

Polymeric membrane formation by wet-phase separation; turbidity and shrinkage phenomena as evidence for the elementary processes

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Abstract

The direct accumulation of polymer, the nucleation and growth of the polymer lean as well as the polymer rich phase and the spinodal phase separation are postulated as four elementary processes of the mechanisms of the polymeric membrane formation by wet-phase separation. With the study of five different polymer/solvent:water systems they are discriminated by the investigation of the turbidity and the shrinkage phenomena taking place during (proto)membrane formation, as well as by the measurement of the pure water permeability and by the inspection of the membranes' cross-section morphology. The general scheme of membrane formation mechanisms is arranged by gathering the groups of different modes of mass transport and the group of nonsolvent/solvent/polymer forms of solidification as elementary processes; by forming combinations of the so postulated elementary processes in time and space particular mechanisms are established. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Mechanisms of membrane formation by wet-phase separation; Elementary processes; Turbidity

1. Introduction

The mechanisms of the polymeric membrane formation by wet-phase separation were previously discussed in common view of the four (elementary) processes [1,2] and presented by the schematised composition paths marked by arrows and encircled numbers 1–4 in the schematised ternary phase diagram nonsolvent/solvent/polymer (Fig. 1) [1–19]. The (elementary) processes were postulated mostly on the basis of a variety of polymeric membranes' cross-section morphologies (figures from 1 to 6 in Ref. [1] and from 3 to 7 in Ref. [2]) are: (1) “the direct solidification” (composition path no. 1); (2) “the nucleation and growth of the polymer lean phase” (end of composition path no. 2); (3) “the spinodal decomposition” (end of composition path no. 3) and (4) “the nucleation and growth of the polymer rich phase” (end of composition path no. 4).

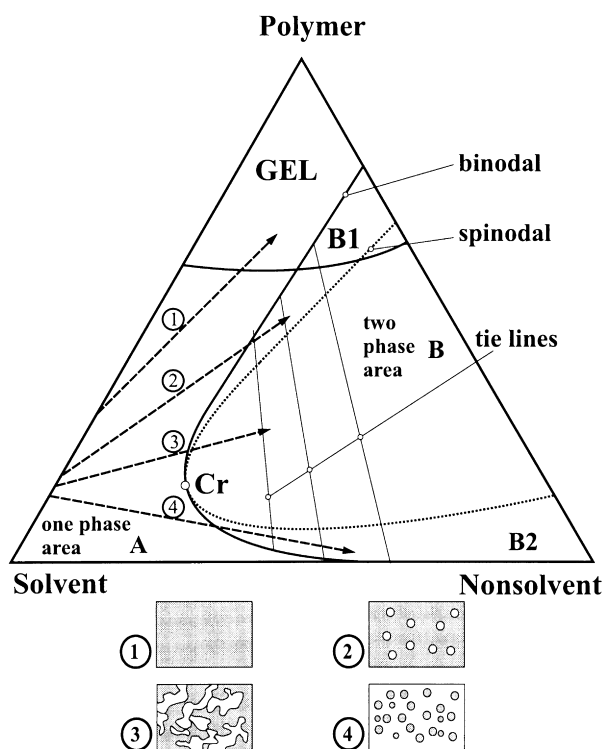
The aim of the present paper is to extend and discuss in depth the meaning and the contents of the above-mentioned set of four (elementary) processes and to add some other

elementary processes which appear to take place in the mechanisms of membrane formation. A broader general scheme of the elementary processes is proposed (Table 1) in which the schematised composition paths and the events on their ends (Fig. 1) are more clearly and precisely correlated and placed among the other elementary processes. In addition we also made some minor changes in the naming of one of them. The scheme with respect to present knowledge presents a complete set of the elementary processes involved in the mechanisms of the membrane formation by wet-phase separation. They are somewhat reasonably arranged into groups of modes of mass transport and into the group of forms of the solidification; in some their time-and-space combinations, taking place during the membrane formation by wet-phase separation, they constitute the mechanism.

The first group of modes of mass transport, namely “the (i) primary nonsolvent/solvent/polymer (ns/so/po) mass transport” consists of “the (ia) direct accumulation of polymer” (previously [1,2] “the direct solidification”), “the (ib) diffusion of ns/so/po”, “the (ic) convection of ns/so/po” and “the (id) hydrodynamic flow of ns/so/po”. All modes of mass transport of this first group are somehow represented in the ternary phase diagram by the four schematised composition paths (Fig. 1). They present the transportation

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- ① direct accumulation of polymer;
- ② nucleation of polymer lean phase;
- ③ spinodal decomposition;
- ④ nucleation of polymer rich phase.

Fig. 1. Ternary phase diagram of a polymer/solvent/nonsolvent system with various composition paths indicated by arrows and numbers; typical membrane structures, composition paths and modes of phase separation are correlated.

of the components only in the direction that is perpendicular to the contact boundary between the solution of polymer and the coagulation bath. The renaming of the (ia) mode of mass transport does not change its content and meaning: it always either takes place (first and) immediately after the cast solution immersion or is absent. It is accomplished without the phase separation by some form of the (iii) solidification. The remaining three modes (ib), (ic), (id) of the (i) primary ns/so/po mass transport as a rule lead to “the (ii) secondary mass transport”, namely to phase separation in the narrower sense. All its three modes, namely “the (iia) nucleation and growth of the polymer lean phase”, “the (iib) spinodal phase separation” as well as “the (iic) nucleation and growth of the polymer rich phase”, have already been mentioned as elementary processes. In these three modes of secondary mass transport the transportation of the components takes place in all directions in space. The next group of elementary processes is “the (iii) solidification of accumulated polymer” (membrane forming system solidification). It

Table 1

Elementary processes arranged into groups (ns/so/po: nonsolvent/solvent/polymer)

Group	Elementary processes
(i) Primary ns/so/po mass transport	Modes of Primary Mass Transport
	(ia) Direct Accumulation of Polymer
	(ib) Diffusion of Components
	(ic) Convection of Components
(ii) Secondary ns/so/po mass transport	Modes of Phase Separation
	(iia) Nucleation and Growth of the Polymer Lean Phase
	(iib) Spinodal Phase Separation
	(iic) Nucleation and Growth of the Polymer Rich Phase
(iii) Solidification of the accumulated polymer	Forms of System Solidification
	(iiia) Gelation
	(iiib) Vitrification (Glass Transition)
(iv) Ternary so/ns/(po) mass transport	(iiic) Crystallisation
	(iva) Leaching of the Polymer Lean Phase
(v) Quaternary ns/po mass transport	(ivb) Leaching of Gel
	(Thermal) Annealing

consists of “the (iia) (thermoreversible) gelation”, “the (iib) vitrification (glass transition)” and “the (iic) crystallisation”. All three phase separation elementary processes, i.e. (iia), (iib) and (iic) are suppressed by some form of (iii) solidification of the polymer rich phase. The same is true with the polymer accumulated via the elementary process of the (ia) direct accumulation of polymer. “The (iv) ternary so/ns/(po) mass transport” contains the elementary process of the (iva) leaching of the polymer lean phase from the protomembrane, usually by a nonsolvent, i.e. by water, and “the (ivb) leaching of the ns/so from a firm gel”. Finally, “the (v) quaternary ns/po mass transport”, that is the annealing of the formed (proto)membrane, can further be arbitrarily added to the set of the elementary processes. Different mechanisms of membrane formation by wet-phase separation that lead to structurally very different polymeric membranes can be established by time-and-space combinations of the above postulated elementary processes.

We prepared polymeric membranes from the five different polymer/solvent:water membrane forming systems. As in the previous case [1,2], no nonsolvent or fourth and further component(s) were added to the polymer solutions. The coagulation bath, too, was without any solvent or other additive(s). The quantitative data on turbidity and the shrinkage phenomena that accompanied the wet-phase separation membrane formation are presented and the pure water permeability (PWP) data and cross-section morphology included. Based on a combined treatment of the obtained experimental results we are able to present new evidence for some postulated elementary processes to broaden our understanding of the mechanisms of polymeric membrane formation by wet-phase separation.

2. Some considerations about membrane formation by wet-phase separation

2.1. Turbidity phenomena

During the polymeric membrane formation by wet-phase separation cast solution of the polymer is immersed into the coagulation bath (mainly) consisting of a nonsolvent for polymer. It is almost regularly accompanied by the turbidity phenomena [1,4,6,7,10,16,18–22]. When being transformed into the protomembrane the cast solution of polymer usually becomes less or practically nontransparent for white light, which also means being more turbid. Parameters of the turbidity phenomena, which can simply be measured by the time dependency of the intensity of the transmitted white light, are the time of the onset of turbidity after the immersion of the cast solution, the rate of turbidity growth and the intensity of the turbidity usually expressed as maximal turbidity at the end of the protomembrane formation. The case when the turbidity does not appear at all or is very small and therefore negligible is also considered a turbidity parameter.

Turbidity is a consequence of the scattering of light on the phase boundaries [23–26] that are characterized by a very (infinitely) steep gradient of physical properties (discontinuity). When the phase separation takes place at any mode of the nucleation and growth (i.e. (iia) and/or (iic)) the conditions for the very (infinitely) steep composition gradient and consequently for the refraction index gradient are fulfilled. The later gradient is responsible for the scattering of light. Considerable concentration fluctuations must take place in the metastable ternary solution to form stable nuclei with a composition that lies on the cross-section of the tie line and the binodal on the opposite side of the miscibility gap. In Fig. 1 the tie line associated with the end of the composition path no. 2 shows the difference in composition of the forming phases and consequently the difference in the refraction indexes; the situation at the end of the composition path no. 4 is in analogy with this. Light scattering and consequently turbidity occurs, irrespective of which phase, namely the (iia) polymer lean phase (end of the composition path no. 2 in Fig. 1) or the (iic) polymer rich phase (end of the composition path no. 4 in Fig. 1), is nucleated. This way, both (iia) and (iic) elementary processes are accompanied by practically the same turbidity phenomena as far as its intensity (maximal turbidity) is concerned. There might, however, be some differences in the rate of the turbidity growth. Namely small molecules of the solvent and nonsolvent might be transported with greater ease towards the concentration gradient during the growth of the nuclei in the case of the (iia) nucleation and growth of the polymer lean phase than the polymer molecules and/or their segments in the case of the (iic) nucleation and growth of the polymer rich phase. A higher rate of the turbidity growth thus could be expected for the (iia) nucleation and growth of the polymer lean phase than

in the case of the (iic) nucleation and growth of the polymer rich phase.

When the phase separation takes place by means of the (iib) spinodal mode, the composition gradient and consequently the refractive index gradient are smoothly changed in space [27–29]. In the unstable region of the ternary phase diagram (end of the composition path no. 3 in Fig. 1) even the smallest concentration fluctuation begins to grow continuously towards the equilibrium compositions of the two phases which are at both ends of the tie line on the opposite sides of the miscibility gap. Some time after the beginning of the process there is no discontinuity in the composition and consequently in the refractive index. Phase boundaries of the formed bicontinuous structure are established towards the end of the spinodal process. So the scattering of light is very low or practically absent when the membrane is formed by means of the (iib) spinodal mode of phase separation.

Turbidity is absent also during the (ia) direct accumulation of polymer and during its (iii) solidification (the composition path no.1 in Fig. 1). The area of the formed phase boundaries between the accumulated and later on the solidified polymer and the coagulation bath on one side as well as between the accumulated and later on the solidified polymer and the binary/ternary polymer solution on the other side is not great enough to contribute some important quantity of light scattering.

Very much the same is the situation during the (iii) solidification of the (ia) direct accumulated polymer and during the (iii) solidification of (iia), (iib), (iic) by any mode of phase separation formed polymer rich phase. As a result of the lack of the refractive index gradient there is no scattering of light and thus no turbidity.

We can summarize that the elementary processes, the (iia), (iic) nucleation and growth of either the polymer lean or polymer rich phase can be recognized through their intense turbidity during the formation of the polymeric membranes by wet-phase separation. Eventually the (iic) nucleation and growth of the polymer rich phase could bring about a slower rate of turbidity growth and thus being discriminated from the (iia) nucleation and growth of the polymer lean phase. On the other hand, the (iib) spinodal mode of phase separation as well as the (ia) direct accumulation of (pure) polymer takes place without the turbidity appearance. The latter elementary processes, namely (ia) and (iib), can, therefore, be distinguished from the nucleation and growth elementary processes solely by the turbidity phenomena. However, they cannot be distinguished from one another by this phenomenon.

2.2. Shrinkage phenomena

During the transformation of the cast solution of polymer into the (proto)membrane by means of wet-phase separation, the dimensions of the cast solution change as a rule

[2,30]. Shrinkage (syneresis) of the cast solution/protomembrane ternary system can practically always be observed.

Compositions of cast solutions for membrane preparation usually range from 10 to 30 wt%. In the extreme (idealized) case when only the outflow of the solvent from the cast solution takes place, the cast solution of the polymer can be converted into a pure polymer. The solvent and/or nonsolvent within the polymer is no longer present and a dense polymer membrane is formed which is evidently much thinner than the original cast solution of polymer. It is the thinnest possible membrane formed. Another idealized extreme situation is when the polymer, the solvent and the nonsolvent somehow maintain their position in space to form a porous structure. Consequently, the formed porous protomembrane is as thick as the original cast solution was.

In the polymeric membrane formation by wet-phase separation in reality the thickness of the (proto)membrane lies somewhere between these two extremes where a more or less porous/dense protomembrane is formed. When the protomembrane is converted into a membrane by leaching out the polymer lean phase, i.e. a solvent and a nonsolvent (usually a nonsolvent, i.e. water, is used for leaching and it remains in the empty space of the membrane), the thickness of the protomembrane does not change. The remaining porous/dense polymeric structure must among other things have satisfactory mechanical properties.

Considering the above-mentioned we can conclude that the elementary process of the (ia) direct accumulation of polymer leads to the densest structure and thus to the thinnest membrane. Both (iia), (iic) modes of the nucleation and growth and the (iib) spinodal phase separation mode lead the process of wet-phase separation to the formation of porously structured membranes which are in principal thicker than the membranes entirely or in part formed in the process of the (ia) direct accumulation of polymer (composition path no. 1 in Fig. 1). By measuring the shrinkage of the cast solution to a (proto)membrane we can distinguish between processes which, at least in one of their parts, take place by means of the elementary process of the (ia) direct accumulation of polymer and the processes which lead to almost entirely porous structures. We could thus distinguish between the elementary process of the (ia) direct accumulation of polymer and the (iib) spinodal mode of phase separation. As we have pointed out at the end of the previous paragraph, such a distinction cannot be done solely on the basis of the turbidity phenomena.

2.3. Cross-section morphology and pure water permeability (PWP)

The mass transport of different media (liquids, vapors, gasses) through/inside the polymeric membrane, beside the properties of the media and polymer themselves, depends on the porosity of the membrane, i.e. on the

space distribution of the polymeric material within the membrane.

In the case when the space distribution of the polymeric material is in the form of a completely dense membrane the adsorption, solubility, diffusivity and desorption of the permeating media to/in/from the polymeric material (solution/diffusion mechanism) are the processes which are decisive for the mass transport through/inside the membrane and thus for its permselectivity.

Another form of space distribution of the polymeric material in the membrane, formed by wet phase separation, is the porous structure. In this case the empty space and the volume of the accumulated solid polymer can be shaped very differently and it results in different types of porosity. Following the modes, i.e. the elementary processes of phase separation in the group of secondary ns/so/po mass transport during the membrane formation by wet-phase separation and variety of membranes cross-section morphologies (figures in Refs. [1,2]) we can distinguish three fundamental types of porosity: (1) cellular porosity, which is the result of the (iia) nucleation and growth of the polymer lean phase mode of wet-phase separation of the ns/so/po ternary system; (2) bicontinuous (cocontinuous) porosity, which is the result of the (iib) spinodal mode of the wet-phase separation of the ns/so/po ternary system; and (3) bead (pearl, particulate) porosity, which comes as the result of the (iic) nucleation and growth of the polymer rich phase mode of the wet-phase separation of the ns/so/po ternary system.

In real events of wet-phase separation we frequently observe mixed types of porosity: (some) cells of the cellular structure are interconnected, (some) beads are found on the web of the bicontinuous structure etc. So, the porosity of the polymeric membranes formed by the wet phase separation process can be arranged into a “continuous porosity spectrum” [1–4,7,8,11–15,17,19,23,31–36]. Although the dense structure is not a porous structure we place it at the beginning of the “continuous porosity spectrum”. The next in the spectrum is the fundamental type of porosity, the cellular porosity. It has a strictly cellular structure with completely isolated, round cells in the solid matrices of the solidified, dense polymer. Then there is the cellular porosity with (some) cells interconnected among each other [1,2,9,11–16,18,19,22,35,37–41]. This interconnectivity can gradually turn into bicontinuous porosity [1,2,8,11–15,17,19,31–34,36,39] (another fundamental type) where the polymer rich phase can dominate or the polymer can spread in space into a more or less dense web (lacy structure). On the other side of the “porosity spectrum” the beads become dominant, at first a few and later in larger numbers appearing on the bicontinuous web [11–15,17,22,26,31–36] as lacy strings of beads, and finally forming the bead (pearl, particulate) porosity itself [1–3,8,11–14,17,32–36,42] (fundamental type). The continuous porosity spectrum ends in the form of latex, which can constitute a solid porous structure only if some “sintering” process (for example shrinkage by means of syneresis

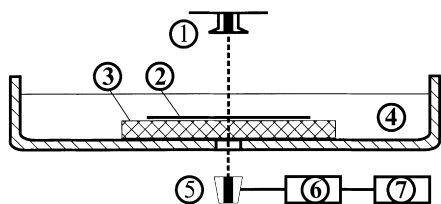


Fig. 2. Turbidity measurement set up: ① source of light (white light); ② cast of polymer solution, (proto)membrane; ③ grinded glass plate; ④ coagulation bath; ⑤ photoresistor; ⑥ amplifier; ⑦ recorder.

pressure) can stick its beads together into a firm membrane, sometimes even as beads of a polygonal (cubic) shape (i.e. nodules) [13,15,33].

In the case of pure cellular porosity, adsorption, solubility, diffusivity and desorption of the permeating media to/in/from the dense polymeric material (solution/diffusion mechanism) are again processes which are decisive for the mass transport of the permeating media (liquids, vapors, gasses) through/inside the dense membrane “matrices” since there is no continuous way through the “empty space” parts, i.e. cells, of its porosity. However, with the increase of cellular interconnectedness, conditions for the mass transport through/inside the membrane can change drastically (increase greatly) since in the bicontinuous porosity a continuous path from one side of the membrane to another through the “empty space” part of the porosity exists, hence, transforming the mass transport through/inside the membrane into a “hydrodynamic transport”. It generally remains unchanged as we move further on in the porosity spectrum: in the bead (pearl, particulate) porosity at the end of the porosity spectrum, a continuous “empty space” part of the porosity still exists which enables the permeating media to pass from one side of the membrane to another without entering the polymer material (hydrodynamic flow). The situation could change in the case of beads of the polygonal (cubic) shape (nodules) since the empty space here is reduced to a minimum or even disappears. Mass transport through/inside this nodular membrane structure can revert again to the “solution–diffusion” mechanism.

Since mass transport through the membrane by means of the solution/diffusion mechanism is slower than hydrodynamic transport, the former is permeability and transmembrane flux determining when the membrane is simultaneously formed from a layer of a dense polymer and from layers of a different porosity.

The PWP of the polymeric membrane reflects the porosity structure which is the result of the elementary processes of phase separation (both modes (iia), (iic) of nucleation and growth and the (iib) spinodal mode) as well as the (ia) direct accumulation of polymer: low PWP suggest that the membrane was formed at least in one layer by the (ia) direct accumulation of polymer and/or its fundamental cellular structure is formed by the (iia) nucleation and growth of the polymer lean phase. On the other hand, high PWP values

suggest that the membrane has a structure which enables a hydrodynamic flow due to its bicontinuous and/or bead (pearl, particulate) structure formed by the (iib) spinodal and by the (iic) nucleation and growth of the polymer rich phase mode of phase separation, respectively.

3. Experimental

About 100 g of the different polymer solutions were prepared by weighting the polymer and the solvent into a 250 cc Erlenmeyer flask and subsequently mixing them for 24–30 h on the KPG mechanical stirrer at about 40 turns per minute. The following polymer solutions were prepared: 12.5, 21 and 30 wt% solutions of cellulose acetate (CA; Aldrich 18,095-5, $M_w = 30$ kD) in acetone (ACE; J.T. Baker), polysulfone (PSf; Aldrich 18,244-3, $M_w = 30$ kD, $T_g = 190^\circ\text{C}$) in *N,N*-dimethylacetamide (DMA; Merck–Schuchard) and polyamide 4,6 (PA4,6; Nylon 4,6 Stanyl KS400) in formic acid (HCOOH; Kemika Zagreb); 12.5, 15 and 21 wt% solutions of poly-(methylmetacrylate) (PMMA; Aldrich 18,226-5, $M_w = 996$ kD, $T_g = 95^\circ\text{C}$) in *N,N*-dimethylformamide (DMF; Merck–Schuchard); 12.5, 18 and 21 wt% solutions of elastomeric thermoplastic polyurethane of the polyether type (TPU; BASF, Elastollan 1190A) in DMF. Polymers and solvents were reagent grade.

The polymer solutions were cast on a $280 \times 250 \times 20$ mm³ grind glass plate the surface unevenness of which was about 5 μm with rectangular knives with a carefully manufactured slit dimension reaching the precision of about 5 μm . The cast solutions were prepared with a 150 and 300 μm nominal cast thickness. A casting took about 5–10 s and the glass plate with a thin layer of the cast solutions was as quickly as possible, i.e. within 5–10 s, immersed into the coagulation bath always consisting of pure water at 25°C.

It can be expected that the solutions’ viscosity will show great differences that have to be taken into consideration during the cast and the immersion process. With less viscous solutions, the cast operation is simple. On the other hand, the manipulation with the glass plate and the less viscous cast solution has to be carried out with caution because gravity can distort the cast thickness. This precaution is especially important during the cast of the 300 μm thick solutions of polymer. With more viscous polymer solutions the situation is the opposite: the cast has to be executed slowly and with great caution, while as a result of immersion there is much less danger of distortion of the cast thickness during the manipulation. Further, the cast speed, irrespective of the viscosity of the polymer solution, is so slow that there is no appearance of the die-swell effect due to dynamic stress. So we take a nominal cast thickness equal to the dimension of the knives’ slits.

The turbidity phenomena accompanying the transformation of the cast solution into the protomembrane were followed by a simple turbidity measurement set up

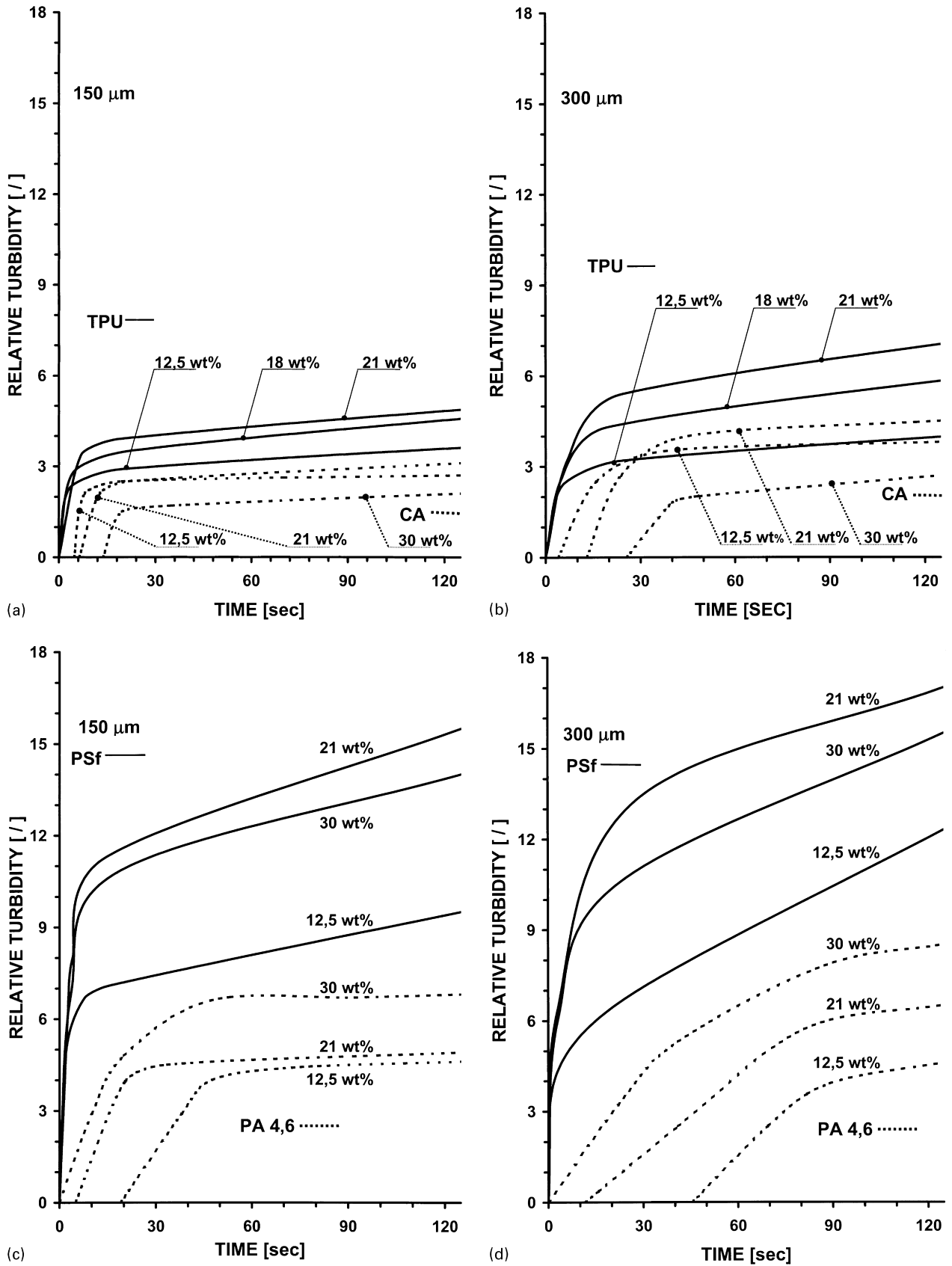


Fig. 3. (a) Course of the turbidity of the CA/ACE:water and TPU/DMF:water membrane forming systems; cast compositions: 12.5; 18; 21 and 30 wt.%; cast thicknesses: 150 μm ; (b) cast thicknesses: 300 μm . (c) Course of the turbidity of the PSf/DMA:water and PA4,6/HCOOH:water membrane forming systems; cast compositions: 12.5; 21 and 30 wt.%; cast thicknesses: 150 μm ; (d) cast thicknesses: 300 μm .

[1,4,6,7,10,16,18–22]. (Fig. 2). We used the amplifier for controlling the sensitivity of the set up since the turbidity intensity is fairly different for different membrane forming systems. The turbidity (nontransparency) of the foils of some semitransparent polymer was used for a comparison with the turbidity of different polymer/solvent:nonsolvent membrane forming systems. These measurements were performed by foils at different levels of sensitivity of the experimental set up. The relative turbidity scale was thus constructed for a direct comparison of the turbidity measurements of the various membrane forming systems. We expressed the turbidity of a particular membrane forming system in terms of the number of semitransparent foils. In the first part of the turbidity measurement experiment a higher speed of the recorder paper was applied (300 mm/min) in order to achieve convincing results in the case of delayed turbidity appearance, whereas the normal speed of the recorder paper was 60 mm/min. From the obtained turbidity curves the time of the onset of the turbidity (instantaneous, delayed), the rate of turbidity growth (high, medium, slow) and the maximal value of the turbidity were determined.

After being formed the (proto)membranes were left in the coagulation bath for the next 10–15 min. Then they were transported into a vessel with a slightly agitated large quantity of water, where they remained for the next 24–48 h.

The shrinkage of the cast solution of the polymer to the (proto)membrane was determined from the difference between the cast knife slit dimension (nominal cast thickness) and the measured thickness of the (proto)membrane. The (proto)membrane thickness measurements were done with the magnetic probe (MINIMER HD1) 24–48 h after the membranes were formed. Owing to the high elasticity of the TPU (proto)membrane the membrane thickness was determined by a magnetic probe with the help of a stiff foil. Ten evenly spaced points on the membrane sheet were chosen for measurement and their average values given as the results.

The cross-section morphology [1,2] was obtained by a scanning electron microscope (SEM; JEOL JSM-840A).

The membranes' permeability for pure water (PWP) was determined by measuring the water flux through the membrane in the AMICON 8400 cell under the ultrafiltration pressure of nitrogen. For membranes with very high PWP cell with 10-l water reservoir was used; membrane surface was practically the same as in the case of the Amicon cell.

4. Results and discussion

4.1. Turbidity phenomena during the formation of the membranes

There are quite a large variety of turbidity phenomena among the different membrane forming systems (Fig. 3).

In cases when solutions of PMMA/DMF, irrespective of their composition and cast thickness, are immersed into the coagulation bath of water, turbidity does not appear. The formed membranes are practically transparent for white light with some blue opalescence, which is why we have omitted the presentation of their “turbidity behavior” in Fig. 3. On the grounds of the considerations from the introductory paragraphs we think that in all cases the elementary process of phase separation takes place by the (iib) spinodal mode and consequently all PMMA membranes have a bicontinuous structure [1,2].

Another obvious phenomenon is the delayed onset of turbidity [1,6,7,9,10] in the case of the CA/ACE: water membrane forming system (Fig. 3(a) and (b)): after the immersion of the solution into the coagulation bath the first few seconds (from five to more than twenty seconds) turbidity does not set on. After this delay, the turbidity of the membrane forming system sets on with a high rate of turbidity growth that stops at a relatively low maximal value. This is the general layout of the turbidity phenomena in the CA/ACE:water system [6,7,43]. This observation can be interpreted as follows: the elementary processes of the (ia) direct accumulation of polymer and its (iii) solidification take place during the delayed onset of turbidity. Later on, during the onset of the turbidity, the elementary process of the (iia) nucleation and growth of the polymer lean phase takes place. Consequently all CA membranes have a polymer rich (dense) skin and a relatively “diluted” cellular structure as is manifested in their morphology [1,2] as well as in the rather low maximal turbidity (Fig. 3(a) and (b)).

The instantaneous onset of the turbidity [1,6,7,9,10] is clearly demonstrated by the TPU/DMF:water (Fig. 3(a) and (b)) and by the PSf/DMA:water (Fig. 3(c) and (d)) membrane forming systems. The instantaneous onset of turbidity takes place in both systems after the contact of the cast polymer solution with the coagulation bath irrespective of the composition of solutions of polymer and their cast thickness. The rate of the turbidity growth is very high for both systems and practically equal to the rate of turbidity growth for the CA/ACE:water system. The difference between the PSf/DMA:water and TPU/DMF:water systems becomes evident at the maximal turbidity value: it is significantly higher in the first of the two systems. In fact, in the PSf/DMA:water system the maximal turbidity value at the end of the membrane forming process is the highest among all the examined membrane forming systems. The described phenomena show that by the PSf and TPU membrane formation the elementary process of the (iia) nucleation and growth of the polymer lean phase takes place during the growth of the turbidity. All membranes, prepared from the PSf/DMA:water and TPU/DMF:water systems, have in their morphology a fairly well developed cellular structure [1,2]. The PSf membranes have larger cells than TPU membranes have; but this difference could not be the reason for the fairly large differences in the maximal turbidity values. One of the possible reasons for that could be the

Table 2
Shrinkage measurements: membrane forming system with a cast composition and a nominal cast thickness; absolute thickness of (proto)membranes and their relative thickness with respect to their nominal cast thickness

SYSTEM ^a	Composition/ thickness (wt%/μm)	Thickness of (proto)membrane	
		absolute (μm)	relative (%)
CA/ACE	12.5/150	18.8	12.5
	21/150	27.8	18.5
	30/150	40.2	26.8
CA/ACE	12.5/300	52.0	17.3
	21/300	49.2	16.4
	30/300	69.9	23.3
TPU/DMF	12.5/150	66.0	44.0
	18/150	71.2	47.5
	21/150	73.1	48.7
TPU/DMF	12.5/300	126.6	42.2
	18/300	141.1	47.0
	21/300	147.0	49.0
PSf/DMA	12.5/150	41.8	27.9
	21/150	71.2	47.5
	30/150	89.9	59.9
PSf/DMA	12.5/300	102.5	34.2
	21/300	127.2	42.4
	30/300	147.2	49.1
PMMA/DMF	12.5/150	41.5	27.7
	15/150	47.6	31.8
	21/150	63.3	42.2
PMMA/DMF	12.5/300	70.5	23.5
	15/300	81.7	27.2
	21/300	105.2	35.1
PA4,6/HCOOH	12.5/150	44.0	29.3
	21/150	52.3	34.8
	30/150	78.6	52.4
PA4,6/HCOOH	12.5/300	74.1	24.7
	21/300	96.2	32.1
	30/300	137.5	45.8

^a CA/ACE: cellulose acetate/acetone; PSf/DMA: polysulfone/*N,N*-dimethylacetamide; PMMA/DMA: poly-(methylmethacrylate)/*N,N*-dimethylformamide; PA4,6/HCOOH: polyamide 4,6/formic acid; TPU/DMF: thermoplastic polyurethane/*N,N*-dimethylformamide.

large differences in the refractive indexes between the polymer lean and the polymer rich phase in the treated systems.

The membrane forming system PA4,6/HCOOH:water shows particular turbidity phenomenon during the membrane formation process (Fig. 3(c) and (d)). After the immersion of the PA4,6/HCOOH cast solution into pure water there is some delay of onset at first or low turbidity appearance. This lasts for a short while, but later the turbidity begins to grow with a rate, which is slower than the rate of the turbidity growth for the CA/ACE:water, PSf/DMA:water and TPUA/DMF:water systems. In all cases, irrespective of the composition and thickness of the

PA4,6/HCOOH cast solution, the turbidity grows to fairly high values, however, slightly lower than the case in the PSf/DMA:water system. Two elementary processes related to phase separation take place in the membrane formation of the PA4,6/HCOOH:water system: the (iib) spinodal mode of phase separation which at the beginning of the membrane formation reflects the absence of or low turbidity, and the (iic) nucleation and growth of the polymer rich phase mode which reflects a medium rate of turbidity growth as well as a relatively high maximal value of turbidity at the end of the process. The nucleation and growth of the polymer rich phase alone would lead the ternary solution to the formation of latex and not to the formation of a firm and solid membrane. Therefore, we could conclude that the (iib) spinodal phase separation, even during a short period of time, can form a basis on which another elementary process, namely the (iic) nucleation and growth of the polymer rich phase, can lead to the formation of a firm membrane consisting of the beads (pearls, particulate) of polymer [1,2].

4.2. Shrinkage of the cast solution–protomembrane system

Shrinkage measurements (Table 2) show that with the exception of CA/ACE: water system practically all the other examined membrane forming systems undergo some comparable loss of thickness when the cast polymer solution is transformed into the (proto)membrane. In the case of the PSf/DMA, PMMA/DMF, TPU/DMF and PA4,6/HCOOH cast solution–protomembrane systems the nominal cast thickness shrinks to between 25 and 55% of their original size. On the other hand, the shrinkage of the CA/ACE cast solution–protomembrane system does not stop until the system reaches 12–25% of the original cast thickness. We can conclude that the porosity is of the same order in the protomembrane that is prepared from less shrinkable membrane forming systems irrespective of the porosity formation mode. The porosity of the membranes, defined as the ratio between the volume of solid polymer and the volume of the membrane, can be the same (is invariant) when it is formed by either of the (iia), (iic) two nucleation and growth mechanisms (cellular or bead (pearl, particulate) porosity) or by the (iib) spinodal mode (bicontinuous porosity) of phase separation. On the other side, the elementary process of the (ia) direct accumulation of polymer when dense polymer is formed can be responsible for the greatest shrinkage in the case of the CA/ACE cast solution–protomembrane system. Considering both, the turbidity and the shrinkage phenomena in all the examined membrane forming systems we can conclude that the experimental facts can be arranged in a consistent way. In the CA/ACE:water system the (ia) direct accumulation of polymer takes place during the delayed onset of the turbidity with not enough area of phase boundaries formation and thus with no scattering of light, while the shrinkage of the cast solution–protomembrane system is great and the membrane's polymer rich (dense) skin is formed. Later when the turbidity sets on, the

(iia) nucleation and growth of the polymer lean phase with the subsequent (iii) solidification of the polymer rich phase take place and form a relatively scarce cellular porosity. The absence of turbidity in the case of the formation of the membrane from the PMMA/DMF:water system has its cause in the fact that during the (iib) spinodal mode of phase separation there is smooth change in the composition gradient and consequently in the refractive index gradient and so no phase boundaries are formed where light could sufficiently be scattered. However, the formed bicontinuous structure is in its porosity comparable with the porosity formed by other porosity forming elementary processes. The nucleation and growth mechanism, in the case of PSf/DMA cast solution–protomembrane systems of the (iia) polymer lean phase and in the case of the PA4,6/HCOOH cast solution–protomembrane system of the (iic) polymer rich phase, is responsible for the occurrence of intense turbidity as well as for the comparable porosity of the PSf and PA4,6 membranes although they are morphologically very different (cellular; some bicontinuous and bead (pearl, particulate) porosity). The shrinkage of the cast solution–protomembrane ternary systems is approximately the same irrespective of which of the three wet-phase separation elementary processes is involved. The same holds for the thickness of the ultimate (proto)membrane.

4.3. Pure water permeability (PWP)

The results of the measurements of pure water permeability (PWP) on polymeric membranes prepared by wet-phase separation are presented in Table 3. They can be classified into three major groups. Membranes prepared from the CA/ACE:water system are practically impermeable to water under ultrafiltration conditions [1,2,6,43]. However, the membranes prepared from the PMMA/DMF:water and especially from PA4,6/HCOOH:water systems have distinctively higher PWP values. Between one and the other are the PWP values of the membranes prepared from the PSf/DMA:water and TPU/DMF:water systems.

These general experimental findings are explicable on the grounds of the porosity of each individual membrane. CA membranes have a polymer rich dense skin that is formed during the turbidity delay and during the intense shrinkage accompanied by the (ia) direct accumulation of polymer. They also contain cellular porosity that is formed after the onset of the turbidity because of the (iia) nucleation and growth of the polymer lean phase and the (subsequent) (iii) solidification of the polymer rich phase. Polymer rich (dense) skin has extremely low permeability for water (solution/diffusion transport) which makes it the decisive part for the PWP of the CA membranes. Bicontinuous spinodal porosity of membranes, formed from the PMMA/DMA:water system, is very permeable since water can penetrate through the membrane via continuous channels (in the form of a hydrodynamic flow), which remain after the polymer lean phase is leached out of them. The structure

Table 3
Pure water permeability (PWP) of the various membranes under the ultrafiltration conditions

SYSTEM ^a	Composition/ thickness (wt%/μm)	Pure water permeability (PWP; 1 m ⁻² h ⁻¹) Pressure		
		2 bar	4 bar	6 bar
CA/ACE	12.5/150	0.0	0.0	2.0
	21/150	0.0	0.0	0.0
	30/150	0.0	0.0	0.0
CA/ACE	12.5/300	0.0	0.0	0.0
	21/300	0.0	0.0	0.0
	30/300	0.0	0.0	0.0
TPU/DMF	12.5/150	10.0	50.0	820.0
	18/150	/	30.0	145.0
	21/150	0.0	0.0	0.0
TPU/DMF	12.5/300	0.5	5.4	63.0
	18/300	2.1	4.4	23.0
	21/300	0.0	0.0	0.0
PSf/DMA	12.5/150	312	467	503
	21/150	0.0	0.0	0.0
	30/150	0.0	0.0	0.0
PSf/DMA	12.5/300	251	393	427
	21/300	0.0	0.0	0.0
	30/300	0.0	0.0	0.0
PMMA/DMF	12.5/150	342	597	784
	15/150	83.0	177	297
	21/150	0.0	11.0	27.0
PA4,6/HCOOH	12.5/150	617	3610	4500
	21/150	4500	3100	6200
	30/300	210	405	720
PA4,6/HCOOH	12.5/300	2700	7100	8200
	21/300	170	1170	1040
	307300	290	645	1040

^a CA/ACE: cellulose acetate/acetone; TPU/DMF: thermoplastic polyurethane/*N,N*-dimethylformamide; PSf/DMA: polysulfone/*N,N*-dimethylacetamide; PA4,6/HCOOH: polyamide 4,6/formic acid; PMMA/DMA: poly(methylmethacrylate)/*N,N*-dimethylformamide.

of the bead (pearl, particulate) porosity is also extremely permeable to water [11,12,14,42] since there are empty spaces among the compactly packed beads where water can easily pass through, again in the form of a hydrodynamic flow. This is the reason for very high PWP values of all membranes prepared from the PA4,6/HCOOH:water system. The partial presence of bicontinuous porosity needed for connecting the beads among each other does not affect the membrane's permeability since it is also very open and thus has a PWP comparable with the PWP of the bead (pearl, particulate) porosity. The changeable PWP observed in membranes prepared from the PSf/DMA:water and TPU/DMF:water systems can also be explained in terms of their cellular porosity. In pure cellular porosity, the cells, which remain in the membrane after the leaching out of the polymer lean phase, are placed in the solidified polymer rich phase

without any interconnectedness hence, water must pass through the dense parts of the membrane during its permeation (solution/diffusion transport). Owing to the appearance of cellular interconnectivity (the (iii) solidification of the polymer rich phase by means of the (iii_a) gelation and subsequent leaching off of the gel; some appearance of the spinodal mode of phase separation; formation and existence of the macrovoids) water passes through the membrane with greater ease and PWP is (drastically) increased because of the hydrodynamic flow. Arguments for PWP through the cellular structure should also be valid in the case of CA membranes since they are also formed by the elementary process of the (i_a) nucleation and growth of the polymer lean phase in its later period of formation. However, the polymer rich (dense) structure, formed in the elementary process of the (i_a) direct solidification of (pure) polymer, is PWP determining.

4.4. Polymeric membrane formation mechanisms

Polymeric membrane formation by wet-phase separation starts with the immersion of a thin cast layer of a thermodynamically stable solution of polymer into the coagulation bath. The very first contact between the cast solution of polymer and the coagulation bath while thermodynamic instability is being induced can be described as the “big bang” of membrane formation; the primary nonsolvent/solvent/polymer mass transport takes place in the direction perpendicular to the cast solution–coagulation bath boundary. The (i_a) direct accumulation of the polymer on the coagulation bath–cast solution boundary usually leads to the formation of a polymer rich (dense) skin [6,7,9,18] which is in most cases decisive for the permselectivity properties of the membrane. The (i_a) elementary process need not always take place, however, some further modes of primary mass transport, namely the (i_b) diffusion and/or the (i_c) convection and/or the (i_d) hydrodynamic flow of components always take(s) place and transform(s) the thermodynamically stable binary solution of polymer into a ternary meta/unstable solution which undergoes the (i_{ii}) secondary ns/so/po mass transport by phase inversion in the narrower sense of the word; now the components are transported in all directions in space. Its three modes, namely the (i_{ii_b}) spinodal mode and the nucleation and growth of the (i_{ii_c}) polymer rich as well as the (i_{ii_a}) polymer lean phase, are the following postulated elementary processes. They are mainly responsible for polymer accumulation and thus for the membrane’s cross-section morphology. The (i_{iii}) solidification of the directly accumulated polymer as well as the one accumulated by phase separation (the next postulated elementary process) is always necessary for membrane formation since it guarantees the firmness of the polymeric membrane. It can take place with the (i_{iii_a}) (thermoreversible) gelation [31,32,44], when some solvent and/or nonsolvent is/are entrapped in the accumulated solid polymer. After the (i_{iv_b}) leaching the

liquids out of such firm gel the remaining pure polymer forms a structure with a finest porosity (microporosity; fundamental porosity type) which is in many cases responsible for the permselective properties of the membranes (dense (part of) membrane, membrane with cellular porosity). The solidification by the (i_{ii_b}) vitrification (glass transition), sometimes followed by the crystallization or the (i_{ii_c}) direct crystallization of some parts of the accumulated polymer forms quite a dense structure which is less permeable than microporous gel. Beside the (i_{iv_b}) leaching of the firm gel, the leaching of the (i_{iv_a}) polymer lean phase from the protomembrane is also an important elementary process: it transforms the protomembrane into a membrane. The various (v) post treatments (temperature annealing etc.) of the (proto)membranes can also be added to the set of elementary processes. Structurally different membranes that also differ in permselective properties are formed by combining these elementary processes in time and in space.

We studied “pure systems”, with only three components, namely the polymer and solvent in cast solutions as well as coagulation baths with always strictly pure water (no solvent or fourth component as additive). In the case of the CA/ACE:water system, the delayed onset of turbidity, great shrinkage of the cast solution into the (proto)membrane and the absence of pure water permeability under ultrafiltration conditions are the result of the (i_a) direct accumulation of polymer and its (i_{iii}) solidification as well as the consequence of the (i_{ii_a}) nucleation and growth of the polymer lean phase and finally of the (i_{iii}) solidification of the polymer rich phase. A membrane with a polymer rich (dense) skin and a relatively scarce cellular structure is formed. The PSf/DMA:water and TPUA/DMA:water systems form membranes by means of instantaneous (i_{ii_a}) nucleation and growth of the polymer lean phase (instantaneous turbidity onset) and by subsequent (i_{iii}) solidification of the polymer rich phase in which a more or less interconnected cellular structure is formed. The former elementary process is also reflected in the changeable pure water permeability and in the moderate shrinkage of the cast solution into the protomembrane. In the case of the PSf and TPU membranes we consciously omitted the problem of the formation of macrovoids. They undoubtedly have (great) influence on the pure water permeability of the membranes. For now we can treat their contribution to membrane permeability only in the context of the “more or less interconnected cellular structure” since it is evident from the PSf membrane cross-section morphology that the macrovoids’ walls also have a “cellular structure”. Practically no sign of turbidity in the case of the PMMA/DMA:water system is the result of the (i_{ii_b}) spinodal mode of phase separation which, after the (i_{iii}) solidification of the polymer rich phase, leads to bicontinuous porosity of the (proto)membrane. Moderate shrinkage and high pure water permeability are also consequences of these elementary processes. In the case of the PA4,6/HCOOH:water system at the beginning to a lesser extent some (i_{ii_b}) spinodal mode and later on to a much

greater extent the (iic) nucleation and growth of the polymer rich phase mode of phase separation take place. The changeable turbidity that occurs during the membrane formation will confirm this statement. After the (iii) solidification of the polymer rich phase, a bead (pearl, particulate) porous structure with great pure water permeability is formed and also the shrinkage of the cast solution into the protomembrane is moderate.

All the postulated elementary processes are, in comprehensive sense, processes of mass transport except the forms of the (iii) solidification of the accumulated polymer. In the present work we differentiate some of them by observing the turbidity phenomena and the shrinkage of the polymer solution to the protomembrane during the polymeric membrane formation as well as by measuring pure water permeability of the formed membrane and by observing their cross-section morphologies.

5. Conclusions

On the grounds of our experiments and by correlating the experimental data on the turbidity phenomena during the transformation of the solution of polymer into the protomembrane as well as the data about the longitudinal shrinkage of the solution of polymer into the (proto)membrane, various polymeric membranes' cross-section morphologies [1,2] and the membranes' pure water permeability we proposed the mechanisms of membrane formation by means of wet-phase separation. We postulated the elementary processes and classified them into some groups that in a way reflect the sequence of events. We also gathered the specific modes of mass transport and forms of polymer solidification. By combining the elementary processes in time and space, different mechanisms of membrane formation by wet-phase separation are established. The proposed mechanisms are general ones. They synergistically and qualitatively, and to some extent also quantitatively, frame several facts and phenomena with very different physical backgrounds into a "unified model". Further work on the quantitative elaboration of particular elementary processes (much has already been done for example on the diffusive mode of primary nonsolvent/solvent/polymer mass transport [5–7,9,10,19,45,46]) and their quantitative coupling into mechanisms still needs to be done.

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