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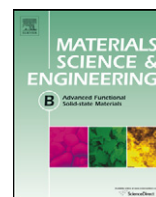
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Supermolecular structure formation of PMP membranes: Theoretical argumentation in terms of the experimental evidences

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ABSTRACT

Experimental and model research lines related to the formation of the polymeric membranes cast from solutions, and associated with their morphologies, are presented. In order to determine the formation's main characteristics, the mechanism governing the polymer crystallisation and/or lamellae aggregation is proposed. It is based on a theoretical Smoluchowski-type argumentation. Poly(4-methyl-1-pentene) has been used as a material for the study. Morphology of the lamellae-containing membrane materials is discussed. Two main topics are addressed: a three-phase model ('real' and 'ordered' amorphous phases, and a crystal phase), and factors affecting the supermolecular structure of the membranes. Special attention is paid to lamellae perfection in the solution of different polymer concentrations and its relation to the thin-film type morphology. The stages of the crystallisation are proposed mainly in terms of the role played by the solvent molecules. The optimal circumstance for the formation of the polymeric membranes with the highest degree of crystallinity is indicated. This optimal circumstance points to consider thoroughly the polymeric membrane formation as a thermodynamic–kinetic process of diffusive nature. As a consequence, the process manifests ultimately in a stationary state of the nucleation-growth and ripening-involving viscoelastic phase transformation. Moreover, it is complemented by explicit involvement of two most relevant interaction contributions, i.e. polymer–solvent and polymer–polymer, typically prevailing in a concentrated binary mixture, with the solvent–solvent interaction in a background. As a result of the experimental data analysis, performed in the frames of the proposed theoretical model, a fitting function is derived explicitly and applied to the crystallinity–concentration relationship.

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1. Introduction

Polymers of sufficient chain's stereoregularity are supposed to be able to crystallise. Different morphologies can be achieved if the crystal forms are obtained from melt or solution. It is due to the fact that polymers, possessing an appropriate asymmetry in their charge distributions, have opportunities to form bonds with the solvent molecules. It is manifested in a way that some parts of the polymer chain show preference to occlude solvent (solvotropic), and some of them do not (solvophobic) [1,2]. Hence, many factors influencing the crystallisation should be taken into account for membrane material formation [3–5]. For instance, the polymer concentration of the solution seems to be an important parameter particularly. A dilute solution usually leads to single chain-folded

lamellae in solution whereas a suspension of these lamellae is obtained at higher polymer concentration [6–9]. Furthermore, the diffusion-limited aggregation with a characteristic one-half exponent, ascribed to the external matter-transportation field, affects the size and the shape of the crystallites and plays a certain role in the organization of the crystallites [10]. Both morphological factors and the aggregation determine whether the formed membrane is transparent or opaque. At sufficiently high polymer concentration, some additional thermodynamic–kinetic effects occurred, such as the ones due to interpenetration and interlocking of the crystallites. These effects can be emphasised by stirring the solution and by increasing the molecular weight of the polymer [3]. The polymer crystallisation and the lamellae aggregation in the solution become more complex when polymers can crystallise into different crystalline modifications [6,7]. The morphological instability, the nucleation and growth rates of different crystals can differ owing to their polymorphism. Supermolecular structure of the polymeric membranes is rather complicated, and then some

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entanglement of chains (such a situation is characteristic of the highly concentrated polymer solution) occurs additionally. The diffusive-in-nature mass transfer in solution and the growth of the lamellae aggregates can be observed with optical microscopy [11,12]. Succeeding stages of the aggregate growth and its comparison with a computer experiment (“statistical” fractals obtained by using the model of diffusion-limited aggregation type) were presented [10]. More advanced experimental techniques, e.g. laser and spectroscopic techniques, have been used to study the composition profiles in the polymer solutions [13,14].

In the present paper, poly(4-methyl-1-pentene) (PMP) diluted in carbon tetrachloride solvent has been used as a material for the study. Mass-transfer processes during the lamellae aggregation and the formation of two miscellaneous fractions of the amorphous phase are considered. The prominent role of the solvent molecules in the processes of the nucleation and the growth of crystallites is emphasised and discussed, whenever appropriate. One of the special purposes of the presented study is to describe the qualitative, and to some extent even quantitative, relationship between the membrane crystallinity and the PMP concentration in solution. In order to propose a theoretical representation of solvent-evaporation-influenced membrane formation, suitable for reflecting the experimental data, we have proposed a certain physico-chemical comprehensive rationale. Thus, we have assumed that the process of matter distribution took place due to the randomly growing germs within the solution and that its nature was (locally) diffusive. Then, an appropriate fitting function is derived for the description of the experimental data concerning the crystallinity–concentration relationship for the polymer solutions, cf. Eq. (7).

The paper is organized as follows. In next two sections (Sections 2 and 3), we make a close inspection of experimental evidences in order to point out a remarkable variety manifested in the morphologies of PMP material, and describe factors responsible for this effect. Then, in Sections 4 and 5, we discuss some theoretical argumentation for the membrane formation, focusing eventually on proposing the fitting function mentioned above. Our efforts are summarized in the Section 6.

2. Experimental evidences

2.1. PMP membrane morphologies

In this paper, the mechanism of the nonequilibrium-thermodynamics membrane formation by thermally induced viscoelastic phase separation [15] is discussed. A crystallographic structure of PMP was described in detail [16–19]. In general, it is not difficult to recognise which crystal unit-cell (modification) is obtained under certain conditions chosen. When the polymer is prepared from melt, one stable crystal phase can be obtained (modification I). The situation is more complicated when PMP is cast from solution as a membrane material. Not only the crystal unit-cells of different structures and dimensions are obtained (modifications I–V) but also, which seems to be more interesting, various crystallites seen in terms of their shapes and sizes can be formed. It is worth noticing that the crystalline phase (crystalline domains, CD) of the solvent-cast PMP membrane includes usually two of five unit-cell modifications. However, it is possible to derive the adequate conditions for the unit-cell formation of one type. The type of the crystalline modification strongly depends on the solvent used and the temperature of the solution preparation. Therefore, only one solvent, carbon tetrachloride, is taken into account in this paper. It was also found that the role of the following factors, except of the type of solvent and temperature of the membrane formation, is important for the process of lamellae aggregation, namely, the polymer concentration, and also the time of the solution stirring [10,12].

One can easily find that the morphology of the solvent-cast membranes is complex, especially, if we take into consideration that the crystalline phase is immersed in the amorphous phase. Moreover, the amorphous phase exhibits distinct duality for semi-crystalline polymer. Thus, two seemingly different fractions of amorphous structure can be recognised in the structural relaxation and glass transition studies, i.e. two α relaxations (α_g , α_c – correlated with the so-called ‘real’ amorphous phase, RAP, and ‘ordered’ amorphous phase, OAP, respectively) and two glass transition temperatures ($T_g(\text{RAP})$ – the lower one, $T_g(\text{OAP})$ – the upper one) [20,21]. RAP and OAP could be treated in some cases as pure *viz* fluid-like and impure *viz* semi-crystalline systems, respectively. A comprehensive view of the morphology of such a complex structure of the PMP membrane was developed in our previous papers [10,12].

The properties of the membranes of different PMP concentrations (0.5–8 wt%) in the solution were investigated by using differential scanning calorimetry (DSC), dynamic mechanical spectroscopy (DMTA), positron annihilation lifetime spectroscopy (PALS) and wide angle X-ray scattering (WAXS) [12,20–22].

2.2. Look at experimental data

Most of presented data is taken from our previous papers [10,12,20–23]. In order to fill in the blanks in the set of (available) data within the polymer concentration range from 0.5 wt% to 8 wt%, additional membranes have been prepared and studied for completing properly the analysis carried out by this paper. Both preparation and studies of those membranes have been performed according to the procedures described previously [10,20,23]. The following three new membranes have been obtained from the solutions prepared at 65 °C: the PMP concentration in the solution was 0.5 wt%, 1 wt%, and 6 wt%, respectively. Both lower and higher concentration solutions (0.5–8 wt% and 0.5–7 wt% at 65 °C and 20 °C, respectively) gave the membranes whose mechanical properties made them rather useless for complex studies, mainly from the membrane science point of view. It was found that the best mechanical properties exhibited the membranes formed from the 2 wt% and 4 wt% solutions [12,20,23].

2.3. Factors affecting the membrane material morphology

When polymer is processed, its supermolecular structure is conditioned by actions taken, especially by thermal treatment. It is commonly accepted that the supermolecular structure of the polymer strongly influences the polymeric material properties. It had previously been found that the supermolecular structure of the solvent-cast PMP membranes depends on the following factors: type of solvent; polymer concentration in the solution; temperature and time of stirring of the solution; temperature of the membrane formation; type of substratum on which the membrane is formed. Some of them strongly influence the crystalline phase, whereas the other affect its amorphous structure. In order to find some relations between the factors mentioned above and the membrane structure, especially the structure of the crystalline phase, certain complementary studies have been performed over several years [24–26]. As for an expected link (or, interrelation) between structure and transport properties of the polymeric membrane material *per se*, let us ascertain the following. The transport properties such as those related to permeation of gases through the membrane structure are customarily linked with the notion of free volume of the polymeric system constituting the membrane material [27]. In general, a rule applies which tells us that the bigger the average free volume of the membrane is, the easier the permeation can be [12,24]. The free volume’s quantitative measure, in turn, which depends on molecular mass and stereospecifics of a macromolecule, can be related

Table 1

The crystallinity of the membrane χ formed at different temperatures, and the corresponding polymer concentration, c_{PMP} , in used carbon tetrachloride solutions: *c* points to temperature of 20 °C – thin membranes cast from the solutions prepared at 20 °C; *g* indicates temperature of 65 °C – thick membranes cast from the solutions prepared at 65 °C, cf. Fig. 4.

c_{PMP} (%)	χ (%)	
	20 °C	65 °C
0.5	14.8	29.51
1	48.3	64.21
2	52.5	61.71
3	46.8	–
4	–	52.99
5	30.3	–
6	–	42.36
7	22.7	–
8	–	38.13

directly with the close-packing index of membrane material. The latter indicates an interrelated structure-property relationship by proclaiming the fact that the bigger the index is the smaller its corresponding free volume should be, cf. [12,24].

3. Experimental results

3.1. Dependence on polymer concentration

The properties of the semicrystalline polymers depend on an amount and a type of crystalline phase. The relation between the membrane crystallinity and the PMP concentration in the solution is presented for carbon tetrachloride as a solvent in Table 1. One can find two sets of data for different temperatures of the solution preparation: low temperature (20 °C) and high temperature (65 °C). All membranes were cast on a glass substrate at room temperature. The degree of crystallinity was determined from calorimetric measurements [28]. The same unit-cell of the crystalline phase was detected by WAXS in all cases. The relationship between the degree of crystallinity and the PMP concentration exhibits the same tendency for both temperatures. It must be emphasised that the solubility of PMP for high polymer concentration was limited at each of two temperatures. It made impossible to prepare the solutions of higher PMP concentration. An apparently additional fact to be uncovered when looking at Table 1: the low-temperature membranes would also possess lower degree of crystallinity. It could be clarified when invoking the role of temperature that activates additional degrees of freedom for the PMP, and readily diffusing solvent molecules. It enables them together, whenever appropriate, to arrange easily in a fairly self-organised way into crystalline lattices – an important property of distinguishing between short- and long-macromolecule crystallisation also manifests this way. Moreover, such a comprehension seems fairly consistent with the three-phase notion exemplified by the underlying study, see discussion below, especially when invoking the fact that each type of the phases mentioned suffers from different close-packing (concentration-influenced) conditions, thus, a different solvent's content [10].

It is worth noticing that both sets of data could reach maximum at the PMP concentration between 1% and 1.3%. According to this assumption, the degree of crystallinity increases initially, reaching the maximum value of 54% and 65% at 20 °C and 65 °C, respectively. The decreased temperature of melting, measured by DSC for the dried membranes [12,20,21], with the raised PMP concentration, would imply that the perfection of the CD diminished. In such a situation the crystalline phase, predominated initially, would be replaced by the OAP in the growth process that occurred in the solutions of sufficient PMP concentration.

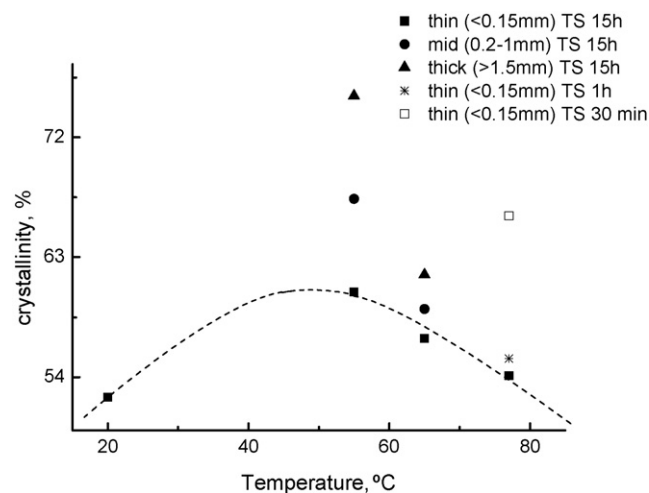


Fig. 1. The crystallinity as a function of the temperature of the solution preparation. Data obtained for the thin membranes are fitted arbitrarily with the inverse parabola function in order to find the maximum value. The thickness of the membrane is signed by the different symbols presented in the picture. The influence of the time of the solution stirring (TS) is shown for the thin membranes at 77 °C for the solvent boiling temperature: 30 min; 1 h, 15 h, respectively.

3.2. Temperature of the solution preparation

As was pointed out above, the temperature of the solution preparation influences the degree of crystallinity markedly. Fig. 1 presents data of the membrane crystallinity for the 2% solutions prepared at various temperatures: 20 °C, 55 °C, 65 °C, and 77 °C (the latter is the boiling temperature of carbon tetrachloride), and upon stirring of the solutions lasting for 15 h. A curve (taken so far arbitrarily from a mathematical textbook in a form of inverse parabola), fitted to the points representing data of the thin membranes, exhibits maximum at 49 °C. Owing to the fact that the curve was fitted to the small amount of data points, from the statistics-involving point of view, this should be taken with caution. However the maximum value is similar to the first glass transition temperature of PMP in a solid state which amounts to about $T_g = 45$ °C [29,23]. The glass transition is a transition during which the mobility of chain is considerably activated [29]. That would lead to the best conformational order of the polymer in solution, resulting in the possibly highest PMP (membrane) crystallinity.

One can find in Fig. 1 several other characteristic points, which reveal the role of the amount of solution cast onto the glass substrate. In order to form the membranes of various thicknesses, some different amounts of the solution were cast. Consequently, a different time of the solvent evaporation was required for the membrane preparation, that might be a true reason for different crystallinity of the membrane but not for the thickness discrepancies of the formed membrane, although this type of factor is pointed out in Fig. 1. (One can note that the degree of crystallinity appears to be dependent upon the duration of membrane formation due to evaporation.) The thickness of the membrane was important from the thermomechanical point of view. It has been found that the membranes prepared from the solution of the PMP concentration higher than 2 wt% could only be investigated by using DMTA [20,21,23]. Therefore our attention was mainly focused on this type of membranes.

Our previous studies revealed that membranes of mid- (0.2–1 mm) and high-thickness (>1.5 mm) included some amount of solvent although the evaporation process had lasted over 2 weeks and the membranes were additionally kept in vacuum conditions after that period of time [23]. As a result, it can be pointed out that the thin membrane (<0.15 mm) did not include residual solvent.

In order to find out, how the time of solution stirring influences the crystallinity, the two additional thin membranes were prepared at 77 °C in two different times of stirring: about 0.5 h and 1 h, respectively. The additional data points can be seen in Fig. 1. (Note that in Fig. 1 the time of stirring is denoted by TS.) It was shown previously that this time was also important for the property called the membrane transparency [10]. After a short time (approximately, 0.5 h) elapsed, the grown crystalline nuclei were rather small and perfect, with an amorphous shell circumventing them. In this case, the membranes were opaque. The bigger crystallites were obtained for some longer time of stirring (1 h and 15 h). Then, the formed membranes were transparent [20]. Thus, the time of stirring would also be recognized as a critical parameter, pointing to a membrane-opaquescence effect so obtained.

3.3. Trapping of solvent molecules

The analysis of solvent amount, occluded in the adequate part of the membrane structure, was performed for the thick membranes (>1.5 mm) by using thermogravimetry, Fig. 2. The procedure was described previously [23]. It was found that the molecules of the solvent (carbon tetrachloride) not only were occluded in both fractions of amorphous phase (RAP and OAP) but also in the CD. The portions of the occluded solvent were estimated from thermogravimetric curves for each of the morphologically different areas of the solid membrane. The thick membranes were formed from the solutions of various PMP concentrations at 65 °C. The results obtained for CD and RAP exhibit quite opposite tendencies. The amount of the occluded solvent increases with the PMP concentration for RAP whereas for CD decreases, showing then a plateau, approximately, when the PMP concentration is higher than 5 wt%. Data obtained for OAP exhibited the maximum about 3.5 wt%, that coincided with the intersection point of the RAP and CD curves. Another two PMP concentrations could be pointed out as characteristic points in the solvent–concentration (phase) diagram: 1 wt% and 9 wt%. The former and the latter values correspond with the PMP concentrations found for the intersection points of the CD and OAP curves and the RAP and OAP curves, respectively. It should be emphasised here that the analysis was done for the amount of occluded solvent, which was determined for a fairly thermodynamic-kinetically stable system, i.e. the weight of the membrane did not change over time at room temperature. This temperature is below both, first and second, glass transition temperatures for every PMP membrane which

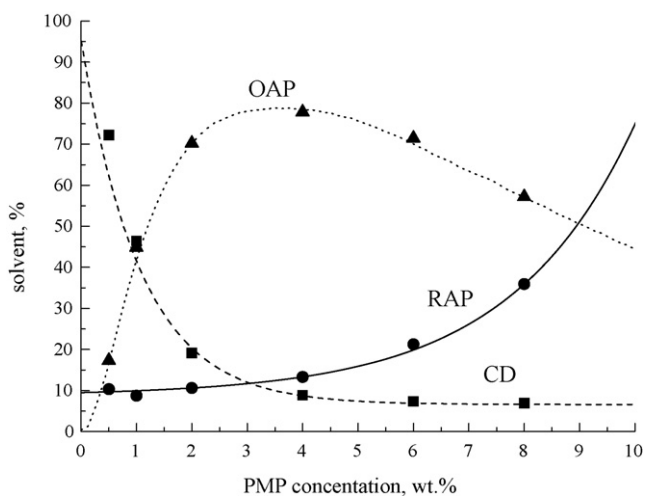


Fig. 2. The content of the solvent molecules in: crystalline domains, CD; 'real' amorphous phase, RAP; 'ordered' amorphous phase, OAP, respectively. Data were obtained for the membrane cast from the solutions of the different polymer concentrations.

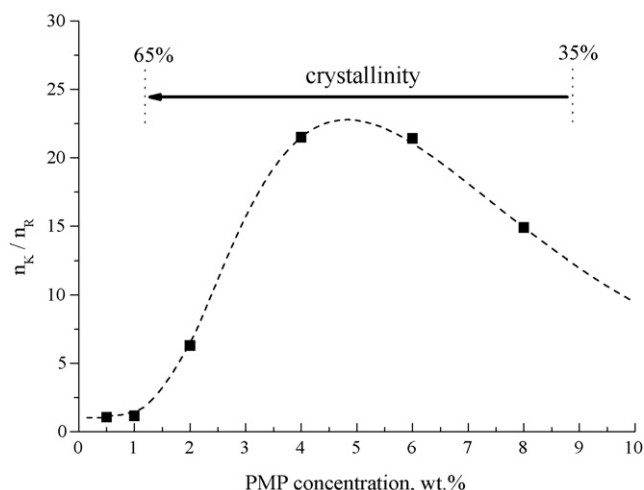


Fig. 3. The ratio of the number of the crystal unit-cell, n_K , and the number of the solvent molecules occluded in the crystalline phase, n_R , as a function of the polymer concentration in the solutions used for the membrane formation. The arrow indicates the respective increase of crystallinity in relation to the polymer concentration.

amount to about 50 °C and 145 °C, respectively [23]. The fluidity of the chains forming supermolecular structures of RAP and OAP is strongly hindered, that made impossible to separate the molecules of the solvent from the non-solvent phase, even in vacuum conditions.

The concept of two glass transition temperatures and their influence on the membrane properties were previously discussed in detail [12]. However, there is still one important question, namely, whether the amount of solvent occluded in some phase ((dis)orderly amorphous or paracrystalline) can give information about the amount of adequate phase. The thermogravimetric results confirmed the three-phase model qualitatively but the quantitative answer is still open. Calorimetric studies showed that the melting temperature of the crystalline phase decreased [20,21]. It means that the perfection of this phase, i.e. the lamella perfection, diminished. This finding is in agreement with the tendencies of the curves if we assumed that the curves in Fig. 2 do reflect the respective amounts of each phase. At low polymer concentration, highly folded lamellae are formed that would result in a small amount of OAP and RAP. At higher concentration both amorphous fractions are predominant in the membrane. Unfortunately, the quantitative agreement between the crystallinity in Table 1 and the crystallinity shown virtually by Fig. 2 cannot be established.

As mentioned in Section 2.1, it is not difficult to find which types of the unit-cell build the CD. Regarding the literature data on the unit-cell [16–19], one can calculate the mole weight of the cells as a value of 4371.4 g/mol (modification I) and that of solvent molecules at 153.8 g/mol. Knowing both values and the amounts of the crystalline phase and the solvent trapped in this phase, the number of the unit-cells, n_K , and the number of the solvent molecules, n_R , were calculated. The n_K/n_R ratio as a function of the PMP concentration in solution is presented in Fig. 3. One can see that the ratio, if set equal to one, would be for the membranes obtained from the solutions of the 2 wt% polymer concentration. A lower ratio means better solvation of the PMP chains. It could be the reason of the highest membrane crystallinity (the maximum of crystallinity is in the range of the 1–1.3 wt% polymer concentration). However the crystallinity decreases for very diluted solutions. It would mean that a large enough solvation ($n_K/n_R \approx 0.15$, i.e. 15 crystal cells per 100 carbon tetrachloride molecules) prevents from the crystallisation of the studied systems. We might conclude that there is the proper PMP concentration for which the highest crystallinity could be achieved and the lamellae of the highest

perfection could be formed. This would suggest that the nucleation stage is determined strongly by the solvent molecules, and in particular, by the solvent–polymer interaction. The polymer–polymer interaction would be predominant at a higher polymer concentration that made the ratio bigger than one. The n_K/n_R value is about 3.3 (Fig. 3) at the maximum of the curve although the crystallinity of the membrane decreased and is less than 50% (see Table 1). It would imply that the solvent molecules are removed from the area of the lamella during its growth stage for the concentrated solutions. When the PMP concentration is very high, higher than 6 wt%, the OAP is formed mainly during the growth stage of the lamellae. Although it is easier to remove the solvent from the amorphous phase of the membrane (fluidity of the chains in this area is higher when compared with the crystalline phase), its amount is very high when compared with the solvent occluded in the crystalline phase, which is almost constant (about 10% of all occluded solvent) for the PMP concentration higher than 4 wt%.

The n_K/n_R ratio varied with the polymer concentration, exhibiting the maximum at some value. This would be a limiting value of polymer concentration for which the chain–chain interaction started to play a decisive role in the process of polymer crystallisation, see a discussion below. It should be emphasised that only this kind of interaction takes place when the polymer gets crystallised from a melt. It was then anticipated that only less than the 50% degree of crystallinity could be obtained [12,21]. Most likely, the entanglement and that very constrained sub-diffusive reptation dynamics of the chains, which is characteristic of dense solutions or melts, would also affect the crystallisation markedly.

3.4. Lamellae formation and aggregation: crystalline-amorphous microstructure

The knowledge on the formation of crystallites and their distribution mechanism seems to be essential for understanding the effect of solvent and polymer concentration in solution on supermolecular structure of polymeric membrane. It was shown previously, that the properties of polymeric membranes depend on the degree of crystallinity and on a distribution of the crystallites over an amorphous matrix [20,21]. Also the size and the shape of crystallites were considered to affect the diffusional membrane properties [12]. Moreover, the scheme of the PMP membrane formation was presented [12]. In this paper, some virtual scenario of the lamellae formation, occurred in different thermodynamic–kinetic conditions, is discussed. It has been already shown that the PMP lamellae are square-shaped and nearly flat, with some defects contained in their bodies. The amount and type of defects depend on the solvent and the thermal treatment history of the solution of the corresponding polymer concentration [6]. It is suggested above that the polymer concentration in solution is possibly a very essential factor influencing the perfection of the lamellae. Hence, we should like to take into consideration all of these factors during the isothermal formation of the supermolecular structure of polymeric membrane. This process could be described in three stages: lamella nucleation; lamella growth; aggregation of the lamellae, to be fairly identified with first-occurring membrane structure formation, especially when its stationary state is attained eventually [30], see Section 6.

The analysis presented in Section 3.3 has shown that the proper solvation of the chains is a main factor determining the degree of crystallinity, hence, the lamellae perfection. The molecules of the solvent are located in the unit-cell due to a random trapping by the adequate segments of the polymeric chains in the initial stage of the nucleation. This stage seems to be independent of the polymer concentration, especially for the low range of concentration (<1.3 wt%). The solvent molecules, due to their high translational mobility, would act as if they were some agents locally deteriorat-

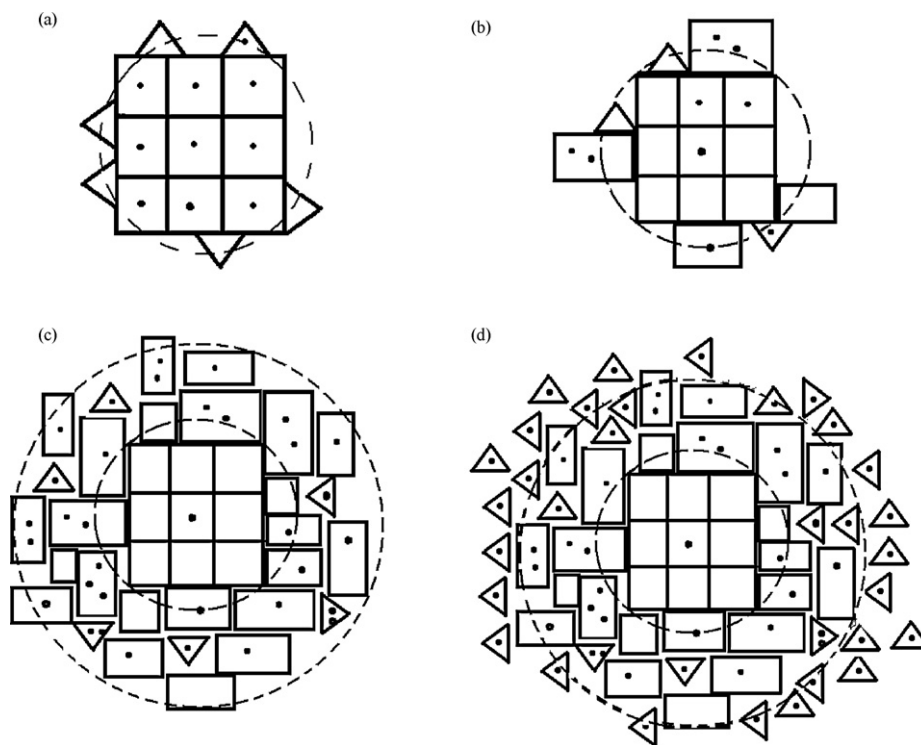
ing the chain conformations. Or equivalently, they affected a local viscous-matrix composition, in which the chains are adequately stretched, being both swollen and influenced by an action of respective mechanical micro-fields. All together they are manifested as a common, interesting, and truly viscoelastic effect. The temperature, staying always for an additional degree of freedom, would affect the translational (diffusive) motion of the solvent molecules, thus influencing the local density of the solution. The higher the temperature, the stronger perturbation of the local structures occurs, also the ones of micro-rheological nature [15]. Most likely, the maximum value plotted in Fig. 1 is a result of superposition of two effects: the local solvent structure and the chain conformation changes (49 °C is placed within the temperature range of the first glass transition, hence, the fluidity of the chains is high).

The second stage, i.e. a growth of lamella, seems to depend markedly on the polymer concentration. Four scenarios, presented in Scheme 1, would occur virtually, depending on the PMP concentration in solution. The following ranges of concentration could be determined: (a) very low, <0.5 wt%; (b) low, 0.5–1.5 wt%; (c) middle and high, 2–6 wt%; (d) very high, >6 wt%. The lamellae formed at very low concentration are the folded chain crystallites with amorphous edges (RAP), where only 15% of the crystal unit-cells gets the solvent molecule trapped ($n_K/n_R = 0.15$). A little higher polymer concentration would produce the lamellae composed of more perfect crystal unit-cell (the number of trapped solvent molecules slightly increases) and some amount of the OAP, which is predominant when compared naturally to RAP. In the third concentration range, the lamella is formed by a rather big amount of crystalline cells (approximately the 45% degree of crystallinity), occluding less than one molecule of the solvent per cell, with still predominant OAP and some amount of RAP, slightly increasing with the polymer concentration. The nonequilibrium, polymer–polymer interaction involving viscoelastic effects of interpenetration and interlocking of crystallites would systematically be observed at sufficiently high polymer concentration. The solvent molecules are mainly occluded in RAP then. The degree of crystallinity tends to a constant value and RAP keeps on being a dominating amorphous fraction then.

The third stage of the membrane formation is temperature- and size-of-lamellae (a ripening effect) dependent. The lamellae grown within one of the polymer concentration range are of different sizes and perfections. Both factors would strictly determine the membranes transparency, and as a consequence, the membrane morphology [20]. At this point, it could be argued that a degree of (optical) transparency of the membrane structure, would also be interpreted in terms of critical opalescence of the system and its respective changes, thus, being likely attributable to a (second-order) phase-change rationale.

4. Theoretical argumentation line of the membrane formation

An argumentation line, addressing the derivation of a function suitable to fit well the experimental data presented in Table 1 is proposed in what follows. The function, pointing to the problem of the crystallinity–concentration relationship in a comprehensive and rationalized way, reflects analytically certain physical phenomena occurring at the principal steps of membrane formation. These steps are as follows. First, the nuclei of lamella should be formed, in a more or less random fashion, in a form of a “fringed micelle” [2]. This step is considered to be purely thermodynamics-controlled. The nucleus is a small (partly) crystalline aggregate of polymer chains but it is assumed as sufficiently large to be stable (ripe). The critical radius of the nucleus can be taken from a description attributable to the hydrodynamic-flow mechanism of coarsening in (bio)polymer–solution systems [31]. Its value is related with the



Scheme 1. The second stage of the amorphous–crystalline membrane formation – growth of the polymer mono-crystal in the solution of various polymer concentration: (a) very low, <0.5 wt%; (b) low, 0.5–1.5 wt%; (c) mid and high, 2–6 wt%; (d) very high, >6 wt%. Squares, rectangles and triangles represent the crystal unit-cells, OAP and RAP, respectively. Dots mean that this area is supposed to contain the molecules of the solvent.

so-called Gibbs–Thomson or capillary constant, γ_1 [32]. This constant reflects mainly a depth associated with the action of surface tension on the (spherical) nucleus' surface. In order to develop our description, we have taken a simplistic picture of the lamella, which is actually a plate-shaped object, i.e. being characterised by one linear size, say L . Second, the description of the growth, realized in time t (and/or possible coarsening, cf. [31]), of a typical lamella should be addressed as an one-seed involving problem, with its kinetics and thermodynamics working properly. The one-seed growth (ripening, cf. [33]), interpreted in a deterministic (thus, oversimplified) sense, is based on absorbing polymer chains into the growing lamellar nucleus within a time interval, dt . It can be described in a natural way by the mass conservation law with the polymer-chain matter flux, $J(L, t)$, prescribed at the surface of nucleus (of radius L) [34,32].

The near-lamella-interface concentration, $c(L)$, included in the flux (cf., Eq. (12) in [34]), involves three main effects which occur at the typically unstable lamella-surroundings border (see, Eq. (1) below): (i) the ones responsible for the nucleation process involving the capillary constant, γ_1 , described above (ii) others, including a finite-size effect due to a polymer-chain persistence length \tilde{r}_{PMP} (the Gaussian-type curvature correction [34]), thus, γ_2 , a Tolman length in thermodynamic notion [35] gives information on how far the part of the surface of lamella can bend locally (or, can become stiff), (iii) the remaining effect, due to a “Goldenfeld-type” spherulitic correction $-\beta_{\text{K}}dL/dt$, [36,37] – this part, cf. Scheme 1, assumes that the surface is quite far away from local thermodynamic equilibrium, and that a deviation from this state is proportional to the local growth velocity of the interface nucleus-surroundings, quite in general. The parameter β_{K} is a positively valued kinetic coefficient, measuring a “local” deviation from the equilibrium – the larger it is the longer distance from the thermodynamic equilibrium can be appreciated. One can easily find that the nonequilibrium term $-\beta_{\text{K}}dL/dt \rightarrow 0$ in the diffusional case, when $t \gg t_0$, hence $L \equiv L(t) \propto \sqrt{t}$ holds, cf. [36].

The near-interface concentration can be expressed as follows [34,36,38]:

$$c(L) = c_0 \left(1 + \frac{2\gamma_1}{L} + \frac{\gamma_2^2}{\tilde{r}_{\text{PMP}}L} - \beta_{\text{K}} \frac{dL}{dt} \right), \quad (1)$$

where c_0 is the equilibrium solution concentration for the planar surface. Surely, the growth occurs when $L > L_c$ for any t value, and especially for the mature stages of growth ($t \gg t_0$). These stages can be seen as the ripening (viz coarsening) process, in which the corresponding viscoelastic effects may prevail substantially [15]. In order to assume the process of matter distribution over the growing germs within the membrane as a (standard, Einstein type) diffusion, $L(t)$ might be expressed as

$$L(t) = bt^{\nu_{\text{G}}} \quad (2)$$

with $\nu_{\text{G}} = 1/2$, and this stands for our basic assumption, enabling to derive in what follows the fitting function; b is a positive (thermodynamic) prefactor. The proposed value stays quite in contrast with $\nu_{\text{G}} = 1$ [34], that is more characteristic of the mass-convective formations, i.e. occurring in high-density polymeric systems¹. It is because we cannot opt fully for this hydrodynamic coarsening scenario since the PMP membranes are made up of the very low-density and partially disorderly polymer components. Therefore, the diffusional matter transfer, more characteristic of diffusive coalescence, more toward Ostwald ripening, must be envisioned in a

¹ In general, the growth rate of the (average) lamella can be obtained while based upon $dL/dt = [\kappa(L)]^{-1}v(L)$, where $\kappa(L)$ represents the (nonequilibrium) solubility, manifested thoroughly within the interface lamella versus solvent-containing surroundings. The $v(L)$ function is the near-surface (stochastic) velocity of the centre of mass of the polymer chain [34,32]. The relation comes from a Smoluchowski-type equation $\partial P(L, t)/\partial t = -\partial J(L, t)/\partial L$, with the probability density $P(L, t)$ (of finding at time t the symmetric lamella of characteristic size L) always mimicking adequately the concentration of the lamellae-involving solution. The matter flux $J(L, t)$ has then to be specified in detail, cf. Ref. [34].

sufficiently plausible way [31]. Thus, it seems to us that the way from the superdiffusive to normal diffusive (Einstein) mode, due to the above offered argumentation line, thus favorably due to the influential presence of polymer–solvent and polymer–polymer interactions, should be seen. These two above mentioned steps are necessary to be addressed since they cause a subsequent solidification of the overall-seeds-containing polymer-rich phase [15]. They can be viewed as a polynuclear and many-cells-involving formation and they are proposed to be accomplished by means of a stochastic (Kramers-type) description [39]. As a result, a cellular membrane structure is finally obtained [12], with a formation-energetics dependent and nucleation predetermined probability which can be inferred from the stationary state $dP/dt=0$ (cf., footnote 1) [30] of the mentioned Smoluchowski equation, cf. Eq. (2) in [34].

Thus, for accomplishing the membrane–structure formation, we utilize the Smoluchowski-type (Kramers' free energy barrier involving [34,39]) equation [40] in L -space which describes the many-seed (stochastic) growth. For the overall stochastic framework of the soft-matter formation one is encouraged to see [34]. However the pure thermodynamic–kinetic Smoluchowski type model, reflecting the entropic character of the formation, does not include the binary polymer–solvent, polymer–polymer and solvent–solvent interactions, more attributable to its generically enthalpic counterpart. Thus, for setting up properly our quantitative rationale, starting from the Smoluchowski type “coalescence” model just offered, mainly the polymer–solvent and the polymer–polymer interactions should be taken into account. It can be done in a phenomenological way. In this approach, the membrane formation time is primarily related to the solvent evaporation time. It indicates that the proper formation commences with a gradual “damping” of polymer–solvent interactions, favouring automatically the polymer–polymer interactions in the subsequent stages. Therefore, the following polymer–solvent and the polymer–polymer terms must appear in a form of two concentration-dependent ansatz'es in the presented model.

The involvement of interactions would suggest to indicate both \tilde{r}_{PMP} and β_K as the quantities being weakly (meaning: powerly) concentration-dependent. It is so because when the concentration increases due to decreasing solvent–molecule occlusion (or nearly equivalently, evaporation) effects, $1/\tilde{r}_{\text{PMP}}$, because of the polymer chain being contracted (unswollen), will tend to increase. Thus, the second L -dependent term on the right-hand side of Eq. (1) must decrease with the concentration. On the contrary, the third L -involving term in Eq. (1), dL/dt , must increase, due to decreasing-with-concentration evaporation, which results inevitably in attaining a possibly close-to-equilibrium state. In the light of the above, we hypothesize the second-term effect to be written in a form of another ansatz, namely

$$\Omega_f(\delta) = B\delta^{\alpha_1}, \quad (3)$$

where $B = \gamma_2^2/\tilde{r}_{\text{PMP}}\bar{b}$, with α_1 – a polymer–solvent interaction exponent, and $\bar{b} = bt_0^{\nu_C}$, cf. Eq. (2). Here, t_0 is an initial instant value. (Realize again that this dependency results from contracting the hydrodynamic radius in the high-concentration regime.)

The third-term effect, involved in Eq. (1) relies on containing β_K [36]. This effect is more accessible at a high-concentration regime because the chains are closer to equilibrium. Thus, it should read, again in a form of the proposed (2nd) ansatz, as follows:

$$\Omega_1(\delta) = C\delta^{\alpha_2}, \quad (4)$$

where $C = \beta_K(\bar{b}/2t_0)$, α_2 – a characteristic polymer–polymer interaction exponent.

Therefore, in order to perform as efficiently as possible such a mechanism-sensitive fitting, both functions should first be pro-

posed in a way consistent with the main observations revealing it, see Scheme 1. The first term of Eq. (1), $A \equiv \Omega_c = 2\gamma_1/\bar{b}$, stands for another purely thermodynamic parameter which we should like to attribute formally to the (background) solvent–solvent interaction.

Then, the next step enters unavoidably: a type of viscoelastic (auto) phase-separation, thus a micro-rheological context [15], mainly due to proper equilibration of the membrane structure. It relies on: (i) restructuring the polymer-rich phase due to evaporation of the solvent, and (ii) somehow expelling the polymer-poor phase, presumably due to thermal stabilisation and solvent evaporation. There are three physical effects which should be considered for the growth of semi-crystalline microstructure which build the polymer membrane [2]. All of them (related to the so-called Avrami–Kolmogorov phase-change phenomenology) should express a physical law showing how the degree of crystallinity changed in time. The first can loosely be mentioned by stating a rule by which the diffusion coefficient of a growing structure is to be proportional to the surface of an individual object. The second, in turn, assumes that the more structural order in the overall phase-changing system, the easier a semi-crystalline matrix may be formed. The third addresses the fact that the growth can also be limited by some interfacial (between-phases-emerging) effects, i.e. the absorption–desorption kinetics within the interface crystallite-surroundings is legitimate to prevail over time as a counter-effect to a facilitated crystal-formation development [41,42]. Such treatment results in the following form for the (algebraic) time-dependence of the overall degree of crystallinity of the membrane, namely

$$X = \bar{X}t^\mu \quad (5)$$

where \bar{X} is an equilibrium reference constant; $\mu = \mu_{\text{bulk}} - \mu_{\text{surf}}$ is a known volume-to-surface effect crystallisation parameter. The $\mu_{\text{bulk}} \approx d+1$ is so-called Kolmogorov random close-packing exponent ($d=2, 3$), capable of expressing virtually the membrane dimensionality; and μ_{surf} is a parameter which is capable of informing us about how strong the interaction between diffusing object on the surface and the surface (spot) itself can be ($0 < \mu_{\text{surf}} < 1$ applies, where $\mu_{\text{surf}} \approx 0$ implies a subdiffusive, nearly chemical-reaction involving case [41], whereas $\mu_{\text{surf}} \approx 1$ indicates a kinetically favourable linear superdiffusive case [34]). In a diffusion-controlled, also time-dependent, adsorption-involving case, $\mu_{\text{surf}} \approx 1/2$ [41,43] holds. Thus, the offered model also emphasizes the lamellae formation as an interface-controlled process, except that it may additionally contain information about the crystallinity in the bulk of the lamellae-containing material as a whole, given by X at each non-early instant of the membrane formation. Thus, for three-dimensional space (and high-temperature diffusive case [41]) $\mu = 3.5$ and this value can be taken for polymer membranes for $t \gg t_0$.

Combining Eqs. (1), (2) and (5) in order to extract (or, reduce) the time variable t , and after assuming the process of matter distribution over the growing lamellae within the membrane as purely diffusive ($\nu_C = 1/2$), a simple power-law non-dimensional (time-less) fitting function, representing a (relative) crystallisation degree, $\chi(\delta) = X/\bar{X}$ in terms of another (near-lamella relative concentration) quantity, δ , can be obtained and applied suitably to experimental data presented in Table 1. The function reads

$$\chi(\delta) = \left(\frac{\Omega_c + \Omega_f - \Omega_1}{\delta - 1} \right)^{2\mu} \quad (6)$$

where $\delta = c/c_0$, $\Omega_c = 2\gamma_1/\bar{b}$, $\Omega_f \equiv B = \gamma_2^2/\tilde{r}_{\text{PMP}}\bar{b}$, $\Omega_1 \equiv C = \beta_K\bar{b}/2t_0$, $\bar{X} = \bar{X}t_0^\mu$, $\bar{b} = bt_0^{1/2}$ for membranes in three-dimensional space. To aim thoroughly at the fitting task, we take, instead of the above, δ to be a linear function of the PMP concentration in solution (c_{PMP}), $\delta \equiv \delta(c_{\text{PMP}}) = Dc_{\text{PMP}} + E$. Owing to the facts mentioned above, the

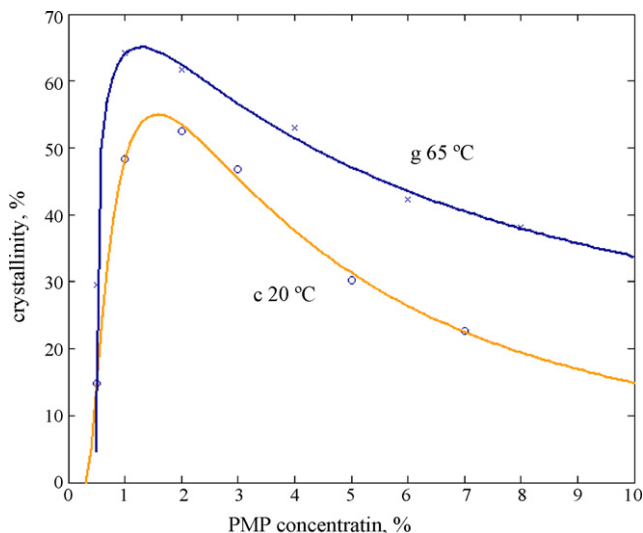


Fig. 4. The crystallinity of the membrane formed at different temperatures as a function of the polymer concentration. The experimental data are satisfactorily approximated by using the proposed fitting function, Eq. (7). The values of the fitting parameters are collected in Table 2.

so-derived function, suitable for fitting the experimental data, can be given ultimately by the following mathematical form, namely

$$\chi(\delta) = \left(\frac{A + B\delta^{\alpha_1} - C\delta^{\alpha_2}}{\delta - 1} \right)^7 \quad (7)$$

assumed finally algebraic dependence for the polymer concentration in the vicinity of the lamella surface, reflected by both principal interaction terms $\Omega_f(\delta)$ and $\Omega_1(\delta)$ (see, Eqs. (3) and (4), respectively). $A, B, C, \alpha_1, \alpha_2$ and D, E , are concentration independent constants (see, Fig. 4).

5. Theoretical results and discussion

The values of the fitting parameters and the corresponding errors, obtained preliminary by a nonlinear least-square regression analysis, using the Matlab software, and strictly by a Chi-square regression after using the Origin 8, are presented in Table 2. The current limitation of the analytical software could not operate without setting the parameters D and E as constant values. It was confirmed additionally by using Matlab nonlinear least-square regression analysis.

The fitting function can be applied for the membrane material density c_{PMP} larger than 0.46% because of the singularity expected to become effective in the denominator of relation (7) for a certain range of parameters. The maximum degree of crystallinity for the first case (20 °C) equals about 54.9% and can be reached for the 1.6 wt% PMP concentration. In the case of higher temperature (65°),

Table 2
The parameter values of the derived fitting function, Eq. (7), mimicking efficiently the polymer–solvent and the polymer–polymer (concentration-dependent) effects, cf. Fig. 4. (Lsqcurvefit function from Matlab Optimization Toolbox and Non-Linear Curve Fit function from Origin 8 were used for fitting).

	20 °C	65 °C
Chi-Sqr	4.2×10^{-4}	4.2×10^{-4}
A	73.08 ± 0.07	74.00 ± 0.08
B	2.9 ± 0.4	1.3 ± 0.5
C	76.0 ± 0.5	75.3 ± 0.8
D	199.8	199.8
E	0.075	0.075
α_1	0.654 ± 0.008	0.88 ± 0.07
α_2	0.014 ± 0.011	0.003 ± 0.017

the degree of crystallinity increases to 64.9% and can be reached from the solution of the 1.3 wt% PMP concentration. The temperature dependence of all parameters can be seen. However, there was another relevant dependence for the studied membranes: the membrane thickness (the thin and the thick membranes were cast from the solution prepared at 20 °C and 65 °C, respectively). We cannot accurately compare both sets of the fitting parameters but we have been able to find some clear tendencies for them. The results show similar values except for the α_2 parameter which differ by one order of magnitude, thus, the last term in Eq. (1) seems to be much more temperature dependent than the other terms. The lower value of A parameter, cf. Eq. (7), results in greater \bar{b} radius of the lamellae, that indicates lower solubility in the 20 °C case than in its 65 °C counterpart. It seems to be in accordance with commonly known physical facts. In the case of the higher temperature, we observed a distinctly smaller value of parameter B . It suggested that the contribution of the polymer–solvent interactions in the process, presumably due to appreciable diffusivity of the solvent molecules, was significantly smaller. Similar tendency can be observed for parameter C . It would also mean that slightly smaller polymer–polymer interactions occurred at the higher temperature. The environment looks as if it was more distant from a local equilibrium than in the case of 20 °C. The parameters D and E translate the concentration in our model into the PMP concentration in the solution, hence it is justifiable that they were the same in both temperature cases, which was confirmed using the Matlab curve-fitting function. There remains still one interesting (open) question on how strong the temperature of the solution preparation influences the hydrodynamic radius \bar{r}_{PMP} and the kinetic non-equilibrium coefficient β_K , which can be inferred, at least qualitatively, from the α_1/α_2 ratio by claiming that $\alpha_1 \gg \alpha_2$ holds typically. Realize, when looking at Table 2, that the fitting procedures were performed at a low-error (Chi-Sqr) level. (It is worth noticing again that we have primarily made an attempt on applying here a generically close-to-equilibrium Smoluchowski type thermodynamic model with its linear flux-force-relation, and entropy-production involving, conceptual basis [44,34].)

It should be underlined that the presented sets of the fitting parameters characterise certain readily best fitted curves which represent well the performed experimental study on the membrane crystallinity versus polymer concentration relationship. However, it does not imply that both sets represent the only possible parameters describing the experimental systems univocally. Moreover, any too large number of the fitting parameters is considered to be a shortage of the proposed fitting procedure. Therefore, we suggest ultimately that we should take the absolute values of all fitting parameters with some system-dependent caution, regarding always in advance with extreme care all available experimental pre-conditions applied [20–23].

6. Conclusions

It should be underscored that the phase separation taking part in the crystallisation is a thermally induced viscoelastic process [15]. Temperature and polymer concentration determine not only the polymer crystallinity but also the lamella perfection. Both factors exhibit their maxima depicted in adequate diagrams that would solely result in the highest crystallinity of the PMP membrane, cf. Figs. 1, 3 and 4. The proposed scheme of the crystalline structure emphasises the relation between two fractions of the amorphous phase and, what is more important, their naturally occurring dynamic coexistence. The polymer concentration in the solution seems to be a decisive (or, sometimes, limiting) factor for the membrane formation, influencing the supermolecular structure of the membrane material greatly. The fitting func-

tion of the crystallinity–concentration relationship for the PMP solutions, thus, our main theoretical finding, Eq. (7), conforms well to the presented experimental data, cf. Fig. 4. It has been obtained while based on the PMP membrane formation seen in terms of nucleation–growth, and viscoelastically auto-separative thermodynamic–kinetic (Kramers-type) process, well immersed in the theoretical Smoluchowski-type truly entropic framework, cf. Ref. [34]. The stationary state of this process, to be estimated crudely from the stationary state of the Smoluchowski dynamics, is fully thermodynamically viz energetically (interaction) controlled [30]. It is responsible for obtaining the membrane structure from an entropic, but also polymer-interactive (more of enthalpic origin) environment. This expresses well a certain appreciable novelty of the presented study. The agreement is good enough after applying two types of ansatz'es, cf. Eqs. (3) and (4), that, in fact, asymmetrise effectively the lamellae, which were first assumed to be symmetrical, in the limit of the membrane-system entropy production [34], acting overwhelmingly. By switching on both principal types of the interactions (polymer–solvent and polymer–polymer), the lamellar form has been found fairly appropriate and consistent enough with basic experimental observations [2]. In the final word, it can be realized that by applying all theoretical assumptions proposed throughout leads unavoidably to obtaining the fitting function with a multi-value number of the fitting parameters. It can be viewed as a certain drawback of the proposed derivation. Thus, our future task shall eventually be focused on how to rationalize the procedure toward minimizing the number of parameters in the model, and to find out whether some well-known strategies, such as entropy-minimisation (thermodynamics) or minimum-entropy production (kinetics), can serve as helpful tools to be applied efficiently, assumed that the interaction map has adequately been provided to complete the overall membrane-material formation task.

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