

ON THE MECHANISM OF FORMATION OF ASYMMETRIC ULTRA- AND HYPER-FILTRATION MEMBRANES.

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SUMMARY

A study has been made of the formation of membranes from solutions of poly(2,6-dimethyl-1,4-phenylene oxide) (P.P.O.***) in trichloroethylene/alcohol mixtures and using methanol as the precipitation agent. The mechanism of the formation of the sponge - like structures proves to be a liquid - liquid phase separation phenomenon with nucleation and growth of the diluted phase. The waterpermeability of this extremely hydrophobic polymer membrane (which only is obtained for high percentages of octanol in the polymer solution) is possibly due to crystallization in the concentrated polymer regions, like the skin at the surface and the concentrated polymer phase which forms the matrix of the sponge-structure. The membranes prepared show good ultrafiltration properties.

INTRODUCTION

In this paper we will report on work which has been done to obtain more information concerning the phase separation involved in the formation of asymmetric membranes. We have prepared asymmetric ultrafiltration membranes of poly(2,6-dimethyl-2,4-phenylene oxide) (P.P.O.) by means of the so called coagulation technique.

Although succes has been achieved in the past in developing various types of noncellulosic membranes, especially for ultra-

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filtration purposes, there are applications where enhanced stability of the membrane material is required e.g. the use of ultrafiltration membranes in the dairy industry. From the literature it is known that P.P.C. has outstanding chemical and physical properties. It has high hydrolytic stability in a broad pH-range and it is resistant to chlorine attack from sodiumhypochloride, which is often used as a membrane cleaning agent. The high glass transition temperature (210°C) of P.P.O. indicates that it is possible to use P.P.O.-membranes at elevated temperatures. Sterilization of the membranes with hot water vapor in the dairy-industry should be possible.

The main objective of our research-programm was to develop an ultrafiltration membrane of P.P.O. for use in the dairy-industry with the following requirements:

- a. high waterflux at moderate pressure: fluxes greater than $20 \text{ cm}^3/\text{cm}^2, \text{ hr}$ at 3 bar.
- b. high permeability for low molecular weight substances, like salts and lactose.
- c. good protein rejection: greater than 95%.

The research programm was initiated from our knowledge of the demixing process, taking the line of the thermodynamics and kinetics of phase equilibria in polymer solutions. Koenhen et al. (1) reported on research done on the system polyurethane dimethylformamide - water, and in this work one can find a review of the results of other workers, in the field of membrane formation mechanisms.

We have tried to verify the mechanism proposed earlier (1) involving a coagulation mechanism along the following scheme:

- a. direct desolvation of the top-layer where most likely gelation or crystallization takes place.
- b. formation of the porous sublayer by means of liquid - liquid phase separation. Nucleation and growth of the concentrated or diluted polymer phase occurs. In the case of nucleation and growth of the diluted phase the concentrated phase forms the continuous matrix, and the final structure, after complete desolvation is the typical sponge - like structure.

The solidification of the dense top-layer is a rather obscure process since in general the rate of phase separation is very

high at this location, where the top-layer comes into direct contact with the nonsolvent. The mechanisms of spinodal demixing is possible, and the result is a favorable fine mazed network, intertwined by finepores. Crystallization in polymer rich regions may follow here. The tendency of a polymer solution to crystallize when high enough in concentration is probably very important for the final membrane structure and performance.

Following Ziabicki (2) and Gröbe et al. (3) in their view on coagulation during wet fiber spinning processes, we believe that the initially formed dense top-layer plays an important role during the membraneformation. The relative rates of mass-transfer of solvents and precipitants are probably determined to a great extent by this skin layer, because of the different diffusion constants in the skin layer for the mobile components leaving or entering the membrane during coagulation. In this way the top-layer strongly affects the kinetics of solidification and thereby the resulting morphology. We feel that that this fact was, until now undervalued by membrane chemists.

THEORETICAL CONSIDERATIONS

Liquid - liquid phase separation

The modeldescription for polymer solutions by Flory (4) and Huggins (5) yields an expression later modified by Koningsveld (6) for the Gibbs free enthalpy of mixing of a polymer and a solvent which is expressed here in weight fractions:

$$\frac{\Delta G_M}{RT} = W_0 \ln W_0 + \sum_i \frac{M_0}{M_i} W_i \ln W_i + g \sum W_i W_0 \quad (1)$$

in which ΔG_M = free enthalpy of mixing, R = universal gas constant, T = absolute temperature, W_0 = weight fraction of solvent, W_i = weight fraction of polymer species i , M_0 = molecular weight of the solvent, M_i = molecular weight of the polymer species i , and g = empirical correction parameter. The entropy of mixing (the first two terms on the right-hand side) is small compared to the entropy of mixing of low molecular weight substances, because the factor M_0/M_i is small for polymers in solution. A small endothermic enthalpy of mixing represented by the term $g \sum W_i W_0$, can cause a phase separation. For an extended explanation of the mechanisms of the phase-separation in the case of an inflection-

point in the ΔG_M -W curve, we refer to the work of Koenhen et al. (1). In this place we should like to confine ourselves to the remark that the different types of demixing will have important consequences on the ultimate structure of the membranes.

Crystallization

Crystallization is a different form of phase separation which can occur in polymer solutions as well (7). It is known that crystallization of P.P.O. is possible from toluene solutions (1,8). Also crystallization of P.P.O. has been reported from other solvents (9,21)

Swelling of linear polymer networks using the concept of the solubility parameter

The solubility behaviour of polymers can be predicted to a reasonable extent by applying the Hildebrand relation (10), which connects the energy of mixing of two components to their individual energies of evaporation:

$$\frac{\Delta E_{\text{mix}}}{\phi_1 \phi_2} = v_m (\delta_1 - \delta_2)^2 \quad (2)$$

$$\delta = [\text{C.E.D.}]^{\frac{1}{2}} = \left[\frac{\Delta E_{\text{vap}}}{v_m} \right]^{\frac{1}{2}}$$

where ΔE_{mix} = energy of mixing, $\phi_1 \phi_2$ = volume fractions of the components, v_m = average molar volume based on mole fractions, δ_1, δ_2 = solubility parameters, C.E.D. = cohesive energy density, and ΔE_{vap} = energy of evaporation. Hansen (11) divided the solubility parameter into contributions from disperse interactions (δ_d), dipole interactions (δ_p) and donor-acceptor or hydrogenbond (δ_h) interactions and he introduced the notation

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (3)$$

If there are no specific interactions upon mixing of two or more components, it is possible to express each term of the solubility parameters for a mixture solvent as:

$$\delta_{m,i} = \sum_{j=1}^n \phi_{j,i} \cdot \delta_{j,i} \quad \begin{array}{l} i = d, p, h \\ n = \text{number of solvent components} \end{array} \quad (4)$$

According to Froehling et al (12) we can predict the interaction of a swelling agent with a polymer, because the affinity of a swelling agent (in our case a mixture of solvent and nonsolvent) with respect to a polymer is inversely proportional to its distance from the polymer in the $\delta_p, \delta_d, \delta_h$ -space. Therefore, swelling value measurements can in principle be used to obtain the correct set of δ -parameters for a polymer. Equation (5) gives the expression for the polymer-swelling agent distance in the δ -space

$$\Delta = \left[(\delta_{p,S} - \delta_{p,P})^2 + (\delta_{d,S} - \delta_{d,P})^2 + (\delta_{h,S} - \delta_{h,P})^2 \right]^{\frac{1}{2}} \quad (5)$$

where the subscript S and P refer to solvent and polymer respectively.

Chen (13) showed that the contribution to the energy of mixing in polymer solutions, caused by dispersion forces and dipole forces could be taken together into one enthalpy parameter χ_H (this is a Flory-Huggins-type correction parameter for the enthalpy of mixing),

$$\chi_H = \frac{V_m}{RT} \left[(\delta_{d,P} - \delta_{d,S})^2 + (\delta_{p,P} - \delta_{p,S})^2 \right] \quad (6)$$

Together with δ_h this parameter produces good predictions for the solubility of polymers.

Diffusion from coagulating polymer films

To measure the transport rates of the mobile components during the coagulation of casted polymer films, we use the diffusion equation from the treatise by Crank (14):

$$\log \left(1 - \frac{M_t}{M_\infty} \right) = \log \frac{8}{\pi^2} - \frac{\pi^2 D}{2,303 \cdot 4} \cdot \frac{t}{l^2} \quad (7)$$

where M_t is the amount of diffusant sorbed or desorbed at time t , M_∞ the same at equilibrium, D is the diffusion coefficient, t is time and l the thickness of the layer through which diffusion takes place effectively. Eq (7) is the solution of the diffusion equation for a sharp boundary layer (sheet), provided that the condition of a homogeneous coagulation bath is fulfilled. The diffusion coefficient can be obtained by plotting $\log \left(1 - \frac{M_t}{M_\infty} \right)$ against t , if the length of the diffusion path l is known.

EXPERIMENTAL

Casting solution preparation

Various membranes have been prepared, from different solution compositions. The solvent trichloroethylene always contained a certain amount of alcohol (between 0 and 22% by weight) from the following range; methanol; ethanol butanol and octanol. The precipitation agent (i.e. the coagulation bath) in all cases was methanol. A 10% (by weight) polymer solution was prepared and casted with a Doctors knife as a 0,2 - 0,4 mm thin film on a glass plate. The P.P.O. sample used had $\bar{M}_n = 21.600$ and $\bar{M}_w = 37.700$ as determined by osmometry and light scattering, respectively. All solvents used were of analytical grade. In all cases the evaporation step after the membrane had been casted, was as short as possible.

Optical microscope studies

The phase separation of P.P.O. was examined with an Olympus E.H.-microscope. The same technique as introduced by Epstein (15) was used. A droplet of polymer solution is placed between two microscope slides. By means of a syringe nonsolvent is placed near the edge and the coagulation process is studied either visually or by taking photographs.

Scanning Electron Microscopy

Cross sections of the membranes were examined with a Jeol J.S.M.-U3 scanning electron microscope (S.E.M.). The samples were prepared by cryogenic breaking and afterwards drying at room temperature (16). Coating with a charge conducting layer was done by means of a Balzer Union "Sputter Unit".

Diffusion experiments

Thin films (0,4 mm) of a 10% P.P.O.-solution were casted on a glass plate using a Doctors-knife. The precipitation bath (methanol) was kept in rocking movement (for stirring action) during the coagulation. The composition of the bath is followed by means of gaschromatographic analysis using a Beckmann model 409 instrument.

Swelling measurements

A 15% P.P.O./chloroform solution was casted on a glass plate and placed in a thermostate oven. After complete evaporation of the solvent, thin (0,4 mm) transparent P.P.O.-films were obtained. Small pieces were immersed in a swelling agent, which was a mixture of trichloroethylene, octanol and methanol, at 20°C for 72 hours. After this time the film was wiped with a filterpaper and weighed in a closed sample vessel. The degree of swelling is expressed as relative weight increase.

Ultrafiltration experiments

Ultrafiltration experiments were carried out in a stirred Amicon low pressure cell at an operating pressure of 3 bars. In the experiments a 100 p.p.m. solution of Human Albumin or a 100 p.p.m. lactose solution was used as a feed solution. The concentrations in feed and product were determined by Total Organic Carbon measurements, using a Beckmann T.O.C.-apparatus, model 915.

RESULTS

Optical microscope studies

The coagulation process was studied for a solution of 10% P.P.O. dissolved in a mixture of trichloroethylene (78%)/octanol (22%). In the same way as reported by Koenhen (1) coalescence of droplets can be seen to occur. This means that liquid - liquid phase separation is the mechanisms for the demixing process.

Membrane casting experiments

10% P.P.O. in trichloroethylene (100%); precipitation agent methanol

The coagulation is very slow. The result is a rather transparant membrane with good mechanical strength and a glossy surface, with no waterpermeability at all.

10% P.P.O. in trichloroethylene (95%)/methanol (5%), precipitation agent methanol

The coagulation is very fast. The result is a white membrane with good mechanical strength. In figure 1 a S.E.M.-photograph is shown. From this picture one can conclude that liquid - liquid phase separation has occurred.

10% P.P.O. in tri (95%)/5% of alcohol from the range, ethanol, butanol, hexanol and octanol; precipitation agent methanol

Cross sections of these membranes show the same structure as seen in fig. 1. In alle cases liquid - liquid phase separation occurred. Membranes of good mechanical strength were obtained but up to a pressure of 40 atm not one of them was permeable for water.

10% P.P.O. dissolved in a mixture of trichloroethylene with increasing amount of octanol

10, 15, 18, 20 and 22, weight % of total solvent; precipitation agent is methanol. From figure 2 to 6 it is seen that starting with composition of 15% octanol in the solvent, the so-called finger like cavaties appear. At a level of 18% octanol the membranees become permeable to water at 3 bars as is shown in table I.

TABLE I

% octanol in solvent	J_w (waterflux) $\text{cm}^3/\text{cm}^2 \text{ hr}$
5	0
10	0
15	0
18	< 0,5
20	1 to 2
22	5 to 25



Fig. 1 5% methanol in solvent

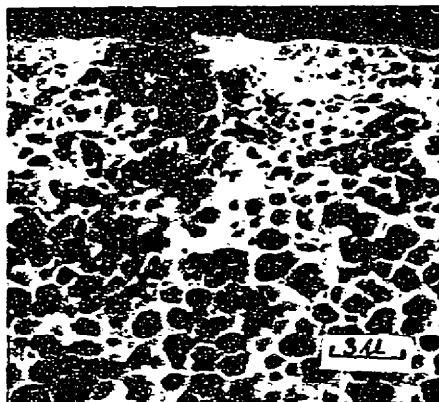


Fig. 2 10% octanol in solvent

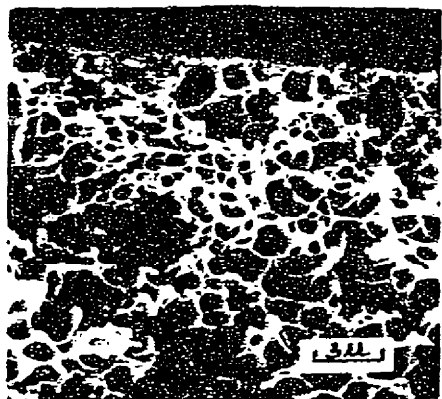


Fig. 3 15% octanol in solvent

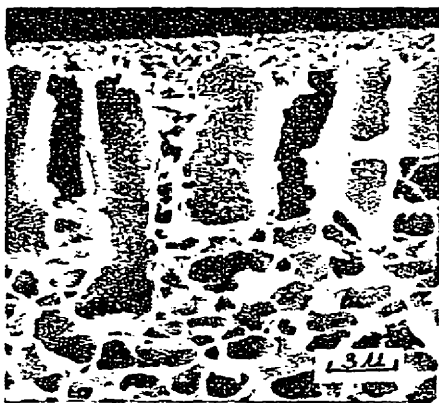


Fig. 4 18% octanol in solvent

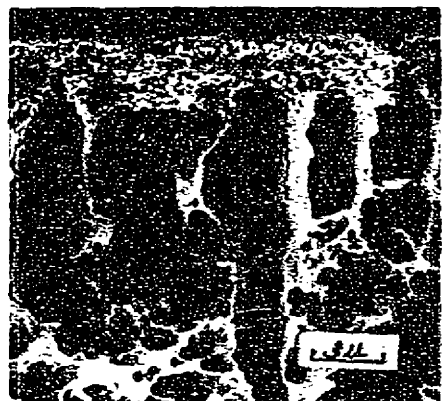


Fig. 5 20% octanol in solvent



Fig. 6 22% octanol in solvent

For the 22% octanol membrane we measured the protein and lactose rejection in a stirred low pressure Amicon cel. Lactose rejection was always zero and rejection for Human albumin was higher than 90% at a flux of about $2 \text{ cm}^3/\text{cm}^2 \text{ hr}$. Note that these are results for membranes whose performances have not yet been optimized.

10% P.P.O. dissolved in a mixture of trichloro-ethylene with increasing amount of octanol. The precipitation agent is now octanol.

From figure 7, 8 and 9 it is shown that when octanol is used as precipitation agent liquid - liquid phase separation determines the overall structure, but crystallization in the concentrated phase obviously has occurred too. The final result is a rather loose, open structure but membranes produced in this way have very little mechanical strength.

Diffusion-measurements

From equation 7 it should be possible to compute the diffusion for trichloroethylene, octanol and methanol, if the diffusion length l were known. In our opinion this distance is equal to the thickness of the skin. The measurement of this thickness however, from S.E.M. photographs is very difficult and not very accurate. It is therefore not possible to calculate the exact diffusion constant but for these coagulating films one can compare the trends in diffusion behaviour of trichloro-ethylene and octanol. Table II and figure 10 give some experimental results.

TABLE II

% octanol in solvent	$\frac{\pi^2 D}{4 \times 2,3 \times 10^2} (\text{sec}^{-1}) \times 10^3$	
	tri	oct
5	5,05	-
10	5,65	1,05
15	5,68	1,41
20	5,96	1,71
22	5,60	2,37

As is shown in figure 10, the applicability of eq (7) for the experimental data is very good.

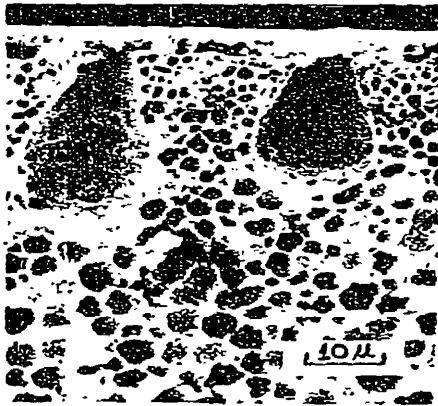


Fig. 7 22% octanol in solvent precip. in octanol

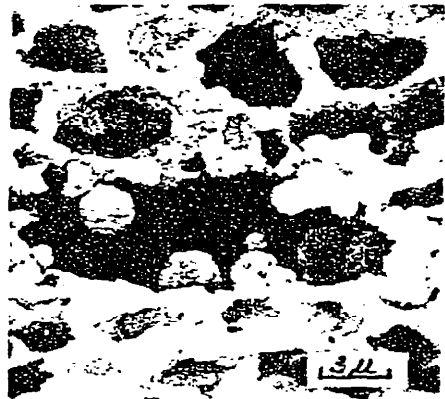


Fig. 8 22% octanol in solvent precip. in octanol

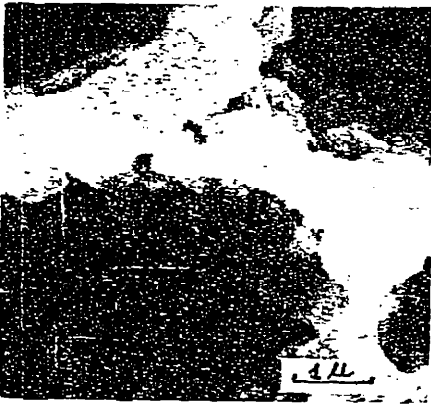


Fig. 9 22% octanol in solvent precip. in octanol

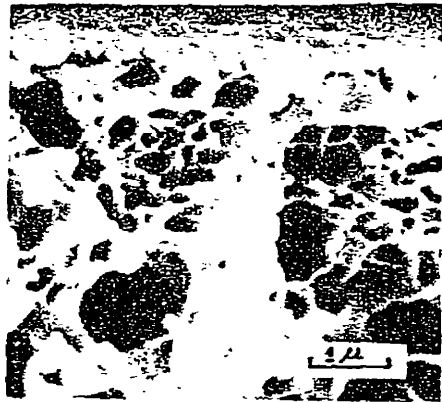


Fig. 12 10% octanol in solvent precip. in methanol



Fig. 13 22% octanol in solvent precip. in methanol

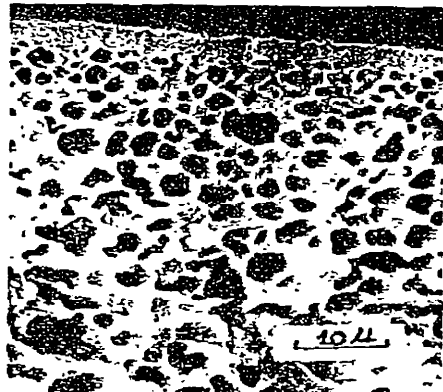


Fig. 14 20% octanol in solvent precip. in methanol/water

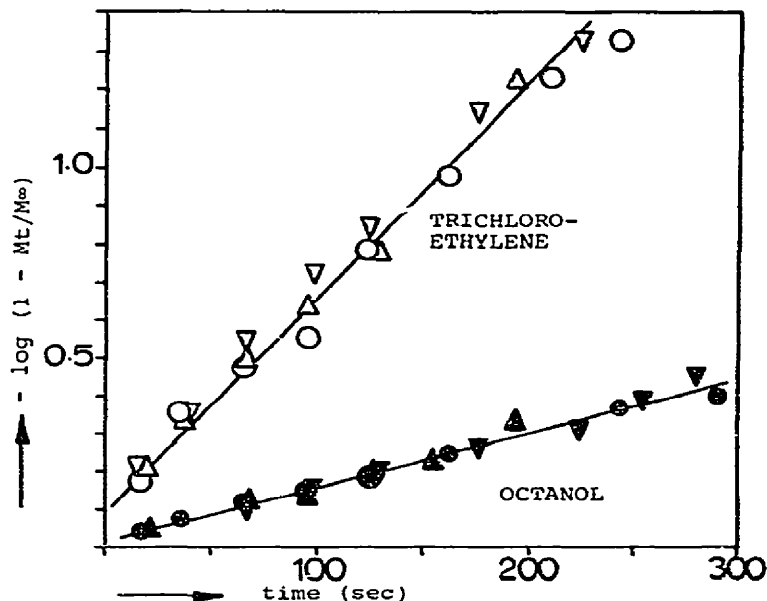


Fig. 10 Values of $-\log(1 - M_t/M_\infty)$ plotted as a function of time, for diffusion of trichloro-ethylene and octanol from coagulating P.P.O. films.

From table II it is clear that the diffusion of the trichloro-ethylene into the coagulation bath is much faster than the diffusion of octanol. The diffusion of tri stays almost constant whereas the octanol diffusion increases with higher octanol contents in the solvent. Together with this result we measure an increased penetration rate for methanol into the membrane.

Swelling experiments

The results for the swelling experiments of P.P.O. in mixtures of tri, octanol and methanol are plotted in figure 11. The magnitude of the relative weight increase (swelling ratio) appears to be inversely proportional to the calculated distance Δ .

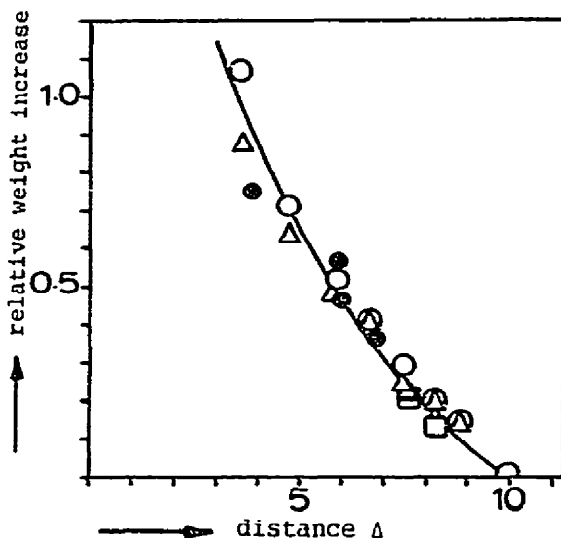


Fig. 11 Relative weight increase for P.P.O. films in mixtures of tri, octanol and methanol, plotted as a function of the distance parameter Δ (see equation 5).

DISCUSSION

The membranes prepared with a low percentage of alcohol in the solvent do not exhibit water permeability. The liquid - liquid phase separation which occurred in this case results in a membrane structure where the walls of the pores or the skin are too dense for any water transport to take place. Since P.P.O. is a very hydrophobic polymer one should not expect water to permeate by a molecular diffusion mechanism through dense polymer regions.

It should be possible to influence the precipitation process in such a way that the walls of the pores in the sponge layer and the toplayer of the membrane become more open by introducing a different kind of structure.

In our opinion, liquid - liquid phase separation accompanied by crystallization of the P.P.O. in the concentrated phase regions can influence to a great extent the membrane structure and performance. Crystallization of a polymer from its solution is from the thermodynamic point of view a more favorable process than the liquid - liquid phase separation, but it is a kinetically slow process. Koehen et al (19) showed that to obtain a liquid - liquid phase

separation in the system P.P.O.-toluene, high values for the Flory-Huggins interaction parameter are needed. From their work it was concluded that the phase separation was due to a crystallization phenomenon, at rather low interaction parameter values. Therefore, for low interaction parameter values, it is possible that at a certain concentration, crystallization is more favorable than the liquid-liquid phase separation. From the literature it is known that P.P.O. can crystallize into irregular spherical shapes (20, 21). From equation (6) we can derive that low interaction parameters are possible when the differences in δ -parameters between the components of the solution are small. From the results of the swelling experiments we conclude that it is permitted to use the concept of the solubility parameters for the system P.P.O./tri, octanol, methanol (fig. 11). So if crystallinity should be introduced into the membrane we must prepare a solvent mixture of trichloro-ethylene with a certain amount of a non-solvent which is more compatible with P.P.O. than methanol (the precipitation agent). Table III shows that the coordinates in the two dimensional δ_d, δ_p -space of the higher alcohols are nearer to the P.P.O.-coordinates than is the case for methanol.

TABLE III

Solubility Parameters		
Substance ¹⁾	δ_p	δ_h
methanol	6,0	10,9
ethanol	4,3	9,5
butanol	2,8	7,7
pentanol	2,2	6,8
octanol	1,6	5,8
P.P.O. ²⁾	1,3	2,4

1) Taken from Hansen and Beerbower (17)

2) Taken from Koenhen en Smolders (18)

The diffusion experiments show that the diffusion rate of trichloro-ethylene into the bath is higher than the diffusion rate of octanol. By this exchange of the solvent, the solution below the initially formed skin becomes more concentrated in octanol and in this way the possibility for P.P.O.-crystallization increases.

The results of experiments using pure octanol as a precipitation agent show (fig. 7, 8 and 9) a grainlike structure in the concentrated phase. The membranes so prepared do not have any mechanical strength. At this high amount (22%) of octanol in the solvent, fingerlike cavities are clearly observed in the membrane (fig. 7). From this result we conclude that liquid - liquid phase separation is involved, with crystallization in the concentrated phase, due to the high concentration of octanol.

At a level of 15% and higher for octanol in the solvent the characteristic fingerlike cavities become visible, see figures 3, 4, 5 and 6, when methanol is used as a precipitation agent. In the same series one observes structural changes in the skin, which becomes more grainlike (figures 12 and 13). The consequence of these structural effects is an improving mass transfer during film formation and a higher waterflux for the final membranes. Indeed we find increasing octanol diffusion and also the penetration rate of methanol increases. Moreover, in all these latter cases we observe the formation of fingerlike cavities. The explanation of the presence of these cavities given by Gröbe et al (3) seems to be the most acceptable: a nucleus of the polymer poor dilute phase just under the skin can precede the solidification front because mass transfer will be favoured in such a liquid region.

Another indication that the properties of the skin determine to a great extent the resulting morphology is illustrated by the fact that a membrane coagulated in a mixture of 20% water in the precipitation bath (methanol) does not show the fingerlike cavities (compare fig. 14 and fig. 5). Further investigations on the thickness and structure of the skin in relation to transport phenomena during coagulation are in progress.

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