

Preparation and Structures of the Poly(vinyl chloride) Porous Membranes

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Synopsis

Formation of membranes from a binary system, poly(vinyl chloride) and dimethylformamide, was studied. Phase separation during membrane formation was caused by absorption of aqueous vapor from the atmosphere. The membrane structure was closely related to the degree of phase separation. The membrane formation process was divided into three stages, i.e., an early stage, a transitional stage, and a late stage. By leaching the solution at the early stage, where the casting solution was still transparent, a membrane with a finger-like structure was obtained. On the other hand, a network structure was obtained by leaching at the late stage which was dependent on the molecular weight and the concentration of poly(vinyl chloride). The membrane structure was predominantly controlled by the mobility of polymer molecules in the casting solution.

INTRODUCTION

Mechanisms for microporous membrane formation through a phase separation process have been reported by several authors.¹⁻³ Kesting¹ first reported that a porous membrane was formed from polyhedra which consisted of spherical droplets or of micelles of polymer molecules. The concept of the membrane formation mechanism studied by Kamiide et al.² is similar to the above. Smolders et al.³ have proposed that nucleation and growth of the diluted polymer phase results in a continuous matrix.

In a previous paper,⁴ we reported the conditions for preparing porous membranes from a poly(vinyl chloride)-dimethylformamide binary system and their properties. The porous membrane could have either a "finger-like" or a "network" structure, and phase separation was suggested to play an important role in the formation of a microporous network structure. However, the mechanism of the phase separation was not studied in detail.

In the present paper, the phase separation during the membrane formation process is investigated with time-turbidity curves, and the relationship between membrane structure and phase separation is studied. The cause of phase separation and the factors determining membrane properties are also discussed.

EXPERIMENTAL

Materials

Poly(vinyl chlorides) (PVC) with different molecular weights were purchased from Kanegafuchi Chemical Co., Ltd. The number-average molecular weights of the PVC were 26,900, 38,200, 48,400, and 67,100, determined by liquid chro-

matography in tetrahydrofuran. Reagent-grade dimethylformamide (DMF) was purchased from Wako Junyaku Co., Ltd., and was used as received.

Membrane Preparation

PVC solution in DMF was cast approximately 400 μm thick on a glass plate ($10 \times 7 \text{ cm}^2$). The glass plate was placed in a sample box in the spectrometer and was left under evaporation condition, i.e., at a given temperature and a given relative humidity, for a given evaporation time. The relative humidity (R.H.) in the sample box was controlled by an air conditioner and measured by a hygrometer. The membrane formed on the glass plate was leached in a gelation bath of water and dried in air.

Cloud Point Curve

The cloud point curve (phase diagram) of the ternary mixture PVC-DMF- H_2O was obtained by titration of PVC-DMF binary mixture with a standard solution of H_2O -DMF. The compositions of the standard H_2O /DMF solutions were 1/1 and 1/9 (v/v). The cloud point was judged by visual observation.

Turbidity Measurements

Turbidity was measured during membrane formation by a Hitachi spectrometer Type 356, as shown in Figure 1. All the measurements were carried out at a wavelength of 500 nm.

Membrane Testings and Viscosity Measurements

The maximum pore diameter was measured according to ASTM-E 128 by using pure water at 25°C. Viscosities of casting solutions were measured with an E-type viscometer made by Tokyo Keiki Co., Ltd., at 30°C and at 50 rpm.

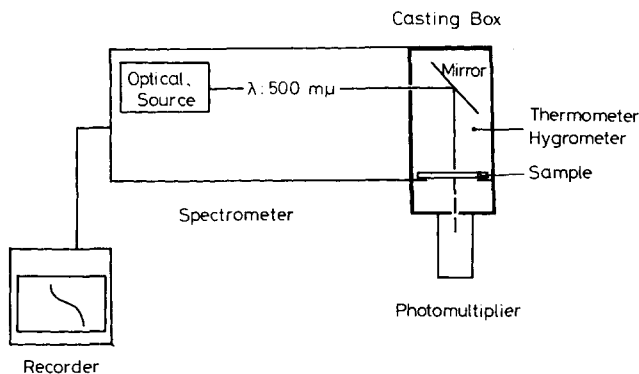


Fig. 1. Apparatus for turbidity measurement.

RESULTS AND DISCUSSIONS

Casting Conditions and Cloud Phenomenon

The DMF solution of PVC, which is initially transparent, becomes opaque a short time after casting on a glass plate. This cloud phenomenon indicates the occurrence of phase separation of the casting solution. Table I shows that the cloud phenomenon is greatly influenced by humidity.

Runs 1 and 2 indicate that the cloud phenomenon is observed after 20 min of evaporation time in 50% R.H. In run 3, the casting membrane becomes cloudy after 20 min and shows no marked change after that time. Runs 4 and 5 show that the cloudy membrane placed thereafter in nearly 0% R.H. becomes reversibly transparent but that exposure to a dry atmosphere after 60 min of being cloudy does not result in a reversible change. In run 6, the cloud phenomenon is not observed even after 3 hr in nearly 0% R.H. The casting solutions in runs 7 and 8 show cloud phenomenon in 50% R.H. but not in nearly 0% R.H.

These results suggest that water vapor is dissolved and diffuses in the casting solution, causing phase separation. Initially the cloud phenomenon should occur in the vicinity of the surface of membranes (evaporating side), and then diffusion of aqueous vapor (water) proceeds to the whole system. If the supply of water vapor is stopped after phase separation occurs and the quantity of water is within a range of soluble composition in the whole system, the cloud phenomenon disappears as the water vapor absorbed in the surface of the membrane diffuses to the whole casting solution. Phase separation does not occur in a dry atmosphere even if any DMF in the casting solution vaporizes. DMF is nonvolatile and highly hygroscopic. Consequently, in high humidity the DMF absorbs enough water from the atmosphere to cause a coagulation of the dissolved polymer (cloud phenomenon). There is no effect of DMF evaporation on the phase separation.

TABLE I
Cloud Phenomena Under Various Evaporation Conditions

Run ¹⁾	Relative Humidity	Evaporation Time (min)			
		0	60	120	180
1	50 %	— t ²⁾			
2		— c ²⁾			
3		— c			
4		— (c) — (c)			
5		— (c) — (c)			

	≈ 0 %	— t			
6	≈ 0 % ³⁾	— t			
7		— c			
8		— t			

1) PVC content 8 wt% , Temp. 25 °C

2) t ; transparent , c ; cloudy

3) atmosphere saturated with DMF vapor

The cloud point curve was determined in order to determine the composition at which the phase separation occurred (Fig. 2). The fraction of water at the cloud point is about 3 wt. % and is almost independent of the PVC concentration and the PVC molecular weight when the polymer content is between 4 and 12 wt. %. Therefore, more than 3 wt. % H₂O should be contained in the vicinity of the surface of the casting solutions when they become cloudy.

Variation of Turbidity During Membrane Formation

The cloud phenomenon was investigated by use of turbidity measurements. The progress of phase separation results in an increase in turbidity (Fig. 3). In every case, turbidity begins to increase rapidly at a certain evaporation time,

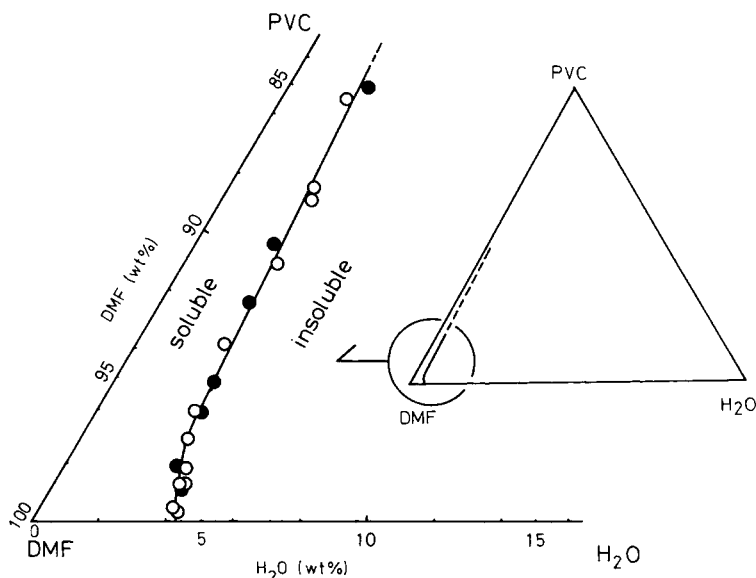


Fig. 2. Cloud point curve at 25°C for PVC/DMF/H₂O. PVC M_n : (●) 26900; (○) 48400.

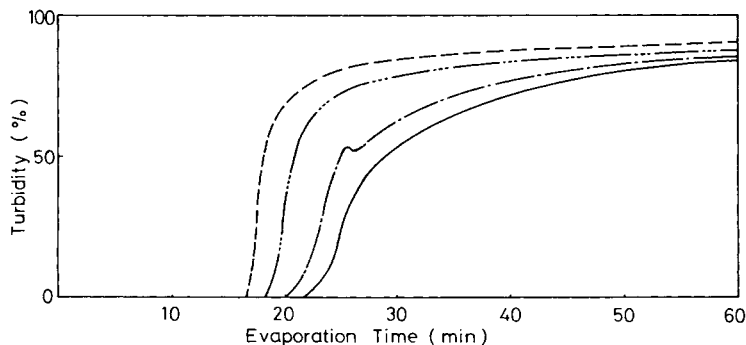
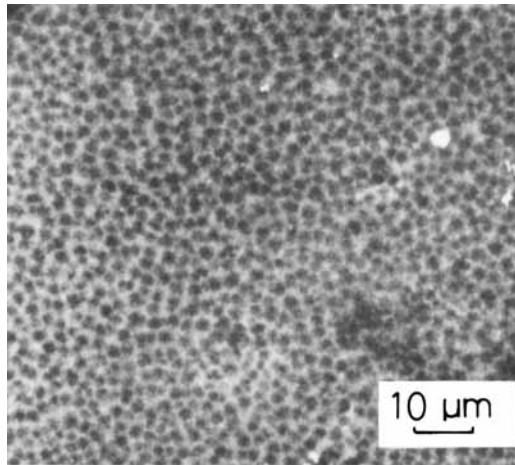
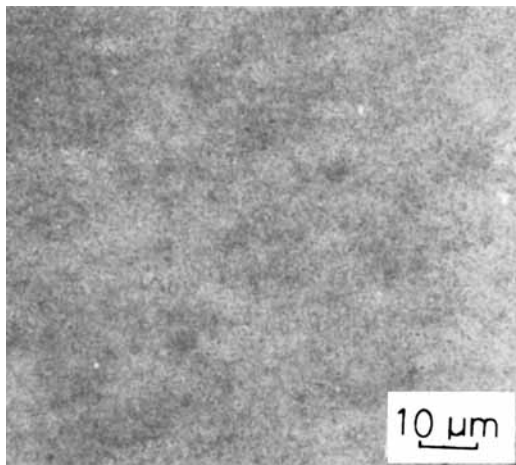


Fig. 3. Relationship between evaporation time and turbidity in the membrane formation processes prepared from PVC of various molecular weights: (—) 26,900; (— · — ·) 38,200; (---) 48,400; (— · —) 67,100. Casting condition: 25°C, 50% R.H., 10 wt. %.



(a)

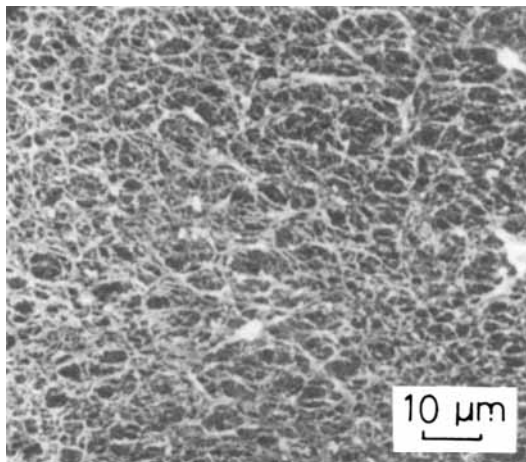


(b)

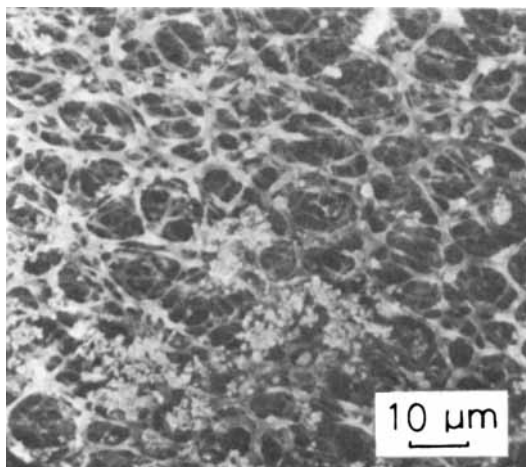
Fig. 4. SEM photographs of the porous membranes from PVC at (a) 5 min, (b) 20 min, (c) 22 min, (d) 25 min, (e) 38 min, (f) 60 min, (g) 5 min, and (h) 60 min.

which is called the “cloud beginning time” here, and the turbidity curve shows a sigmoidal feature.

The turbidity curve indicates that three stages of membrane formation exist. The first is the early stage, where the turbidity of the casting solution can hardly be detected. Nevertheless, aqueous vapor in the atmosphere dissolves in the casting solution. The second is the transitional stage, where the turbidity shows a rapid increase and the progress of phase separation of the casting solution becomes visual. The third is the late stage: the turbidity increase slightly and becomes nearly constant. The “cloud beginning time” clearly distinguishes between the early and the transitional stages and is considered a measure of the rate of phase separation in the early stage. It is rather difficult, however, to find an obvious distinction between the transitional and the late stages.



(c)



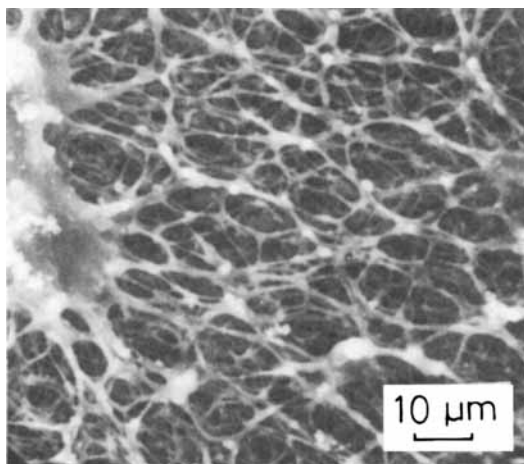
(d)

Fig. 4. (Continued from previous page.)

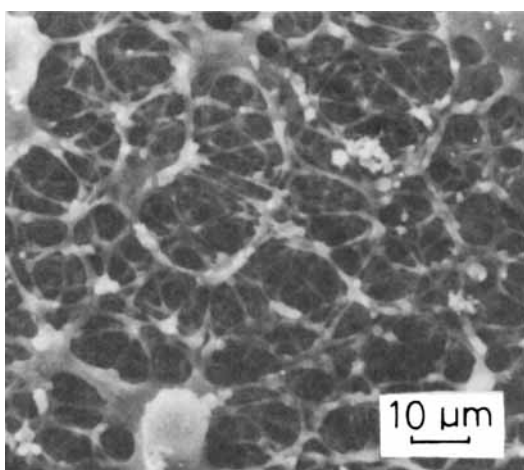
Effect of Phase Separation on Membrane Structure

Figure 4 shows the SEM photographs of the top surfaces and the cross sections of the membranes which were prepared at different evaporation times. In Figure 4(a), no pores are observed on the surface of the membrane. In Figure 4(b), micropores begin to appear. In Figures 4(b), (c) and (d), the micropores grow larger as the evaporation time becomes longer. Figures 4(e) and (f) show no more change. Figures 4(g) and (h) indicate a "finger-like" and "network" structure which are obtained by leaching at evaporation times of 5 and 60 min, respectively.

The above results show that the membrane structure is closely related to the three stages of membrane formation as observed by the turbidity. At the first stage, evaporation time from 0 to 20 min, the membranes have a nonporous skin layer and a finger-like structure, Figures 4(a) and (g). At the transitional stage, corresponding to an evaporation time of 20 to 30 min, nascent and growing mi-



(e)



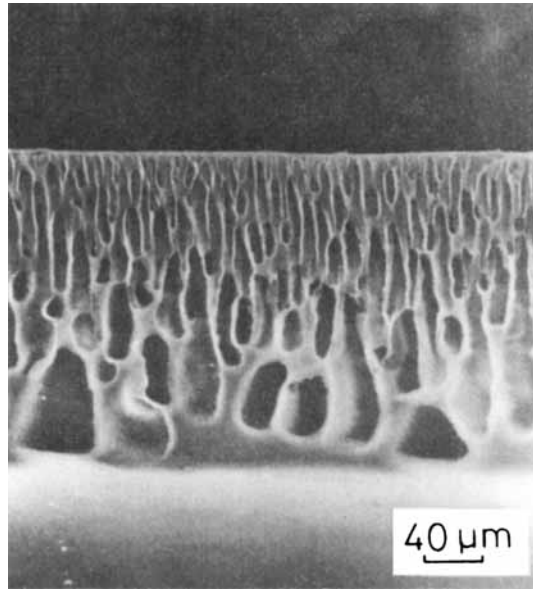
(f)

Fig. 4. (Continued from previous page.)

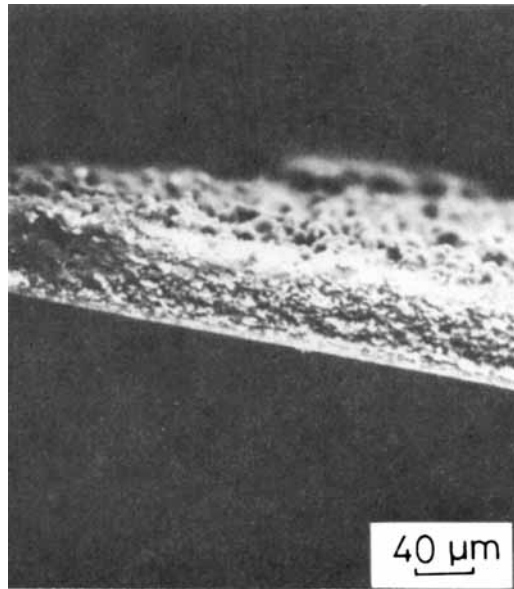
cropores are observed on the surface, Figures 4(b), (c) and (d). The late stage, after 30 min of evaporation time, Figures 4(e), (f), and (h), does not show any marked change in the network structure, and the phase separation becomes saturated.

Relation Between “Cloud Beginning Time” and Relative Humidity

The relative humidity influences the cloud beginning time, as shown in Figure 5. The cloud beginning time becomes shorter with increasing relative humidity and more diluted casting solutions, but it becomes remarkably longer at less than 30% R.H. The aqueous vapor dissolves faster into the surface layer of the casting solution when the R.H. is higher. This makes the phase separation faster and the cloud beginning time shorter.



(g)



(h)

Fig. 4. (Continued from previous page.)

Although the water content required for phase separation is about 3 wt. % independent of the PVC concentration as shown in Figure 2, the cloud beginning time increases as the PVC concentration increases. This means that the rate of aqueous absorption and/or the rate of PVC coagulation becomes slower as the PVC concentration increases.

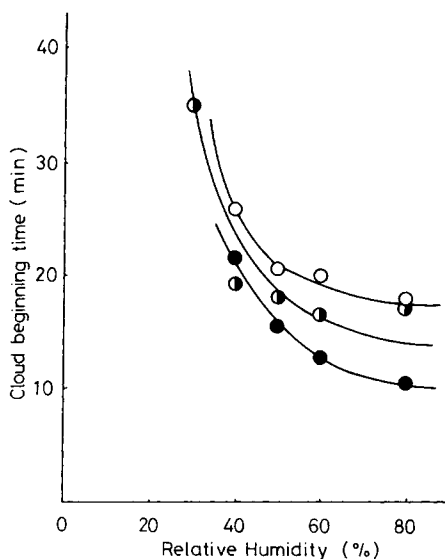


Fig. 5. Cloud beginning time during membrane formation processes for various PVC concentrations: (●) 6 wt. %; (◐) 8 wt. %; (○) 10 wt. %.

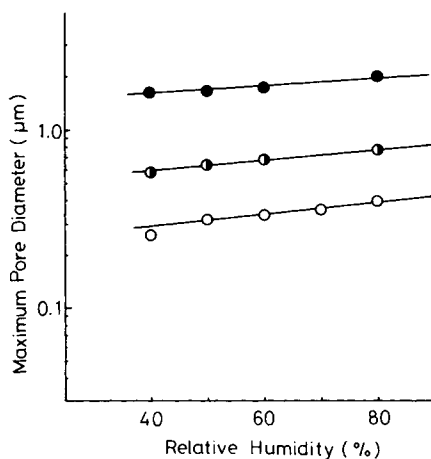


Fig. 6. Relationship between relative humidity and maximum pore diameter. PVC concentration: (●) 6 wt. %; (◐) 8 wt. %; (○) 10 wt. %.

Casting Conditions and Membrane Properties Obtained at Late Stage

The maximum pore diameters obtained at the different PVC concentrations are shown in Figure 6. The R.H. has only a slight effect on the maximum pore diameter, although the R.H. influences the cloud beginning time as shown in Figure 5. Therefore, noticing that the above membranes were leached at the late stage of the membrane formation process, one can consider that the states of phase separations under the various humidities are similar to each other at the late stage of evaporation, even if the rates of phase separation in the early and transitional stages depends greatly on the R.H.

The maximum pore diameters as a function of the concentration for different molecular weights of PVC are shown in Figure 7. The maximum pore diameter

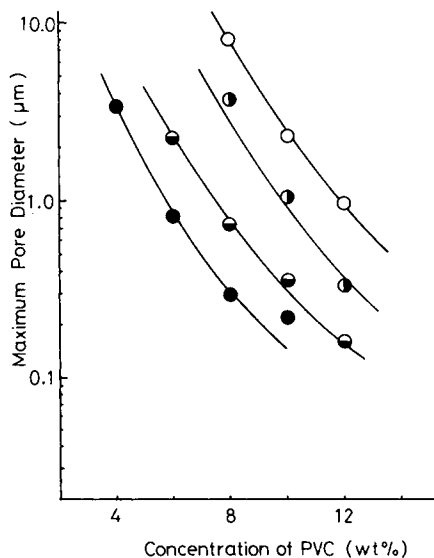


Fig. 7. Influence of concentration and molecular weight of PVC on maximum pore diameter. PVC M_n : (O) 26,900; (◐) 38,200; (◑) 48,400; (●) 67,100.

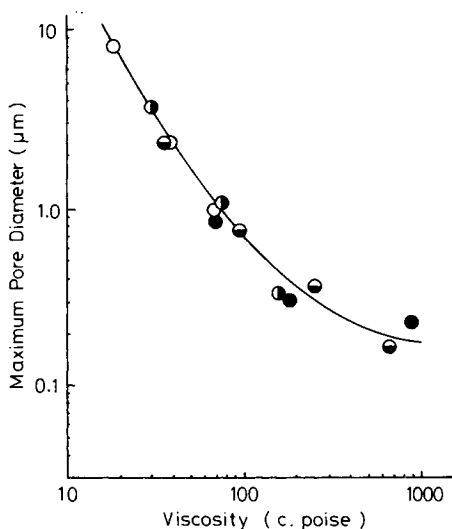


Fig. 8. Maximum pore diameter as function of viscosity of PVC solutions. PVC M_n : (O) 26,900; (◐) 38,200; (◑) 48,400; (●) 67,100.

becomes smaller either as the PVC concentration of the casting solution increases or as the molecular weight of PVC increases. Since these membranes are obtained at the late stage of the membrane formation processes and have reached the final structure at which phase separation ceases, the above change in maximum pore diameter with concentration and molecular weight may reflect the change in the membrane structure at the late stage.

GENERAL DISCUSSION

The above results suggest that the membrane structures are formed and immobilized as follows:

1. The phase separation and cloud phenomenon start as the result of aqueous vapor absorption. The PVC molecules begin to coagulate.
2. The phase separation progresses and the coagulated PVC is finally immobilized.
3. The membrane structures are fixed by leaching in a water bath.

The membrane structure is determined by the stage of the phase separation just before leaching. When the casting solution is leached before being cloudy, a finger-like structure with a surface skin layer is obtained. In this case, the polymer phase is forced to separate from the solvent by water leaching. The pattern of the finger-like structure indicates the direction of the extraction of excess solvent. On the other hand, a network structure is obtained after phase separation has occurred, namely, at the late stage of the membrane formation process.

The maximum pore diameter of the membrane obtained at the late stage depends strongly upon the molecular weight and the PVC concentration but little upon the relative humidity. These dependences of membrane structure (maximum pore diameter) cannot be interpreted in terms of the difference in the compositions of the casting solution (PVC/DMF/H₂O) at the cloud point and/or the cloud beginning time. This is because composition at the cloud point is independent of the molecular weight and the PVC concentration, according to the cloud point curve (Fig. 2), and cloud beginning times have a close relationship to the relative humidity (Fig. 5).

One should note that the membrane structure is determined by the state of the phase separation just before leaching, as previously mentioned. Therefore, the micropore dimension may also be determined by the membrane structure just before leaching. In general, two important features of phase separation are correlation length of concentration fluctuation in the early stage and rate of separation throughout. They are basically determined by thermodynamic stability and mobility. Then, if the thermodynamic stability is the secondary factor in the present experimental conditions, the maximum pore dimension should be determined by the mobility.

This provisional condition is realized in Figure 8, which shows the relationship between the viscosity as a measure of the mobility of PVC molecules in the casting solution and the maximum pore diameter. Obviously there is a good correlation between them. Other casting conditions such as evaporation time and relative humidity have little effect upon the membrane structure. These factors should be minor in the membrane formation at the late stage in comparison with the profound effects of the mobility of the casting solution, within the present experimental conditions.

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