

The Surface Tension of Polymer Solutions and Asymmetric Membrane Formation

G. B. TANNY, *Department of Plastics Research, The Weizmann Institute of Science, Rehovoth, Israel*

Synopsis

The surface concentration of polymer molecules in solution has been combined with the three-component bulk-phase diagram of Strathmann et al. to describe the complete equilibrium thermodynamic precasting situation. The polymer surface concentration is estimated according to the theory of Prigogine and Marechal as used by Siow and Patterson, and is governed by the relative values of the polymer and solvent surface tension, γ_p and γ_s , respectively. In general, when $\gamma_p > \gamma_s$, the cast membrane will tend to form with the asymmetric layer on the support side; for $\gamma_p < \gamma_s$, it will tend to form on the gelation bath side. This was found to be the case for several cellulose acetate casting solutions, including the acetone/formamide mixture of Manjikian. The surface tension of cellulose acetate in the latter mixture appeared to be much lower than in single solvents such as DMSO. The effects of surface tension were used to prepare asymmetric gels of poly(phenylene oxide) and nylon 11 by cooling high-temperature solutions in which $\gamma_s > \gamma_p$ at the gel transition point.

INTRODUCTION

One of the most intriguing and complex sets of problems in polymer science is encompassed by the phrase "coagulation of polymer solutions." Included within this framework is the spinning of fibers, the casting of membranes for various types of dialytic and pressure-driven separations, and the hybridization of both applications within the context of the hollow fine fiber.

It was known for a considerable time in the textile industry¹ that fibers spun from polymer solutions occasionally possessed an asymmetric structure consisting of a dense polymer layer ("skin") resting on a porous substructure, and this was often regarded as an undesirable phenomenon. On the other hand, efforts aimed at the creation of such a polymeric structure only began with the discovery by Riley, Merten, and Gardner^{2,3} that the highly successful Loeb-Sourirajan cellulose acetate membrane⁴ owed its properties to the existence of a dense, typically 0.1- to 0.2- μ -thick layer of cellulose acetate resting on a porous supporting film.

Without recapitulating all the theories advanced to explain this structural formation, it is possible to recognize two distinct sets of factors: (a) The equilibrium thermodynamic properties of the polymeric casting solution and the three-component (polymer, polymer solvent, and coagulating

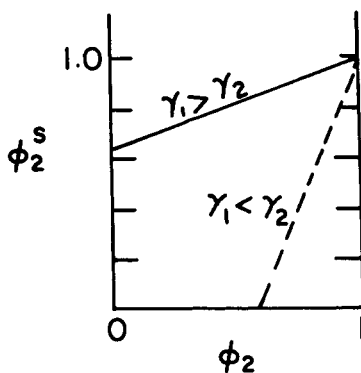
solvent) phase diagram,^{5,6} and (b) irreversible, thermodynamic phenomena occurring during the actual coagulation process, in which flows of polymer solvent and coagulation solvent are governed by gradients in the free energy of mixing and the diffusion coefficients of each species.⁷⁻⁹

In the present contribution, we shall be concerned primarily with the role of the surface tension, which, as a part of set (a), has not been given the quantitative evaluation it deserves. Although Kesting and Menefee⁵ made the first intuitive suggestion that the surface tension plays a role in the formation of asymmetry in Loeb-Sourirajan membranes, Matz et al.¹⁰ were responsible for the first serious attempt to measure and correlate the surface tension of cellulose acetate solutions. Unfortunately, these authors used the maximum bubble pressure technique, which is not well suited to viscous solutions. The data obtained were very irregular in the sense that for some compositions the surface tension measured was much smaller than that of either component, while other systems displayed sudden unexplainable jumps or drops at certain polymer concentrations. For this reason, the work of Matz et al. was repeated using the Du-Nouy ring technique developed by Schonhorn and Scharpe¹¹ for the surface tension measurement of high-temperature polymeric melts.

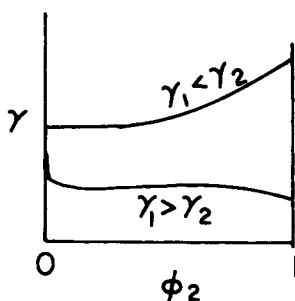
Equilibrium Thermodynamic Considerations

Through the Gibbs-Duhem relationship, every solution can be conceived of as two separate but related thermodynamic entities—the bulk phase and the surface layer with which it is in equilibrium. Since we are dealing with a system whose final form is usually determined by phenomena occurring at and across a gelation boundary, it is reasonable to believe that the equilibrium concentration of polymer in both the bulk and surface phases prior to casting must set the boundary conditions for what occurs subsequently in the process of coagulation. In order to discuss the equilibrium solution concentration of polymer in the surface layer, we shall refer to the theory of Prigogine and Marechal¹² which was recently tested by Siow and Patterson.¹³ The latter found that this theory constituted a reasonable, approximate treatment of the surface tension and adsorption of polymer solutions. In the present context, we will only refer to the qualitative conclusions and predictions of this theory as outlined by Siow and Patterson.

Consider the polymer solution-air interface. In Figure 1a, the theoretical surface volume fraction of polymer, ϕ_2^s , is plotted versus the bulk polymer volume fraction, ϕ_2 , for the case where the surface tension of the polymer, γ_2 , is less than that of the solvent, γ_1 , and vice versa. Figure 1b demonstrates the surface tension behavior expected for both possibilities. The surface layer has here been assumed athermal, i.e., the polymer-solvent interaction parameter, χ , is 0, but this assumption does not change the basic pattern. For $\chi > 0$, the behavior of the polymer will be even further exaggerated for either situation. Thus, it is clear that in systems for which



(a)



(b)

Fig. 1. (a) Surface volume fraction of polymer as a function of bulk volume fraction for $\gamma_1 > \gamma_2$ and $\gamma_1 < \gamma_2$ (after Siow and Patterson, *J. Phys. Chem.*; **77**, 356 (1973)). (b) Surface tension as a function of volume fraction of polymer for $\gamma_1 > \gamma_2$ and $\gamma_1 < \gamma_2$.

$\gamma_1 > \gamma_2$, a substantial fraction of the surface (far out of proportion to the bulk concentration) is already occupied by polymer molecules, and such a situation should lend itself toward asymmetric membrane formation. On the other hand, since a system with $\gamma_1 < \gamma_2$ is almost completely solvent at the interface, only a very special ratio of the polymer solvent-coagulant fluxes will be able to create a dense surface layer, and one would require this flux ratio to be altered thereafter, in order for the overall membrane porosity to be substantial.

To further visualize these arguments, we may consider a generalized three-component phase diagram similar to that determined by Strathmann et al.⁶ for cellulose acetate/acetone water (Fig. 2).

For the case in which $\gamma_1 > \gamma_2$ and the bulk volume fraction of polymer, ϕ_2 , is denoted by A , the surface polymer volume fraction, ϕ_2^s , is A^s . Let AB represent the path determined by the volume flux ratio of solvent and coagulant during the casting process. Assuming a similar ratio for the surface, one arrives at a surface membrane composition, B^s , which is clearly much less porous than the bulk. Even if the surface layer were to follow

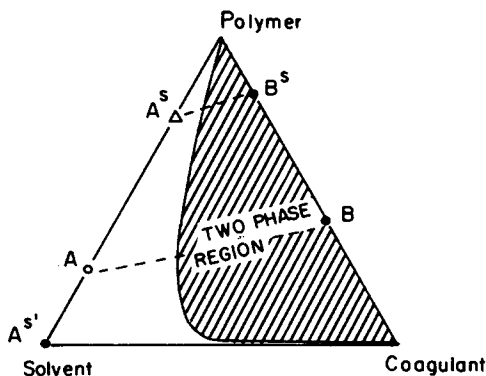


Fig. 2. Generalized three-component equilibrium phase diagram for a polymer-solvent-coagulant system: A is the bulk concentration in the casting solution; A^s and A' are the surface concentrations in the casting solution for $\gamma_1 > \gamma_2$ and $\gamma_1 < \gamma_2$, respectively; B and B^s are the bulk and surface porosities of the asymmetric membrane.

a somewhat different path from that of the bulk, it would appear to be difficult to avoid forming a membrane possessing asymmetry.

The situation is clearly reversed for the situation $\gamma_1 < \gamma_2$. In this case, A' lies well below that of the bulk composition and must take a very different path in order to reach B^s . This should not be taken to mean that "skin" formation at this boundary upon gelling such a system is impossible; only that it would seem in principle to be less favored.

DEFINITION OF "ASYMMETRY" AND SPECIAL CASES

Before proceeding further, it would be useful to define more precisely what may be meant by the term "asymmetry." In the context of the present discussion, it will be used to refer to a *difference between the surface porosity and the bulk porosity*. It does not necessarily imply anything with regard to the manner in which the surface porosity is distributed, i.e., many small pores or a relatively few large holes. Thus, according to this definition, a membrane which possesses a surface porosity much smaller than that of the bulk but whose pores are the same size as those found in the bulk would be considered "asymmetric." The term nonuniform will be used to describe a difference between the size of surface pores and those in the bulk (conceivably for a situation in which no "asymmetry" exists).

This distinction is important because of its ramifications with regard to the various rationales offered for the formation of Loeb-Sourirajan-type membranes. Such membranes are clearly "asymmetric" as well as "non-uniform." The supersaturation-nuclei growth explanation of Strathmann et al.⁶ clearly predicts "nonuniformity," but not necessarily "asymmetry." Furthermore, it cannot rationalize asymmetric membranes forming with a dense layer at the boundary adjacent to the supporting tube or plate used to cast the membrane. Such phenomena as "reverse skinned" membranes^{7,8} can be understood by examining ϕ_2^s at each interface, e.g., certain systems may have $\gamma_1 < \gamma_2$ and thus be polymer free at the air-solution

interface, while ϕ_2^s at the plate-solution interface will be quite large due to preferential polymer adsorption. Thus, one would once again have the situation depicted in Figure 2, except that it would apply to the supporting solid-solution and not the air-solution interface.

It should be noted that the two most popular techniques for detecting the presence of a "skin," i.e., the absorption dye test and changing the membrane face adjacent to the feed in a reverse osmosis cell, are tests for "nonuniformity" rather than "asymmetry," because they measure a difference in the selectivity of the pore. In many instances, nonuniformity and asymmetry appear to go together; it is important, however, to recognize that this need not be the case.

EXPERIMENTAL

Surface Tension Measurements

The surface tension measurements were performed using a du Nuoy platinum-iridium ring, $R/r \simeq 54$, where R is the ring radius and r is the wire radius (Fisher Scientific). An Instron automatic strain-gauge test instrument equipped with a regulated oven was used in place of the manual du Nuoy apparatus in a manner similar to that described by Schonhorn and Sharpe.¹¹ Used on its most sensitive scale (1 g full scale), the apparatus could resolve 5-mg tension, and the tension was continuously recorded as a function of the head motion. Since polymeric solutions are viscoelastic, the rate at which the ring was lifted from the surface had the effect of slightly increasing the maximum load. This was corrected for by measuring the load as a function of pulling speed and extrapolating to zero. In general, this correction lowered the final result by 0.5-1.5 dyne/cm. In a number of instances, the difference between the values at the fastest speed, 0.5 cm/min, and that at 0.005 cm/min was very small, and the latter value was used without correction. A constant atmosphere was maintained by continually passing a slow stream of nitrogen saturated with solvent at the measurement temperature through the glass cup containing the ring and the solution. The cup was made from the two halves of a B60 joint and was equipped with entry and exit ports for the gas in addition to a probe for a thermocouple and a hole through which the brass rod linking the gauge and the ring was passed.

The surface tension γ was calculated from the equation

$$\gamma = (mg/4\pi R)F \quad (1)$$

where m is the maximum mass of liquid supported by the ring, g is the gravitational constant, and F is the ring correction factor of Harkins and Jordan.¹⁴ The latter is a function of R^3/V , where V is the volume of liquid supported. To determine V , densities of two-decimal accuracy were determined in accordance with Archimedes' principle by suspending a calibrated weight of known volume in a given liquid and measuring the weight displacement with the Instron.

At least three surface tension measurements were made for every concentration or at every temperature. A very slight decrease in surface tension (1%) was noted for samples aged more than 70 min. For the nylon 11/(benzyl alcohol/formamide) and the PPO/ α -bromonaphthalene systems, the surface tension in the vicinity of the sol-gel transition was obtained by extrapolation of $d\gamma/dT$ to the transition point. Transition temperatures were measured either by DSC or thermomechanical penetration of the gel on a Perkin-Elmer DSC-TMS unit.

Polymers and Solvents

The cellulose acetate was Eastman E-398 powder, which was dried and used without further purification. The nylon 11 was BESNO-P40, while the poly(phenylene oxide) (PPO) was General Electric GFD-111. All solvents were Fluka puriss grade which were used directly, after checking their measured surface tension with that quoted in the literature.

Membrane Preparation

Cellulose Acetate/Methylethyl Ketone. A 0.1-mm film of a 20% solution (w/w) of cellulose acetate in methylethyl ketone was scraped onto a clean glass plate with a doctor blade. After a 30-sec "holding time," the membrane was cast into a bath of chlorobenzene at room temperature and left for 30 min. The chlorobenzene was solvent exchanged with a series of solutions of chlorobenzene and methanol (80/20, 60/40, 40/60, 20/80, 100%) and the methanol exchanged in similar fashion with water. The membrane was then heated in a water bath at 82°C for 1 hr.

Cellulose Acetate/Acetic Acid. A 0.1-mm film of a 25% (w/w) solution of cellulose acetate in acetic acid was scraped onto a clean glass plate with a doctor blade. After a hold time of 30 sec, this was then cast into a water bath at $\sim 2^\circ\text{C}$ and left for 30 min. The membrane was then heated at 82°C in a water bath for 1 hr.

Electron Microscopy

Photomicrographs of acetic acid and methylethyl ketone cast membranes were obtained with a Phillips 300 electron microscope from pre-palladium-shadowed (20° incident angle) carbon replicas of freeze-dried membrane. The nylon and poly(phenylene oxide) gels were prepared in sealed DSC pans, leached (with water and isopropanol, respectively), fractured after freezing in liquid air, and vacuum coated with a Pd/Au alloy prior to their examination in the scanning electron microscope.

RESULTS AND DISCUSSION

General Observations on the Surface Tension of Cellulose Acetate Solutions

As Siow and Patterson¹³ point out, it is difficult to find systems in which $\gamma_1 > \gamma_2$, since by their nature polymeric liquids usually have a higher cohe-

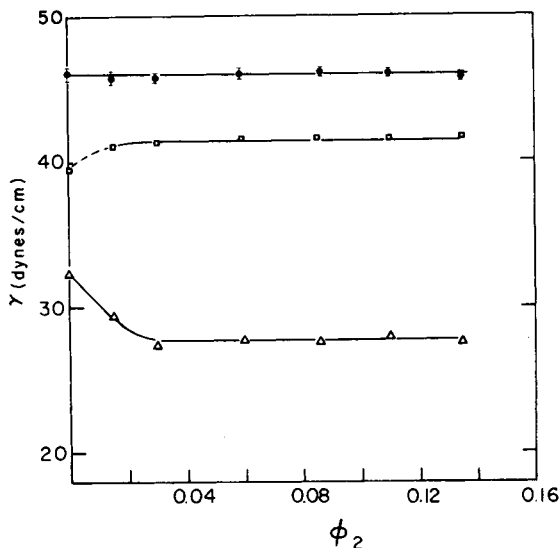


Fig. 3. Surface tension as a function of volume fraction of cellulose acetate: (\bullet) dimethylsulfoxide, $T = 25 \pm 0.5^\circ\text{C}$; (\square) (DMF/H₂O) (4/1) (mole/mole), $T = 27 \pm 0.5^\circ\text{C}$; (Δ) (acetone/formamide) (1/1) (mole/mole), $T = 27 \pm 0.5^\circ\text{C}$.

sive energy density than the "monomeric" organic solvent. Thus, for a material such as cellulose acetate, which decomposes before melting, it may be assumed that γ_2 is quite large. For the DMSO/cellulose acetate system (Fig. 3), the behavior is typical of the case $\gamma_1 < \gamma_2$, since the surface tension remains approximately constant with the introduction of the polymer. (The volume fraction of polymer has been calculated assuming no ΔV of mixing takes place.) On this basis, one expects $\gamma_2 > 46$ dynes/cm, and therefore solutions of cellulose acetate in solvents possessing γ 's below this value should display a behavior similar to that of the DMSO/C.A. system. This result is indeed found for solutions of cellulose acetate in acetic acid and methylethyl ketone (Fig. 4).

Thus, it is rather interesting to note the quite different behavior in Figure 3 of the two ternary systems studied, cellulose acetate/(dimethylformamide/water), and cellulose acetate/(acetone/formamide). Both systems consist of a polymer, a solvent, and a nonsolvent. For both systems, the cohesive energy density parameter, δ , of the solvents are similar, as are the nonsolvent δ 's, ($\delta_{\text{H}_2\text{O}} = 23.4$, $\delta_{\text{formamide}} = 18.0$; $\delta_{\text{acetone}} = 9.9$; $\delta_{\text{DMF}} = 12.1$). Thus, the value for the solvent-polymer and nonsolvent-polymer parameters must parallel one another in the two systems. However, the surface tension behavior of the two ternary systems is diametrically opposed (Fig. 3).

In the cellulose acetate/(dimethylformamide/water) system, the surface tension shows a sharp rise and remains constant. This may be explained on the basis of one or a combination of both of the following

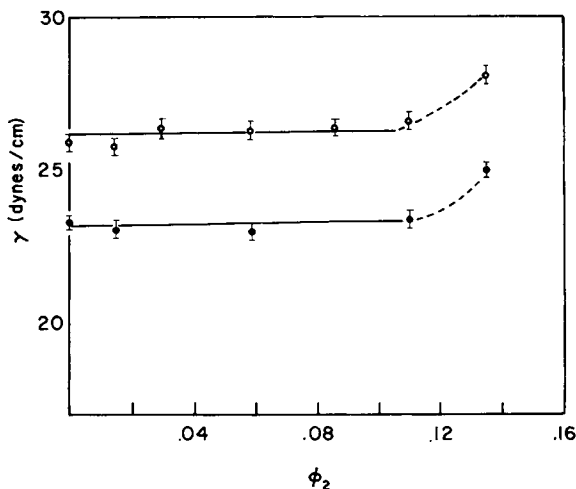


Fig. 4. Surface tension as a function of volume fraction of cellulose acetate: (●) methyl ethyl ketone, $T = 27 \pm 0.5^\circ\text{C}$; (○) acetic acid, $T = 28^\circ\text{C}$.

possibilities: (i) The total free energy is minimized by replacing surface dimethylformamide molecules by water molecules so that unfavorable nonsolvent-polymer contacts are replaced by favorable solvent-polymer contacts in the bulk solution, or (ii) the surface tension rise represents the introduction of a small volume fraction of high-surface tension polymer into the surface phase.

In view of the similarity between the two ternary systems, one would, therefore, predict an increase rather than a drop in the surface tension of the cellulose acetate/(acetone/formamide) solution, unless some special effect occurs. One such possibility is that the acetone/formamide mixture changes the polymer conformation in solution.

It is known¹⁵ that the skeletal rigidity of cellulose acetate varies with composition in solutions of mixed solvents such as methylene chloride/methanol. In addition, cellulose acetate has been shown to form large supermolecular aggregates¹⁶ in acetone, even at very low concentrations in solution. Kesting and Menefee⁵ found that the turbidity of cellulose acetate/(acetone/formamide) solutions decreases as the concentration of formamide approaches 50 mole-% of the solvent. They concluded that the formamide/acetone mixture is a better solvent than pure acetone and breaks down the aggregates into individual molecules. One would, therefore, hypothesize that the surface tension of these individual molecules must be substantially smaller than that of the aggregate.

On this basis, the drop in surface tension is due to the appearance of a substantial volume fraction of cellulose acetate molecules (nonaggregated) in the surface layer, as one expects for the case $\gamma_1 > \gamma_2$ (where 1 and 2 refer to the mixed solvent and dissociated C.A., respectively).

Surface Tension and Membrane Structure

As stated earlier, in cast systems the final membrane structure is a result of the interaction between the equilibrium factors, of such as polymer concentration in the bulk and at the boundaries, and the phase diagram and the dynamic factors such as the ratio and direction of the osmotic fluxes of solvent and nonsolvent. This separation of factors is complicated by the fact that many casting processes also make use of an intermediate evaporation or "holding" period between the time that the polymer solution is spread and its actual immersion in the nonsolvent. Hence, the polymer concentration in the boundary layer exposed to the atmosphere will also depend on the rate of solvent diffusion out of the polymer solution as well as surface tension considerations. Indeed, a theory involving concentration-dependent diffusion coefficients¹⁷ has been proposed to explain the appearance of asymmetric membranes. If, for the moment, the choice of systems is restricted to those in which the precasting evaporation period is short and/or the solvent is relatively nonvolatile, the predominant factor establishing the equilibrium surface polymer concentration should be the surface tension. Thus, the surface tension behavior may be used to elucidate the extent to which the equilibrium and dynamic parameters play a role in asymmetric structure formation.

In Table I, the results for a number of systems may be found. For all the binary solutions, the surface tension measurements indicate that the surface concentration of polymer is very low at the air-solution interface. This is because the polymer has a higher cohesive energy than that of the organic "monomeric" solvent. However, as Siow and Patterson¹³ suggest, for such a system *ipso facto* the interfacial tension between polymeric liquids and a solid surface should be lower than the corresponding interfacial tension between organic solvent and the solid. Thus, we predict that the polymer will adsorb at the supporting surface-solution interface and elevate ϕ_2^s at this boundary. Since the effect suggests itself on general energetic grounds, we would further predict that it should occur independent of the chemical nature of the supporting surface (providing, of course,

TABLE I
Surface Tension and Membrane Structure for Various Cellulose Acetate Solutions

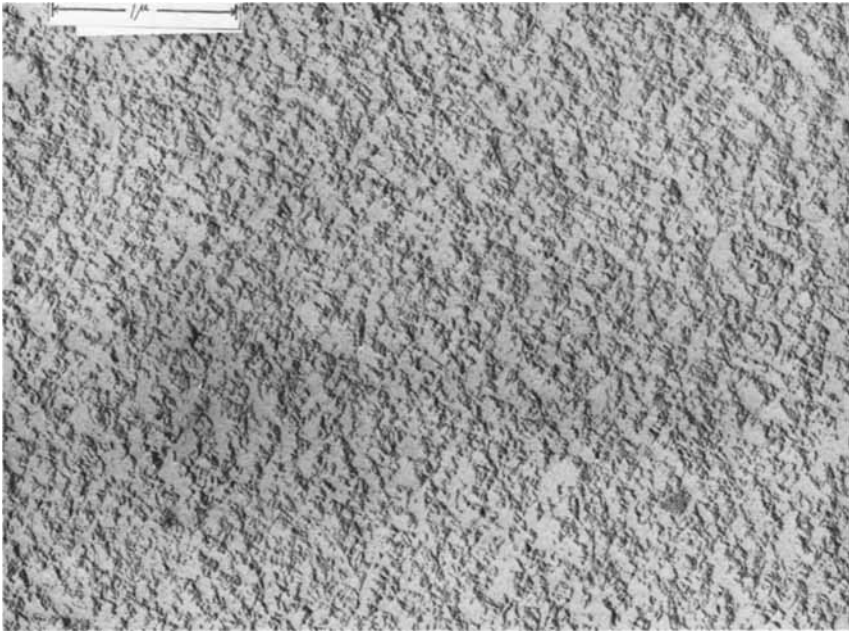
Solvent	Surface tension behavior	Theoretical surface volume fraction of polymer	Membrane structure
Dimethylsulfoxide	$\gamma_2 > \gamma_1$	~ 0	"skin" on supported side
Dimethylformamide/H ₂ O (4/1) (mole/mole)	$\gamma_2 > \gamma_1$	~ 0	"skin" on supported side
Methylethyl ketone	$\gamma_2 > \gamma_1$	~ 0	"skin" on supported side
Acetic acid	$\gamma_2 > \gamma_1$	~ 0	"skin" on gelation bath side
Acetone/formamide (1/1) (mole/mole)	$\gamma_2 < \gamma_1$	0.7-0.8	"skin" on gelation bath side

that no specifically unfavorable interaction exists). One would therefore expect that, *if the equilibrium polymer concentration at the boundaries is the predominant factor in structure formation*, the membrane should be asymmetric with the "skin" on the supported side of the cast film. For DMSO and DMF solutions, this was found to be the case by Bloch and Frommer.⁷ In addition, they determined that the skin formation on the support side was independent of the nature of the support. In a second work,⁸ it was tentatively suggested that the support side skin might be due to a boundary effect of the solvent/nonsolvent flows. However, such an effect seems intuitively more difficult to rationalize than an explanation based on surface tension and surface concentration of polymer.

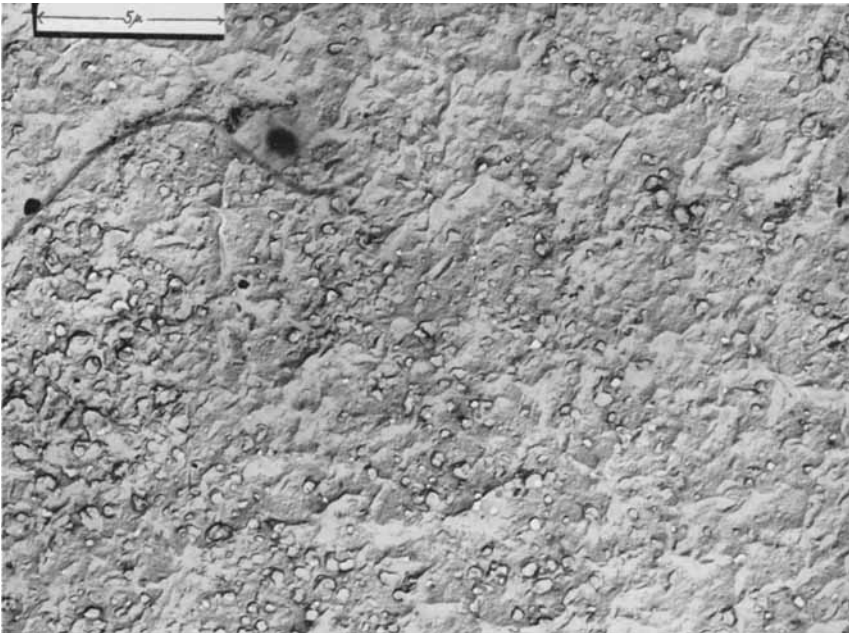
Klein and Smith¹⁸ have demonstrated the usefulness of determining a solubility map for a polymer in terms of the δ_H, δ_P solubility parameters of Hansen.¹⁹ An empirical rule was formulated that membranes possessing a dense layer should be cast from solvent systems close to the solubility boundary into nonsolvents which do not require the total system to pass through the solubility maximum. For this reason, the methylethyl ketone/cellulose acetate solution was cast into chlorobenzene rather than water (cf Fig. 1 in reference 18). The same surface tension arguments used in connection with the DMF and DMSO solutions would predict that the asymmetric layer should form on the glass support side of the membrane, which is in fact the case (Table I).

At this point, it would be useful to examine the cellulose acetate/acetic acid system. Although ϕ_2^s at the air-solution boundary is very low, the membrane turns out with the dense selective layer on the gelation bath side. Thus, the asymmetric layer must arise either due to the dynamic processes or from concentration dependence of the solvent diffusion coefficient.¹⁷ However, inspection of electron micrographs of replicas of the surfaces (Fig. 5) reveals that the surface porosity of *both* sides of the membrane is far smaller than the bulk porosity. Hence, there must also have been adsorption of polymer at the support-solution interface. The only system which appeared from the surface tension measurements to contain evidence of polymer surfactancy ($\gamma_1 > \gamma_2$) was the cellulose acetate/(acetone/formamide). Assuming this to be the case, one would predict that in casting this system (a) the asymmetric layer should be on the gelation bath side and (b) the existence of the asymmetric layer should be almost independent of the evaporation time. Both of these predictions are fulfilled, the latter confirmed by several workers.^{20,21}

The membranes with the best fluxes and rejections have been made with an evaporation or holding period of only 2-3 sec,²² while longer evaporation times cause a decrease in the water flux without improving the salt rejection. If the casting is made directly into water without any holding period, the asymmetric layer disappears.^{20,21} This is explicable in terms of the surface tension effect, because a minimum time of 2-3 sec will be necessary for diffusional processes to reestablish the equilibrium polymer concentration in the newly formed surface.



(a)



(b)

Fig. 5. (a) Replica of the gelation bath side of acetic acid cast membrane. (b) Supporting side of acetic acid cast membrane.

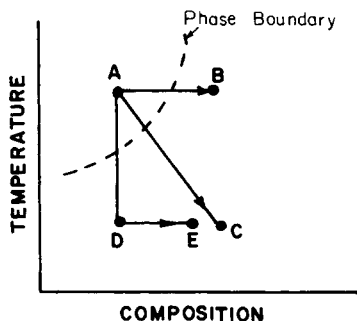


Fig. 6. Schematic temperature-composition diagram: AB, casting solution and gelation bath at same temperature; AC, casting into gelation bath of lower temperature; ADE, temperature of casting solution lowered below the phase transition boundary and solvent removed either by leaching or freeze drying.

One last but very important question which must be dealt with is whether or not the surface concentration argument is really compatible with the observed thickness of the "skin" in the membrane. The work of Riley, Marten, and Gardner^{2,3} showed the skin to be $\sim 1000\text{--}2000$ Å thick and since cellulose acetate is known to form aggregates $800\text{--}1500$ Å in diameter in solution,¹⁶ the answer to the question would seem to be positive. Indeed, recent work²³ would suggest that concentrated polymer solutions generally form surface layers which are far in excess of a monolayer.

In sum, it seems possible to conclude that the relative values of the surface tension of the polymer and the solvent can be used to prejudice the ultimate membrane structure. In general, *for systems in which the equilibrium factors are dominant*, if the surface tension of the polymer is *greater* than that of the solvent, the "skin" will appear on the supported side of the film. If the surface tension of the polymer is *less* than that of the solvent, the "skin" will be on the gelation-bath side of the film. Since "dynamic" factors will also play a role in some systems (such as acetic acid/cellulose acetate), in order to exercise complete control on the final membrane structure one must change the gelation route itself (*vide infra*).

Thermally Gelled Asymmetric Structures

Consider a schematic temperature-composition diagram, such as that in Figure 6, for a polymer solution of composition A. This solution may be gelled by (a) casting at the same temperature in a nonsolvent (path AB), (b) casting at a lower temperature (path AC), and (c) lowering the temperature below the phase separation point and removing the polymer solvent at a constant temperature (path ADE). Of the three possible gelation routes, the latter (ADE) is the simplest in the sense that it consists of two distinct processes, a heat flow followed by a flow of mass *subsequent to the formation of the gel structure*, as opposed to a flow of mass which creates structure. In path ADE, the resulting polymeric entity should reflect the polymer concentration gradient present in solution.^{24,25}

TABLE II
Surface Tension of Polymer Solutions in the Vicinity of the
Gel-Sol Transition Temperature

Polymer	Solvent	Solution-gel transition temperature		Surface tension, dyne/cm	
		Wt-% of polymer	°C	Pure solvent	Solution
Nylon 11	benzyl alcohol/formamide (1/1) (mole/mole)	30	145	29.5	24.2
Poly(phenylene oxide)	α -bromonaphthalene	25	90	31.5	20.0

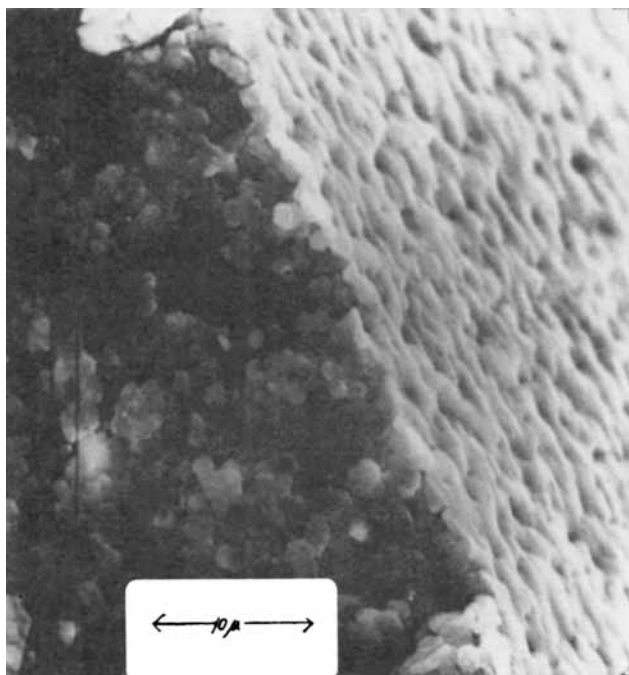


Fig. 7. Surface and partial cross section of gel formed from 40% nylon 11 in benzyl alcohol/formamide (1/1) (mole/mole).

Thus, it should be generally possible to form porous asymmetric structures by cooling polymeric solutions for which the condition $\gamma_1 > \gamma_2$ exists in the vicinity of the sol-gel transition temperature. Since most polymers have high surface tensions and do not usually form concentrated solutions at room temperature in solvents of high surface tension, the systems must be prepared at higher temperatures. However, this is not necessarily a disadvantage, because they can be extruded into tubular form.

Two of the systems found in which $\gamma_1 > \gamma_2$ in the vicinity of the sol-gel transition are nylon 11/(benzyl alcohol/formamide) and poly(phenylene

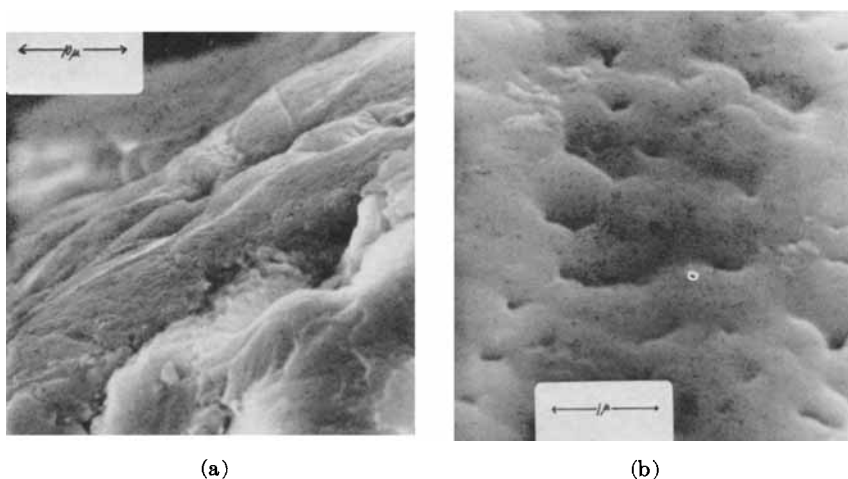


Fig. 8. (a) Surface and partial cross section of gel formed from solution of poly(phenylene oxide) in α -bromonaphthalene (25/75). (b) Surface of gel formed from solution of poly(phenylene oxide) in α -bromonaphthalene (25/75).

oxide) (PPO)/ α -bromonaphthalene (Table II). As may be seen from Figures 7 and 8, the expectation of achieving an asymmetric layer has been fulfilled. The degree of pore "nonuniformity" is not sufficiently great for these membranes to display salt rejection, although they could usefully serve as ultrafilters. Further work on these systems and several others is in progress.

The author is indebted to Prof. D. Patterson of McGill University and Professors D. Vofsi, O. Kedem, and J. Jagur of the Weizmann Institute for stimulating and useful conversations and encouragement in the course of this work. Dr. H. K. Lonsdale is to be thanked for his useful comments in the preparation of the final manuscript. The dedicated technical assistance of Miss Celia Honey in performing many of the surface tension measurements is gratefully acknowledged.

References

1. F. Morehead and W. Sisson, *Text. Res. J.*, **15**, 443 (1945).
2. R. Riley, J. O. Gardner, and U. Merten, *Science*, **143**, 801 (1964).
3. R. Riley, U. Merten, and J. O. Gardner, *Desalination*, **1**, 30 (1966).
4. S. Loeb and S. Sourirajan, *Advan. Chem. Ser.*, **38**, 117 (1963); S. Manjikian, *Ind. Chem. Eng., Prod. Res. Develop.*, **6**, 23 (1967).
5. R. E. Kesting and A. Mennefee, *Kolloid-Z. Z. Polym.*, **230**, 341 (1968).
6. H. Strathmann, P. Scheible, and R. W. Baker, *J. Appl. Polym. Sci.*, **15**, 811 (1971).
7. R. Bloch and M. A. Frommer, *Desalination*, **7**, 259 (1969).
8. M. A. Frommer, I. Feiner, O. Kedem, and R. Bloch, *Desalination*, **7**, 393 (1969).
9. M. A. Frommer and D. Lancet, in *Reverse Osmosis Membrane Research*, H. K. Lonsdale and H. E. Podall, Eds., Plenum Press, New York, 1972.
10. R. Matz, G. Herscovici and O. Kedem, in Technical Report 7005, Final, Hydro-nautics Inc., November 1971, for the Office of Saline Water, Contract No. 14-30-2529, U.S. Dept. of the Interior, Washington D.C., 1971, Chap. II.
11. H. Schonhorn and L. H. Sharpe, *J. Polym. Sci. A*, **3**, 569 (1965).

12. I. Prigogine and J. Marechal, *J. Colloid Sci.*, **7**, 122 (1952); R. Defay, I. Prigogine, A. Bellemans, and D. H. Everett, *Surface Tension and Adsorption*, Wiley, New York, 1966, Chap. 13.
13. K. S. Siow and D. Patterson, *J. Phys. Chem.*, **77**, 356 (1973).
14. W. D. Harkins and H. F. Jordan, *J. Amer. Chem. Soc.*, **52** 1751 (1930).
15. M. I. Shakhparanov, N. P. Zakurdaeva, and E. K. Podgorodetskii, *Vysokomol. Soedin. Ser. A*, **9**, 1212 (1967).
16. V. I. Klenin and O. V. Klenina, *J. Polym. Sci. C*, **16**, 1011 (1967).
17. J. E. Anderson and R. Ullman, *J. Appl. Phys.*, **44**, 4303 (1973).
18. E. Klein and J. K. Smith, in *Reverse Osmosis Membrane Research*, H. K. Lonsdale and H. E. Podall, Eds., Plenum Press, New York, 1972, Chap. 3, p. 61.
19. C. M. Hansen, *Ind. Eng. Chem., Prod. Res. Develop.*, **8**, 1 (1969).
20. R. Matz, Chap. 7 in reference 10.
21. M. Weintraub and S. Loeb, University of the Negev, Beersheba, Israel, private communication.
22. H. E. Grethlein, *Proceedings of the Fourth International Symposium on Fresh Water from the Sea*, A. Delyannis and E. Delyannis, Eds., Heidelberg, Sept. 9-14 (1973); Vol. 4, p. 147.
23. Y. M. Malinsky, V. V. Protopenko, and N. M. Titova, *Proceedings International Symposium on Macromolecules, IUPAC*, Helsinki, July 2-7, 1972; Vol. 4, 1972, p. 199.
24. M. Panar, H. H. Hoehn, and R. R. Herbert, *Macromolecules*, **6**, 777 (1973).
25. R. E. Kesting, *J. Appl. Polym. Sci.*, **17**, 1771 (1973).

Received November 21, 1973

Revised January 15, 1974