

Diffusion induced phase separation with crystallizable nylons. II. Relation to final membrane morphology

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Abstract

Intermediate stages during membrane formation by means of immersion precipitation were studied by cryo-substitution for the system nylon 4,6, formic acid and water. The presence, nature and size of solid particles was determined as a function of time and of the distance from the interface. The spherulitic nature of these particles was confirmed by staining the samples. It was shown that at a relatively low nucleation density the concentration profile in the film was hardly influenced by a starting phase separation process, while in a situation with a relatively high number of nuclei per volume concentration patterns must be considerably altered.

Keywords: Membrane formation; Cryo-substitution; Transmission electron microscopy; Spherulitic crystallization

1. Introduction

Since immersion precipitation is one of the most widely used techniques for membrane preparation [1], the mechanisms behind the membrane formation are essential for understanding and predicting membrane morphology. Therefore two phenomena must be understood: (i) equilibrium thermodynamics, i.e. knowledge about the stability borders of the mostly ternary system and the type of phase separation that occurs, and (ii) kinetics, i.e. insight in to the diffusional processes.

In membrane science equilibrium thermodynamics of a membrane forming system is usually (semi-quantitatively) described by the Flory–Huggins theory [2,3]. The theory is used in order to describe the liquid–liquid phase separation border [4–8] as well as solid–liquid phase separation [9,10].

For the description of the mass transfer models for immersion precipitation have been developed [8,11,12].

The calculated concentration profiles may no longer be valid as soon as any kind of phase separation has started. Insight in the intermediate and later stages of membrane formation must still be obtained by deduction. The development of the concentration profiles in time passes through different stages. During the whole process the diffusion front enters deeper into the film and shifts to sites further away from the interface. In the early stage the interfacial concentrations are assumed to be constant. During the first second of our calculations this condition is maintained as is assumed by Reuvers [11]. In the later stages, however, the levelling off of concentration gradients at the interface, takes place [8]. The driving forces will decline resulting in lower fluxes

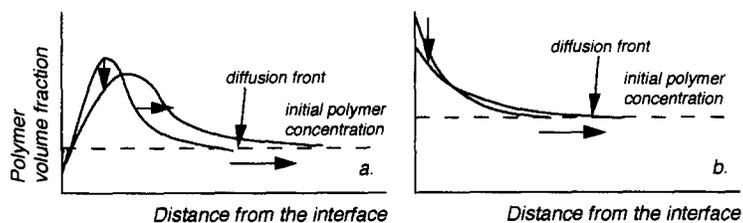


Fig. 1. Schematic changes of the polymer concentration profile in time. The interface concentration changes; the “wave” becomes wider and the diffusion front moves away from the interface. The moving interface is not included in this scheme.

of solvent and non-solvent. The profiles will become more flattened. These two effects are schematically given in Fig. 1.

The morphology of the top-layers (the “slices” near the interface) is determined by the concentration profiles at the moment phase separation sets in. The predictions from the model are only valid for those parts of the membrane that are located close to the interface if turbidity is observed within a few seconds or deeper into the film if it takes place after a longer period of time. Concentration profiles in the still homogeneous layers certainly will develop with a diffusion front proceeding towards the support (see Fig. 2).

Especially the morphology of the sub-layer of a membrane sometimes cannot always be related to the mass transfer models available.

Experimentally it is difficult to determine the intermediate stages of immersion precipitation.

Membranes in which the morphology of the sub-layer is determined by liquid–liquid phase separation are not easily isolated. Solid particles, on the other hand, nucleated in a sub-layer in which solid–liquid phase separation takes place, can be isolated with techniques that enable the removal of the still liquid material while the coagulation process is stopped. Samples can then be examined by transmission electron microscopy (TEM). The solid crystalline particles can be made visible by using a staining agent.

In the first part of this series the system: nylon 4,6, formic acid and water was studied [13]. The membrane morphology obtained under different circumstances is correlated to corresponding compositions paths resulting from the mass transfer model

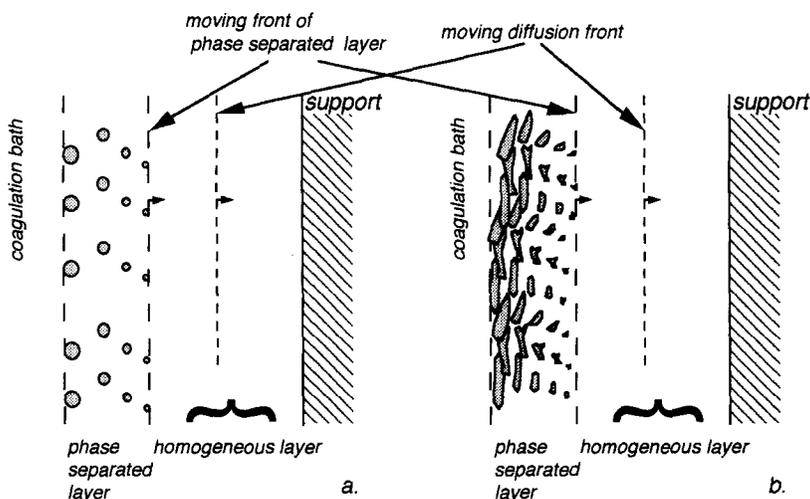


Fig. 2. The situation in the film after phase separation has started in the upper layers for a situation with (a) a small nucleation density and (b) a large nucleation density.

making use of the earlier developed knowledge of the thermodynamics of the system [10].

This paper will emphasize whether intermediate stages in membrane formation can be experimentally studied and related to final membrane morphology. Therefore it will be essential that electron microscopy experiments will confirm the spherulitic nature of the solid particles, that must correspond to size and shape of particles observed with scanning electron microscopy [14].

2. Experimental

2.1. Sample preparation

Nylon 4,6 (Stanyl KS 400) kindly supplied by DSM was dissolved at 30°C in formic acid in the concentrations 20 and 32 wt%. Prior to use the polymer was dried in vacuo at 70°C for at least 24 h. The membranes were cast on a metal plate and immersed in a coagulation bath containing demineralized water. The coagulation process was stopped at different intervals by quick immersion of the metal support with the film into liquid nitrogen. Small samples were cut from the frozen film and immersed in Lowicryl K4M resin at –20°C in a Balsers FSU 010 cryo-substitution unit. The liquid resin was exchanged several times, because of accumulation of formic acid. The solid components present in the prepolymer were embedded by polymerizing the resin with UV light. The samples were used to prepare thin slices by a microtome for transmission electron microscopy (TEM).

Samples of a film that was completely coagulated were also immersed in the prepolymer resin, in order to prepare TEM samples of the final membrane structure.

2.2. Transmission electron microscopy

Microslices were stained with phosphor tungsten acid (PTA), a staining agent, in order to make the lamellae visible in the membranes. Photographs were taken at magnifications between 5000 and 20 000 times. The presence and nature of solid particles present during membrane formation was studied as a function of coagulation time and of the distance from

the interface. TEM pictures were prepared from samples at different sites: from sites near the top-layer to sites closer to the support layer.

3. Results

TEM pictures of a membrane cast from a 20 wt% and from a 32 wt% solution are shown in Fig. 3. The lamellae, visible in both the spherulitic (20 wt%) and the axialitic (32 wt%) morphology, clearly indicate that spherulites are formed in nylon membranes. The size of the spherulites is in agreement with the results of the SEM pictures [14]. It can be observed that the centers of both structural units are quite similar in nature, which indicates that the mechanism

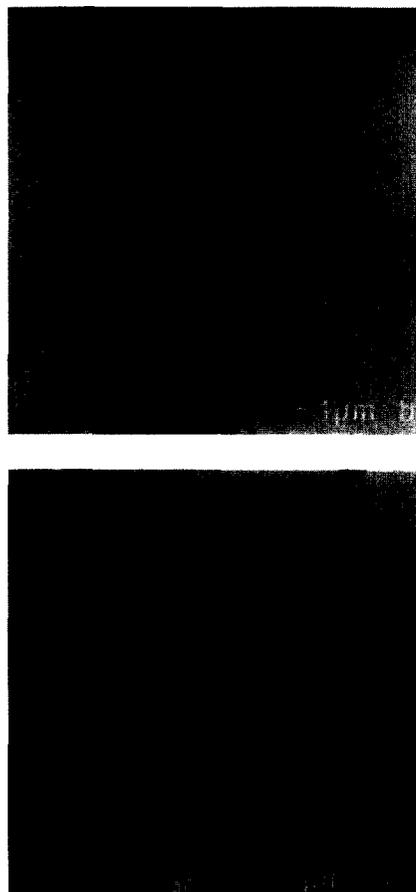


Fig. 3. TEM photographs of membranes cast from a 20 wt% solution (a) and a 32 wt% solution (b).

of spherulitic growth in case of both spherulitic and axialitic morphology is equal. Different mechanisms have been reported [15] to explain axialitic and

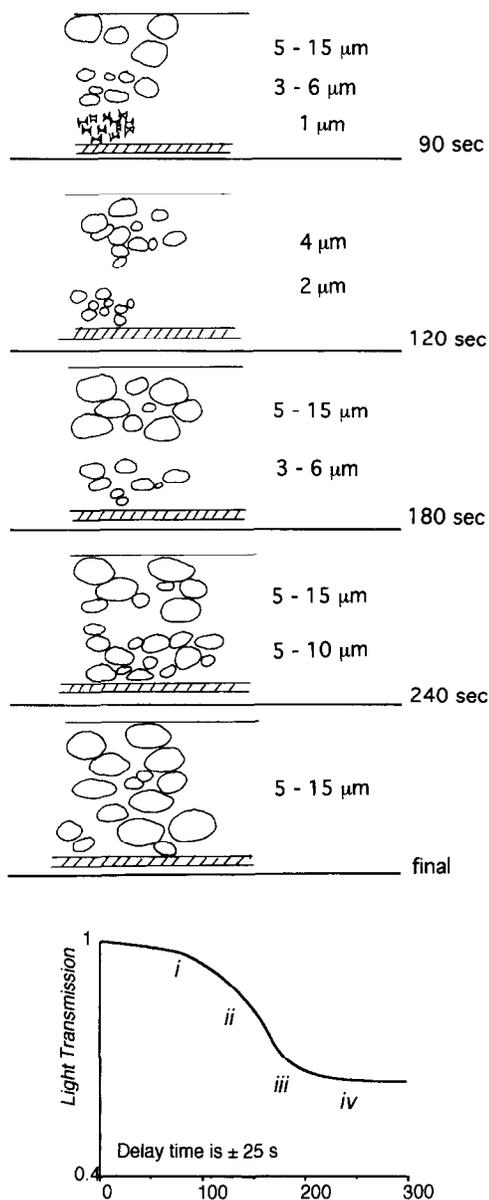


Fig. 4. An overview of the results obtained from the cryo-substitution experiments with membranes cast from a 20% solution of nylon 4,6 in formic acid, with the circles representing the spherulites and the "clock houses" representing the axialites. The sizes of the solid particles and the coagulation times are given in the right hand column. The light transmission profile during membrane formation for this membrane is taken from the first part of this series [13]; the different stages are indicated with i to iv.

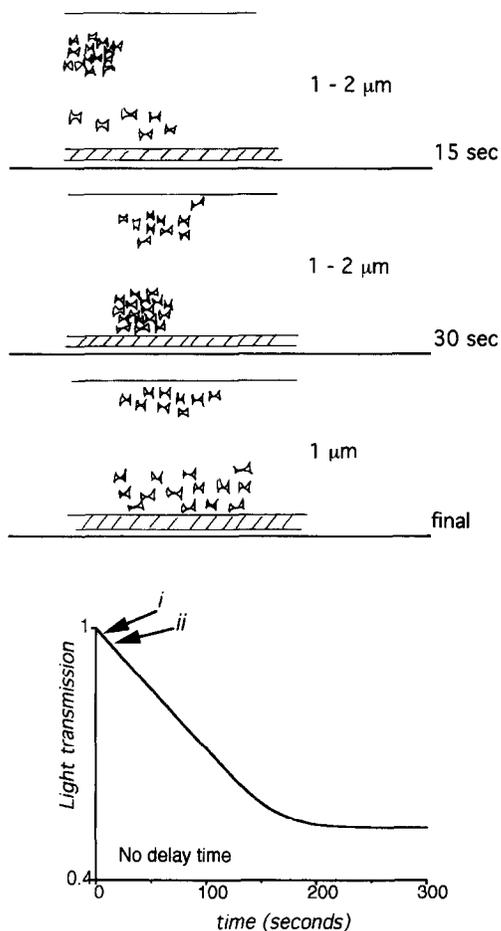


Fig. 5. An overview of the results obtained from the cryo-substitution experiments with membranes cast from a 32% solution of nylon 4,6 in formic acid, with the "clock houses" representing the axialites. The sizes of the solid particles and the coagulation times are given in the right hand column. The light transmission profile during membrane formation for this membrane is taken from the first part of this series [13]; the different stages are indicated with i and ii.

spherulitic morphologies when polymers are crystallized from the melt. Axialites have been observed when the material is crystallized at low undercoolings and spherulites at larger degrees of undercooling. Here, this analogy is not observed since the 20% membrane would be comparable with a low degree of undercooling and the 32% membrane with the largest driving force for crystallization. In these cases the difference can only be explained by a large difference in nucleation density. The axialites simply cannot grow to complete spherulites.

The results of two casting solutions with a polymer concentration of 20 and 32 wt% are schematically shown in Figs. 4 and 5, respectively. The transmission curves during the formation of these membranes are shown as well [13].

For the 20 wt% casting solution the first stage after 90 s shows the larger spherulites formed near the top with a size of spherulites of 5–15 μm , as observed in the final membrane [15]. Smaller spherulites are found in the middle of the membrane, and some axialitic structures near the bottom. After 180 s the larger spherulites can be found deeper in the membrane and smaller spheres near the metal plate. Then after 240 s the spherulite size deeper in the film has increased and in the final stage a uniformly distributed spherulite size is observed. In combination with the light transmission profile it can be seen that after 240 s the line is bending towards a horizontal direction just at the moment that the morphology has almost reached its final state. This uniform morphology is not a result of simultaneously nucleated and grown spherulites. During the progress of the diffusion processes nucleation takes first place near the interface. The differences in size of the spherulites in the first stages of the membrane formation process are levelled out during the later stages. The density of the spherulite population is not consistent over the whole result. This might be caused by some disturbance of the nucleation during the quenching and the substitution processes.

Phase separation in the membranes cast from a 32 wt% solution sets in during a much shorter time scale compared to a 20 wt% solution. During the membrane formation all stages show axialites through the membrane. The bottom side of the film was still “sticky” after melting of the cryogenically frozen sample in a water bath at room temperature, which is an indication that up to 45 s demixing in the layers close to the bottom part of the film was still far from complete.

4. Discussion

A continuous “interplay” exists between the proceeding of the phase separated layer (which is not equal to the moving diffusion front in case of delayed onset of demixing or if solid–liquid demixing

takes place) and the proceeding of the diffusion pattern. A concentration profile near the growing crystals superimposed on the overall concentration profile exists. Several cases are schematically given in Fig. 6. The conditions at the interface of a growing crystal unit is dictated by the solid–liquid equilibrium. At the crystal-side of the interface the polymer concentration is one, at the liquid side the composition is given by a point at the crystallization line. At a semi-infinite distance from this growing surface the composition is dictated by the overall concentration profile, which continuously changes. The two cases examined with the cryo-substitution experiments will be worked out. The first one is for a spherulitic morphology; the second in case an axialitic morphology is obtained.

4.1. Spherulitic morphology

According to the results of the cryo-substitution the average rate of spherulitic growth is in the order of 2–5 $\mu\text{m}/\text{min}$. With a spherulite size of 10 μm it takes approximately 2–5 min before they impinge for this specific case. From the calculated concentration profiles the rate of movement of the diffusion front is in the order of 5 μm per square root of time ($5 \mu\text{m}/t^{-1/2}$). The layer in which phase separation sets-in has been will stay in a stage in which spherulites still can grow freely before they impinge after 2 to 5 min. With an average spherulite size of 10 μm the nuclei, formed in earlier stages of the membrane formation process, have an average distance of 10 μm from each other. In the first stages of immersion (30 s) the main part of the layer where crystallization has taken place is still in the “homogeneous” composition dictated by the overall concentration profile (see also Fig. 4a). The propagation of the concentration profiles through the film is then hardly influenced by the already started phase separation. Since the composition path of the 20% solution [13] is already rather shallow it will become even more levelled out in time; the morphology of the final membrane can be thus expected to be quite homogeneous as indeed is observed.

Two conditions can cause spherulites to stop growing.

1. They touch upon neighboring spherulites.
2. The surrounding matrix is depleted of polymer.

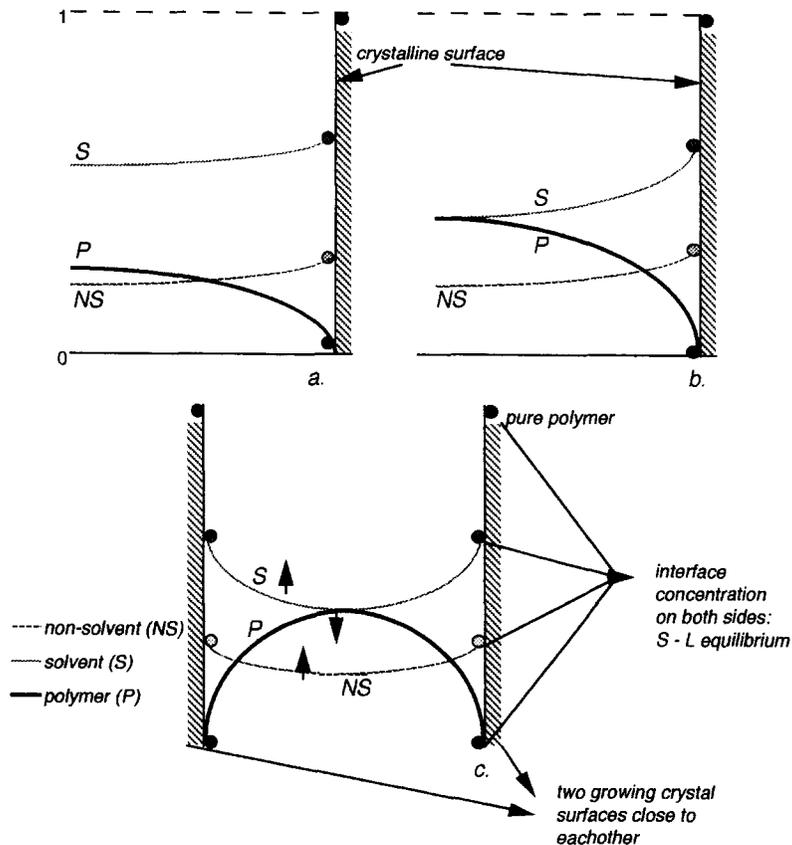


Fig. 6. Concentration profiles in the presence of a growing crystal surface, with concentrations at the interface that are given by the solid-liquid equilibrium. A schematic profile for a crystalline unit grown from a film with initial polymer concentration of (a) 20%, (b) for 32% and (c) when two surfaces grow in the vicinity of each other; in the latter case the layer between the growing crystal surfaces is exhausted in polymer, therefore the solvent and non-solvent concentration will increase. This will effect the overall composition throughout the film. The local equilibria are schematically drawn on the same scale.

When spherulites impinge, it is not necessary that the growth of the spherulite completely stops. In other directions than the site of contact there would still be a possibility to continue growth.

Around the contact-points of the spherulites the crystallization process continues; the points of fusion must give the membrane its mechanical strength. It can be concluded that the growth of spherulites is ceased by the absence of more polymer molecule, because a precipitated film is porous. The entire space will not be filled up with polymeric material as is the case for crystallization from the melt.

4.2. Axialitic morphology

This morphology is observed for the membrane cast from a 32% polymer solution. Almost immedi-

ately after immersion the growth of a layer consisting of crystalline units starts. In the concentration profiles [13] it can be observed that the interfacial polymer concentration is almost 50%. The concentrations at the growing crystal surface, as given by the crystallization line, gives an equilibrium concentration with a lower polymer content. The high nucleation density results in growing centers that are very close to each other (see also Fig. 2b.). In Fig. 6c it is shown how the concentration profiles near these surfaces can no longer be considered as "semi-infinite" in the first stages. The profiles between two growing centers are largely influenced by crystallization, and will be "refreshed" by the newly set overall concentration profiles as given for the whole film, that on their turn are strongly influenced by

these local phenomena. Polymer molecules will tend to diffuse towards growing crystal surfaces; polymer diffusion may also take place from the still homogeneous layer. Compared to diffusion of low molecular weight components, however, diffusion of macromolecules is relatively slow. In the regions between the growing crystal centers (Fig. 6c) both the solvent and the non-solvent concentration have increased, which will enhance solvent and non-solvent transport by an increase of driving forces. It can be considered as an iterative process each superimposed on the preceding stage. The concentration profiles can undergo iterative changes, with the initial profile, however, propagating in every stage. A steady state growth of the phase separated layer can be expected, with the upper layer, which contains in their pores only solvent and non-solvent, hardly contributing to resistance for solvent and non-solvent transport. Actually the “porous” part of the upper layer can then be considered as part of the coagulation bath. The growth of the porous layer can be compared to a linearly grown oxidation layer, that also is porous or cracked in nature [16]. This contrary to parabolic oxidation, known from corrosion theories [16], in which the dense oxidation layer grows with the square root of time. Parabolic oxidation kinetics leads to the formation of impervious adherent oxide layer, protecting metals against further degeneration. This analogy might be of importance for formation of a porous sub-layer, when a thick skin is formed as a result of the diffusion processes.

The concentrations at which nucleation takes place are the same throughout the immersion of the film in the water bath. A sub-layer in such cases will have a isotropic morphology.

4.3. Interface and roughness of the surface of the membrane

An important characteristic of the final membrane is the texture, i.e. roughness, of the top-layer. The typical separation properties of the membrane are determined by the pore size and the largest resistance for transport in a separation system. It is relevant to consider in more detail the mechanism of formation of this top-layer. A crystal surface near the interface has a similar concentration profile as given in Fig. 6. The difference, however, is that no semi-infinite

“bulk” concentration of polymer is present. The polymer concentration must drop to zero at the interface film–bath, since the coagulation bath does not contain polymer. During growth of the crystal surface the film near the interface gradually is exhausted in polymer. Two phases, the coagulation bath and the polymer lean phase in the film with both only low molecular weight components will merge. The top-layer of the membrane is composed of surfaces that are grown in this way. Such a surface never is smooth because growing surfaces of the structural crystalline units have axialitic or spherulitic geometrical forms, that are reflected in the surface at the top. A roughness of the surface is a characteristic for membranes that are determined by crystallization or solid–liquid phase separation. The preparation of a well-defined top-layer in systems in which crystallization is involved requires special precautions.

5. Conclusion

TEM has confirmed the spherulitic nature of the “solid” particles in nylon membranes. Size and shape of the particles corresponds to the crystalline entities observed with SEM [14].

Cryo-substitution experiments show that the nucleation of a crystalline phase and the growth of spherulites continues throughout the membrane. In earlier stages a gradient in spherulite size exists, which levels out in later stages. The growth of spherulites is limited by depletion of polymer.

With a large nucleation density the concentration profiles are influenced by crystallization process. The exchange rate of solvent for non-solvent is not hindered in those layers which contain mainly low molecular weight components in the pores. Despite the fact that the calculated concentration profile for the polymer shows a rather high polymer concentration at the interface, the morphology in most parts of the membrane (the sub-layer) is more or less isotropic. A close look to the situation at the top shows a very thin denser layer [13].

In general cryo-substitution enables experimental study of intermediate stages in immersion precipitation in a membrane forming system with solid–liquid phase separation determining the membrane morphology.

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