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MICROPOROUS MEMBRANES FROM POLYCAPROLACTAM

Microporous membranes were prepared from PA6 solutions in 6 M HCl coagulated in water. Before immersion in water the casting solutions were subject to maturation for 24-96 h. It was shown that during that period a reduction of the average molecular weight of PA6 took place. As a result, viscosity of the casting solutions decreased, which had direct effect on the membrane structure. Pores in the membranes appeared as void volume among PA6 nodules (aggregates). When PA6 concentration in the casting solution was increased from 15 to 25%, the size of the nodules decreased from ca. 10 μm to 0.2 μm . The soaking rate parameter was introduced to quantify how open the porous structure was.

1. INTRODUCTION

Membranes from polyamides have been widely applied because of their good mechanical, thermal and chemical stability [1]. The membranes are also attractive because of the ease of chemical functionalization to obtain a good support for enzyme or catalyst immobilization (membrane reactors). Polyamide microfilters can be also used in environmental monitoring for isolation of suspended particulates dispersed in the atmosphere and in all types of water [2].

From a variety of polyamides two kinds have found widespread applications as membrane materials, namely Nylon 6 and polycaprolactam (PA6). Although the mechanical, chemical and thermal properties of Nylon 6 are slightly better, the higher hydrophilicity of PA6 makes it a good alternative in many applications.

There are only few reports giving a detailed description of the preparation of microporous membranes from polyamides. PALL [3] patented a procedure based on the phase inversion from PA6 solutions in anhydrous formic acid and CASTRO [4] patented a method based on the thermal phase inversion. SOLDATOV et al. [5], [6]

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described preparation of symmetric microfiltration membranes with controlled pore diameter in the range from 0.05 to 0.3 μm by phase inversion from PA6 solution in N,N-dimethylacetamide and LiCl. Applying the same solvent system they obtained membranes from Nylon 6 and from a copolymer of caprolactam and AG-salt [5]. McDONOGH et al. [6] and YAO et al. [8], [9] obtained asymmetric microfiltration membranes from PA6 solutions in HCl gelled in water. The structure and properties of the membranes depended on the relative content of PA6 and HCl in the starting solution and on the maturation time.

The purpose of this paper is to investigate the relationships between the preparation procedure characteristics and both the structure and properties of microporous membranes from PA6.

2. EXPERIMENTAL

The polycaprolactam (PA6) used was Tarnamid T-30 (Tarnów, Poland) with relative viscosity of 3.3 measured at 25 °C in 96.5% H_2SO_4 . The material was in the form of textile yarns.

Viscosity of 0.2–1 wt.% PA6 solutions in 85.0% HCOOH at 25 °C was measured by means of a Lauda VISCOBOY 2 equipped with a microcomputer unit. Average molecular weight (M_v) was calculated basing on Mark–Houwink equation:

$$[\eta] = KM_v^a \quad (1)$$

where $[\eta]$ denotes the intrinsic viscosity, and the constants $K = 22.6 \cdot 10^{-3}$ and $a = 0.82$ [10].

Casting solutions were prepared by mixing a given amount of PA6 with 150 cm^3 of 6 M HCl. Then, the solutions were allowed to mature for a specific period of time (24–96 h). All the data are gathered in table 1.

Membranes were cast on a dry glass plate to the thickness of 100 μm . The plate was then immersed in a water bath kept at ambient temperature (18 °C). The membranes formed were peeled off and washed with distilled water for the next 24 h.

Water content W (porosity) of the membranes was calculated from the equation (2):

$$W = \frac{m_w - m_d}{m_w} \quad (2)$$

where:

m_w – weight of the wet membrane,

m_d – weight of the membrane dried in the air for 120 h.

Bubble point and water flux at 0.05 MPa were measured in a standard way with the use of equipment constructed in our laboratory [11]. Basing on the bubble point

Table 1

Procedures of the membrane preparation

Membrane number	PA6 concentration (wt.%)	Maturation time (h)	Membrane thickness (μm)
152	15.0	48	180
153	15.0	72	210
154	15.0	96	300
202	20.0	48	170
203	20.0	72	190
204	20.0	96	200
252	25.0	48	150
253	25.0	72	190
254	25.0	96	200

data, the pore radii (r) were calculated according to the Laplace-Young equation:

$$r = \frac{2\sigma \cos(\theta)}{P} \quad (3)$$

where:

σ – interfacial tension (0.07277 N/m for water–nitrogen system),

θ – wetting angle (10 deg for PA6–water system),

P – pressure applied to remove water from the pores of radius r .

Tensile strength and elongation at break of the wet membranes were measured using an INSTRON model 1126 at room temperature and at elongation rate of 50 mm/min.

The scanning microscope Cambridge Stereoscan 180 was used for section and surface examinations.

3. RESULTS AND DISCUSSION

It is known that the final structure of a porous membrane depends on several factors, the main ones being the polymer concentration in the casting solution, strength of the coagulation bath, viscosities of both the casting solution and coagulation bath, and, finally, temperature. Additionally, in the case of the PA6–HCl solutions, a maturation time is very essential because of the acid-induced cleavage of the polymer chains. We can take advantage of this phenomenon to fix 'precisely' the molecular weight of the PA6 and in this way to control porosity of the resultant membrane.

The influence of the maturation time of casting solution on the PA6 average molecular weight is shown in fig. 1. A substantial reduction of the average molecular weight is observed (from 43 000 to 11 000–17 000 daltons). The effect is slightly

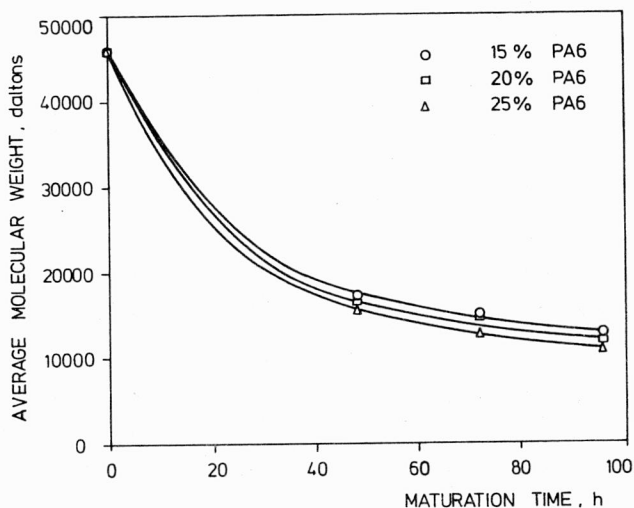


Fig. 1. Influence of maturation time of casting solution on PA6 molecular weight

more pronounced for higher casting solution concentrations. In similar studies YAO et al. [8] reported an initial increase of molecular weight attributed to protonated polymer-counterion complex formation. After about 10 h slow hydrolysis was observed. Because of the greater size of the PA6 yarns used in the present study the dissolution process itself proceeded 24 h and it was not possible to observe the above effect.

Tensile strength and elongation at break data are shown in table 2. A very pronounced effect of PA6 chains cleavage is visible. Both the tensile strength and elongation at break decrease with the prolonged maturation of the casting solution. The membranes prepared from solutions matured for more than 100 h were mechanically weak and desintegrated while peeling from the glass plate. As can be predicted the mechanical characteristics improve with the increasing PA6 concentration in the casting solution.

The effect of maturation on mechanical properties of the membranes can be analyzed basing on the critical molecular weight necessary for entanglement [12]. Decrease in the molecular weight (here by hydrolytic chain cleavage) causes change in the state of molecular aggregation of the polymer in the casting solution. For molecular weights much higher than the critical molecular weight there exists a continuous aggregate network. As the result of gelation a membrane with continuous pore wall structure is formed. The process can be called an infinite network gelation [8]. This structure is characterized by a high tensile strength.

When molecular weight of the dissolved polymer is lower than the critical molecular weight, a non-overlapping aggregate structure is formed. After gelation a membrane with pore walls composed of clustered aggregates is obtained. This process can be called a polymer aggregate gelation [8] or just coagulation. The resultant structure is characterized by a very low tensile strength.

In order to test the influence of both the PA6 concentration in the casting solution and maturation time on the porous structure of the resultant membranes the porosities, bubble point and water fluxes have been determined. The results are shown in table 2.

Table 2

Properties of the membranes

Membrane number	Pore radius (μm)	Water content $t_s = 10 \text{ s}$	Water content $t_s = 24 \text{ h}$	Water flux ($\text{cm}^3/\text{cm}^2 \cdot \text{s}^{-1}$)	Elongation at break (%)	Tensile strength (MPa)
152	2.4	0.63	0.84	0.320	35.4	1.19
153	2.9	0.58	0.84	0.463	16.7	0.69
154	—	0.58	0.84	—	12.4	0.46
202	0.9	0.77	0.80	0.311	48.7	1.80
203	1.4	0.78	0.80	0.486	36.2	1.31
204	1.6	0.78	0.80	0.536	12.6	0.74
252	<0.6	0.72	0.77	0.040	58.7	2.83
253	<0.6	0.74	0.77	0.041	54.6	2.52
254	<0.6	0.74	0.77	0.048	7.6	1.17

t_s - time of soaking.

Analysis of the bubble point data leads to the conclusion that with the increasing PA6 concentration in the casting solution the average pore radius of the resultant membranes decreases. In extreme cases, the pore radius is shorter than 0.6 and 2.9 μm for the concentrations of 25 and 15%, respectively. The influence of the maturation time is slight which may indicate that the state of molecular aggregation is not critical as compared to the PA6 concentration in determining the effective size of the porous paths through the membranes studied.

Valuable information can be gained due to comparison of the data on water content in membranes initially dry that were put into water for $t_s = 10 \text{ s}$ and $t_s = 00 (24 \text{ h})$, respectively. The reciprocal of the difference can be named a 'soaking rate' and is a very important parameter in many practical applications. It can be seen that in general the soaking rate is high. The only exception are the membranes prepared from 15% PA6 solutions which may be indicative of significant con-

tribution to the total porosity of the pores weakly connected with the rest of porous structure. On the contrary, the membrane obtained from 20 and 25% PA6 solutions should possess an open pore structure. Water content can be a measure of total porosity of the membranes. From table 2 it can be seen that water content is relatively high and slightly decreases, from 0.84 to 0.77, with the increasing PA6 concentration in the casting solution. Recalculation of the above values into pore volume ratio gives 0.86 and 0.79 cm³/cm³, respectively.

From the water flux data in table 2 it is evident that the flux decreases with the increasing PA6 concentration in the casting solution and increases with the prolonged maturation. This dependence is consistent with the relation established for the bubble point.

Mechanical properties of the membranes, i.e. elongation at break and tensile strength, support predictions based on porosity analysis also. Here, however, the influence of the maturation time is particularly clear.

The above discussion can be well illustrated by the SEM micrographs shown in figures 2 and 3. The first figure gives scans of the upper part of the membrane cross-section. The second one shows the upper surfaces of the membranes. Very significant differences in membrane structure depending on the maturation time and, in particular, on the PA6 concentration in the casting solution are evident.

Careful analysis of figure 2 does not fully support the early conclusion that the molecular weight of the polymer and, further, its state of molecular aggregation are essential. In fact, it is clearly evident that the prolonged maturation of the casting solution results in the increase in macropore dimensions and changes the porous structure into more open. This effect is characteristic of the improved kinetics of diffusional exchange of solvent and nonsolvent between the coagulation bath and the casting solution. This, in turn, can be caused by decreasing viscosity of the solution. Thus, it is viscosity reduction that governs the membrane structure change when the maturation is prolonged.

The influence of PA6 concentration in the casting solution on the membrane structure can be well understood due to the analysis of figure 3. It can be seen that the membranes consist of a large number of interconnected nodules or domains. The pores appear as a void volume between the domains. At higher magnification each domain reveals its aggregate-like structure resembling that typical of a diffusion-limited aggregation (DLA). This evidences that in the studied case membrane formation did not proceed as a result of spinodal decomposition, but due to nucleation and growth probably induced by crystallization of polycaprolactam.

It can be observed that the domain size decreases, from about 10 μm to about 0.2 μm, when PA6 concentration in the casting solution increases from 15 to 25%. The shift in concentration to higher values modifies both the kinetics of the phase separation and the so-called 'coagulation path'. With increasing PA6 concentration the coagulation path becomes closer to the binodal line, as can be projected in the phase diagram, which results in generation of stable nuclei at higher PA6 concentration and thus greater number of smaller domains.

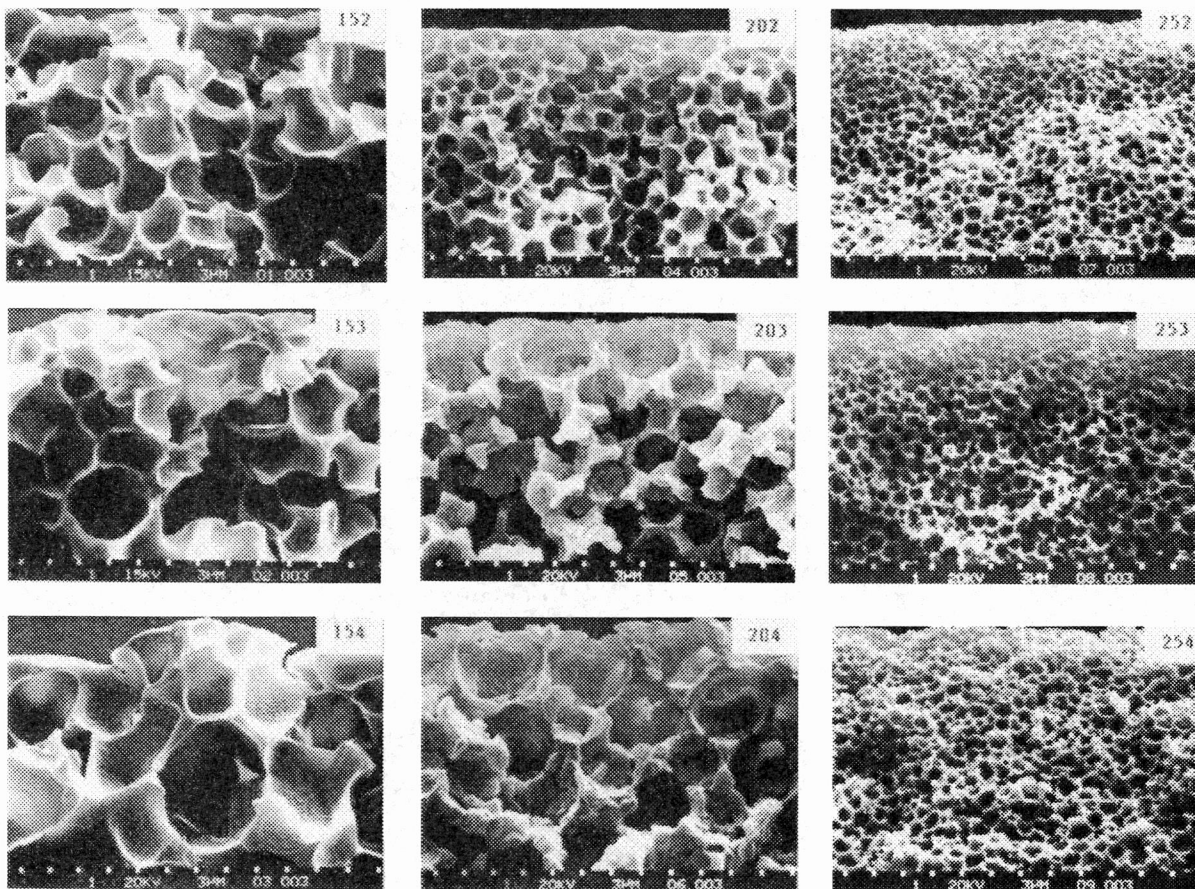


Fig. 2. Micrographs of the upper part of the membrane cross-sections by scanning electron microscopy. Magnification $3000\times$

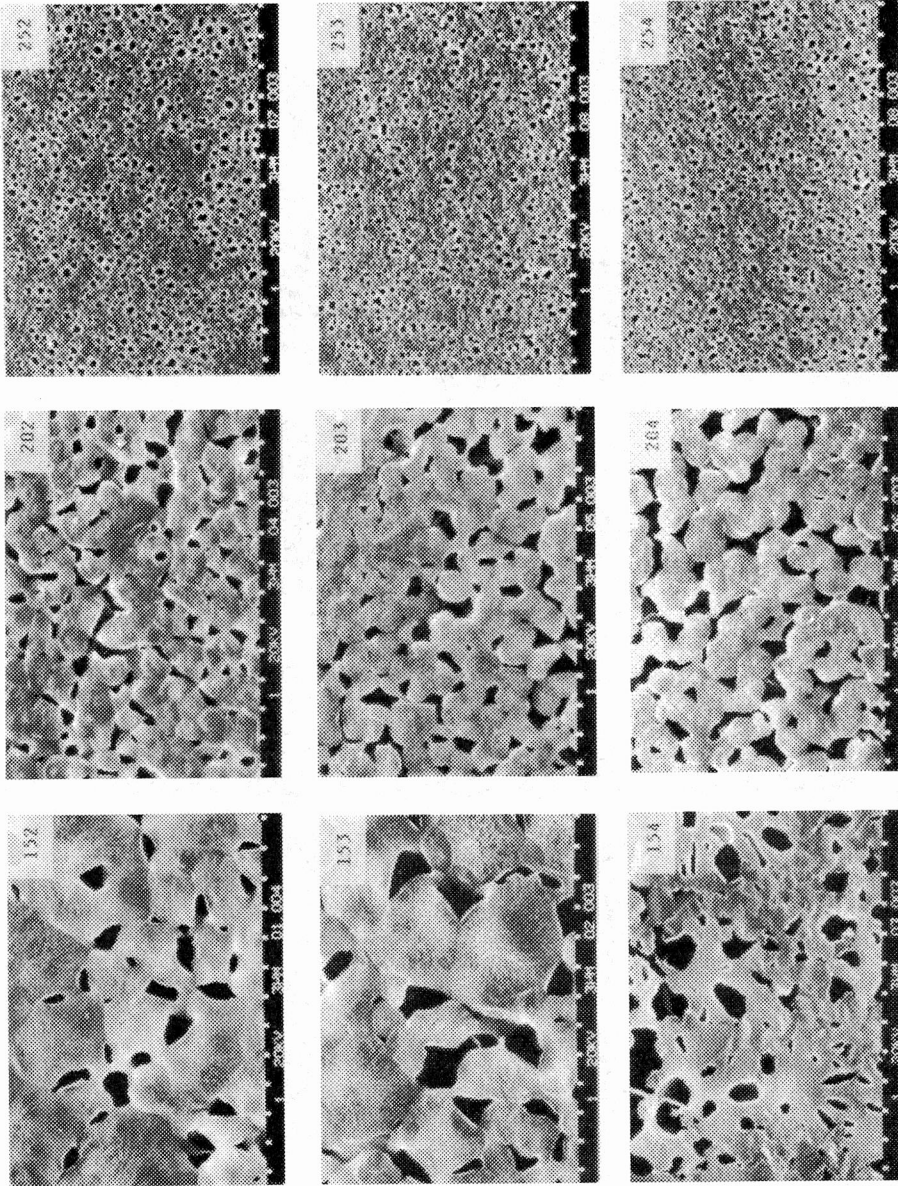


Fig. 3. Micrographs of the upper surfaces of the membranes by scanning electron microscopy. Magnification 3000 ×

4. CONCLUSIONS

Reduction of the polycaprolactam (PA6) average molecular weight from 43 000 to 11 000 daltons is observed in the casting solutions matured for 96 h.

As a result both the tensile strength and elongation at break of the membranes obtained by phase inversion decrease with prolonged maturation. The membranes prepared from the casting solutions matured for more than 96 h were mechanically weak and desintegrated while peeling from the glass plate.

The pores in the membranes appear as a void volume between the PA6 domains. Each domain has an aggregate structure with sizes decreasing from 10 μm to 0.2 μm when the PA6 concentration in the casting solution increases from 15 to 25%.

A soaking rate parameter was introduced to quantify how open the porous structure was. In general, the soaking rate is high. The only exception are the membranes prepared from 15% PA6 solutions which may be indicative of significant contribution of pores weakly connected with the rest of the porous structure.

As a final conclusion it may be stated that prolonged maturation of the casting solution results in increased pore dimensions of the membranes. Moreover, the porous structure becomes more open. The primary cause of these changes is the reduction of viscosity of the casting solution and thus improvement of kinetics of diffusional exchange of solvent and nonsolvent between the coagulation bath and the casting solution.

REFERENCES

- [1] BLAIS P., *Polyamide membranes*, [in:] S. Sourirajan (Ed.), *Reverse Osmosis and Synthetic Membranes*, National Research Council of Canada, Ottawa 1977.
- [2] BAKER J., *International Lab. News*, April 1994, 16.
- [3] PALL D.B., U.S. Patent 4, 340, 479, 1982.
- [4] CASTRO A., U.S. Patent 4, 247, 498, 1981.
- [5] SOLDATOV V.S., MOSTOVLYANSKIY O.A., ARTAMONOV V.A., *Synthesis, Properties and Application of New Polyamide Microfiltration Membranes*, [in:] T.Z. Winnicki and A. Mika (Eds.), *Membrane Phenomena and Processes*, Technical University of Wrocław, Wrocław 1986.
- [6] SOLDATOV V.S., ARTAMONOV V.A., *Preparation and Structure of Microfiltration Membranes*, [in:] A. Mika and T.Z. Winnicki (Eds.), *Advances in Membrane Phenomena and Processes*, Wrocław Technical University Press, Wrocław 1989.
- [7] McDONOGH R.M., FELL C.J.D., FANE A.G., *J. Membrane Sci.*, 31 (1987), 321.
- [8] YAO C.W., BURFORD R.P., FANE A.G., FELL C.J.D., McDONOGH R.M., *J. Appl. Polym. Sci.*, 34 (1987), 2399.
- [9] YAO C.W., BURFORD R.P., FANE A.G., FELL C.J.D., *J. Membrane Sci.*, 38 (1988), 113.
- [10] BRANDRUP J., IMMERGUT E.H. (Eds.), *Polymer Handbook*, John Wiley and Sons, New York 1975.
- [11] BROK T.D., *Membrane Filtration. A User's Guide and Reference Manual*, Science Tech., Inc. Madison 1983.
- [12] MATSUMOTO T., NAKAME K., OCHIUMI T., HORIE S., *J. Membrane Sci.*, 9 (1981), 109.

MEMBRANY MIKROPOROWATE Z POLIKAPROLAKTAMU

Membrany porowate przygotowano metodą inwersji faz z roztworów PA6 w 6 M HCl. Jako kąpiel koagulacyjną stosowano wodę. Przed zanurzeniem w wodzie roztwory poddano procesowi starzenia przez 24–96 godzin. Stwierdzono, że w tym okresie następowało zmniejszenie średniej masy cząsteczkowej PA6. W rezultacie lepkość roztworu zmniejszała się, co miało bezpośredni wpływ na strukturę membran. Uzyskiwano membrany mikroporowate typu domenowego (*nodular structure*), gdzie wolne przestrzenie między domenami stanowiły pory. Gdy stężenie PA6 w roztworze błonotwórczym zwiększano z 15 do 25%, wielkość domen zmniejszała się z ok. 10 μm do 0,2 μm . Wprowadzono nowy parametr, „szybkość nasączania”, aby określić stopień zwartości struktury porowatej.

МИКРОПОРИСТЫЕ МЕМБРАНЫ ИЗ ПОЛИКАПРОЛАКТАМА

Пористые мембраны, изготовленные методом инверсии фаз из растворов PA6 в 6 M HCl. В качестве коагуляционной ванны была применена вода. Перед погружением в воду растворы были подвержены процессу старения в течение 24–96 часов. Было установлено, что в это время наступало понижение средней молекулярной массы PA6. В результате вязкость раствора понизилась, что непосредственно влияло на структуру мембран. Получались микропористые мембраны доменного типа (англ. *nodular structure*), где свободные пространства между доменами составляли поры. Когда концентрация PA6 в блендообразующем растворе повышалась от 15 до 25%, размер домен понижался с ок. 10 μm до 0,2 μm . Введен новый параметр – „скорость промокания” – для определения степени плотности пористой структуры.