoher Flüchtigkeit) lieferten eine hohe Reproduzierbarkeit der Filmdicke und eine ausgezeichnete Einheitlichkeit des Films.