Membrane Formation via Phase Separation Induced by Penetration of Nonsolvent from Vapor Phase. I. Phase Diagram and Mass Transfer Process

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Received 13 October 1998; accepted 27 February 1999

ABSTRACT: The isothermal phase diagram for poly(vinylidene fluoride)/dimethyl formamide/water system was derived. The binodal and spinodal were calculated based on the Flory–Huggins theory and the calculated binodal was approximately in agreement with the experimental data of the cloud points. The isothermal crystallization line was also obtained according to the theory of melting point depression. Mass transfer of the three components during membrane formation by the precipitation from the vapor phase has been analyzed. During this process, phase separation of the polymer solution is induced by the penetration of water vapor in the solution. The calculated result on the changes of the cast film weights indicated the good agreement with the experimental data. The time-course of the polymer concentration profile in the film was calculated for various cases of different humidity of the vapor phase and different initial polymer concentration. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 159–170, 1999

Key words: membrane formation; mass transfer; phase separation; crystallization; poly(vinylidene fluoride)

INTRODUCTION

Porous polymeric membranes developed for the industrial applications such as microfiltration, ultrafiltration and reverse osmosis are mainly fabricated by phase separation process.¹ Phase separation of polymer solutions can be induced in several ways. Four different techniques² can be used such as immersion precipitation, air-casting of a polymer solution, precipitation from the vapor phase and thermally induced phase separation (TIPS).

In order to predict and control the membrane morphology such as pore diameter and porosity,

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membrane formation mechanism must be clarified. Phase separation techniques are governed by two complex phenomena of equilibrium thermodynamics and kinetics. The clarification of equilibrium thermodynamics enable us to know the stability borders of system and the type of the phase separation. Analysis on the kinetics gives insight into the stages of the phase separation process and the origin of the skin layer.

The immersion precipitation is most widely used for preparation of commercially available membranes. Reuvers et al.^{3,4} analyzed the mass transfer of components in the immersion precipitation process on the basis of earlier work of Cohen et al.⁵ Since then, several authors have computed the composition profile in the film prior to the phase separation.^{6–8} Tsay and McHugh improved the numerical model to investigate the

Journal of Applied Polymer Science, Vol. 74, 159-170 (1999)

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combined effect of the solvent evaporation and quench step on the membrane structure.⁹ Recently, mass transfer in systems with crystalline polymers have been analyzed,^{10,11} where solid–liquid phase separation, that is, crystallization^{12–14} occurs in addition to the liquid–liquid phase separation.

In air-casting process, on the other hand, a polymer is dissolved in a mixture of a volatile solvent and a less volatile nonsolvent. The evaporation of the solvent decreases the solubility of the polymer, which leads to the phase separation. Shojaie et al. developed a predictive model which incorporates coupled heat and mass transfer to describe the evaporation of both solvent and nonsolvent.¹⁵ They showed that the model can describe the wide range of structures associated with dry-cast membranes.¹⁶ We analyzed the mass transfer in the dry-cast process and simulated the polymer concentration profiles in the film during the membrane formation.¹⁷ Based on the calculated thermodynamic and kinetic properties, obtained membrane structures were discussed.

Precipitation from the vapor phase is another phase separation method. In this process, a polymer solution is cast as a thin film and placed in a vapor atmosphere where the vapor phase consists of a nolsolvent. Phase separation of the polymer solution is induced by the penetration of nonsolvent vapor into the solution. Although this method was used as early as 1918 by Zsigmondy,¹ very few reports exist in the literature on this phase separation method. Wijmans et al. prepared poly(2,6-dimethyl-1,4-phenyleneoxide) membrane by phase separation from the vapor phase using a vapor of octanol as a nonsolvent.¹⁸ Several types of membranes were found to be formed by changing the initial compositions in dope solutions. Kinetics of phase separation of poly(p-phenylenebenzobisoxazole) in methanesulfonic acid were examined by the time-resolved light scattering measurements.¹⁹ Diffusion of the water vapor into the polymer solution film resulted in phase separation. These solutions appeared to undergo a spinodal decomposition-like phase separation. Park et al. investigated the phase separation of polysulfone/N-methyl pyrrolidone system by introducing a precipitant (water) from the vapor phase.²⁰ The pore size was increased under a lower humidity and for a lower polymer concentration. The optical microscopy study showed that the pore sizes seemed to be determined by the coarsening in the late stage of the phase separation process. As far as we know, however, no quantitative analysis has been reported so far on this membrane formation process.

In this work, the formation of porous structure via phase separation induced by the penetration of nonsolvent from the vapor phase was investigated in poly(vinylidene fluoride) (PVDF)/dimethvlformamide (DMF, solvent)/water (nonsolvent) system. The crystallization of polymer must be considered as well as the liquid-liquid phase separation because PVDF is a crystalline polymer. The object of this work is to clarify the phase diagram and to calculate the mass transfer of components during this diffusion process for a better understanding of the effect of the preparation condition on the membrane morphology. Membrane structure will be discussed in Part II of this work based on the phase diagram and the calculated polymer concentration profiles.

THEORY

Construction of a Phase Diagram

The Gibbs free energy of mixing for ternary component system ΔG_m can be expressed according to the Flory–Huggins theory.^{21,22}

$$\Delta G_m / RT = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + g_{12} n_1 \phi_2 + g_{13} n_1 \phi_3 + g_{23} n_2 \phi_3 \quad (1)$$

Here, subscript 1, 2, 3 denote nonsolvent, solvent and polymer, respectively. n_i and ϕ_i are the number of moles and the volume fraction of component i. R and T denote the gas constant and temperature. g_{ij} is the interaction parameter between component i and j. As described below, constant values were used as g_{13} and g_{23} in this work.

When an equilibrium is established between two liquid phases, that is, a polymer-lean phase α and a polymer-rich phase β , the chemical potential difference $\Delta \mu_i$ of the component *i* in these two phases are equal:

$$\Delta \mu_i^{\alpha} = \Delta \mu_i^{\beta} \quad (i = 1, 2, 3) \tag{2}$$

The liquid–liquid miscibility gap in the ternary system can be calculated from eq. (2) and mass balance equations ($\Sigma \phi_i = 1$ for polymer-rean phase and polymer-rich phases) and thus, the binodal is obtained.

The equation for the spinodal is given by the following equation: 23

$$G_{22}G_{33} = (G_{23})^2 \tag{3}$$

where

$$G_{ij} = \{\partial^2 \Delta G_m^t / (\partial \phi_i \partial \phi_j)\} \nu_1 \tag{4}$$

 ΔG_m^t is the Gibbs free energy of mixing per unit volume and ν_i is the molar volume of component *i*. The spinodal can be calculated from eq. (3) and the mass balance equation if the interaction parameters are given.

According to the theory of melting point depression,²¹ the chemical potential of the polymer repeating unit in the crystalline state μ_u^c can be represented by

$$\mu_u^c - \mu_u^0 = -\Delta H_u (1 - T/T_m^0)$$
(5)

where μ_u^0 is the chemical potential of the polymer repeating unit in the standard state and ΔH_u and T_m^0 denote the heat of fusion of the polymer repeating unit and the melting point of pure polymer, respectively. The chemical potential of the polymer repeating unit in a polymer solution μ_u is given by eq. (6):

$$\mu_u - \mu_u^0 = (\partial \Delta G_m / \partial n_3)(\nu_u / \nu_3) \tag{6}$$

Here, ν_u is the molar volume per repeating unit in the polymer. The condition of equilibrium between crystalline polymer and the polymer in the solution can be expressed as follows:

$$\mu_{u}^{c} - \mu_{u}^{0} = \mu_{u} - \mu_{u}^{0} \tag{7}$$

By substituting eqs. (5) and (6) into eq. (7), we obtain the following equation for the melting point depression:

$$(1/T_m) - (1/T_m^0) = -(R/\Delta H_u)(\nu_u/\nu_1)$$

$$\times \{r \ln \phi_3 + r(1 - \phi_3) - \phi_1 - s\phi_2$$

$$+ (g_{13}\phi_1 + sg_{23}\phi_2)(\phi_1 + \phi_2) - g_{12}\phi_1\phi_2\} \quad (8)$$

Here, *r* and *s* denote ν_1/ν_3 and ν_1/ν_2 , respectively.

Evaluation of Interaction Parameters

It is assumed that the binary Flory–Huggins parameters g_{ij} are only dependent on the components i and j and not on the third component in the ternary situation. Solvent-nonsolvent interaction parameter g_{12} is now dependent on the following composition variable u_2 .

$$u_2 = \phi_2 / (\phi_1 + \phi_2) \tag{9}$$

Table IParameters Used in the Calculationof Phase Diagram

$\nu_1 \text{ [cm}^3/\text{mol]}$ $\nu_2 \text{ [cm}^3/\text{mol]}$	18.0 77.4
$ u_3 \text{ [cm^3/mol]} $ $ u_u \text{ [cm^3/mol]} $ $ s \text{ []} $	307000 36.8 0.233
$egin{array}{lll} r & [] \ \Delta H_u \; [{ m J/mol}]^{ m a} \ T_m^0 \; [{ m K}]^{ m a} \end{array}$	0.000059 5962 473

^a Ref. 27.

 g_{12} in DMF-water system was evaluated according to the following equation reported by Altena and Smolders.²²

$$g_{12}(u_2) = 0.50 + 0.04u_2 + 0.80u_2^2 - 1.20u_2^3 + 0.8u_2^4 \quad (10)$$

The nonsolvent-polymer interaction parameter g_{13} was determined from the swelling experiment by using eq. (11).²⁴

$$g_{13} = -\{\ln(1 - \phi_3) + \phi_3\}/\phi_3^2 \tag{11}$$

The obtained value was 2.09.

The solvent-polymer interaction parameter g_{23} can be roughly estimated from eq. (12) with the help of solubility parameter δ .²⁵

$$g_{23} = 0.35 + \nu_2 / (RT) (\delta_2 - \delta_3)^2 \tag{12}$$

Values²⁶ of 24.8 (MPa)^{1/2} of δ_2 and 23.2 (MPa)^{1/2} of δ_3 gave 0.43 as g_{23} . Other parameters used in the calculation of phase diagram are summarized in Table I.

Mass Transfer Model

Precipitation from the vapor phase is governed by a solvent and nonsolvent fluxes perpendicular to the film. Geometry for the mass transfer in this system is shown in Figure 1. The film consisted of polymer and solvent is placed in the atmosphere including nonsolvent. Thus, inflow of nonsolvent (component 1) into the film and out-flow (evaporation) of solvent (component 2) occur simultaneously. The polymer does not evaporate in the gas phase, that is, component 3 stays in the film. In order to describe the change of the polymer concentration profile with time, a ternary diffusion model is needed. If we assume a one-dimen-



Figure 1 Geometry for the mass transfer.

sional diffusion process and constant partial specific volume, the following expressions for the diffusion fluxes can be obtained.^{6,28}

$$j_{1}^{\dagger} = -D_{11}(\partial \rho_{1}/\partial z) - D_{12}(\partial \rho_{2}/\partial z)$$
(13)

$$j_{2}^{\ddagger} = -D_{21}(\partial \rho_{1}/\partial z) - D_{22}(\partial \rho_{2}/\partial z)$$
(14)

Here, j_i^{\ddagger} and ρ_i are the mass flux with respect to the volume-average velocity and the mass density of component *i*, respectively. D_{ij} is the appropriate phenomenological diffusion coefficient for the ternary system and *z* represents the position from the glass-facing surface shown in Figure 1. As described below, because ρ_1 is fairly lower than ρ_2 in this case, the following solvent flux equation in the quasi binary system (polymer-solvent system) was used instead of eq. (14) as first approximation.

$$j_2^{\ddagger} = -D_2(\partial \rho_2 / \partial z) \tag{15}$$

Here, D_2 is the mutual diffusion coefficient of the solvent in the binary system. If eq. (14) is used for the calculation, many parameters such as friction coefficients must be determined. Considering errors generated in the estimation of these parameters, we used eq. (15).

From eqs. (13) and (15), the following diffusion equations are given.⁶

$$\partial \rho_1 / \partial t = \partial \{ D_{11} (\partial \rho_1 / \partial z) + D_{12} (\partial \rho_2 / \partial z) \} / \partial z \quad (16)$$

$$\partial \rho_2 / \partial t = \partial \{ D_2 (\partial \rho_2 / \partial z) \} / \partial z$$
 (17)

Initial and boundary conditions are

$$t = 0 \qquad \rho_1 = \rho_{10}, \ \rho_2 = \rho_{20} \tag{18}$$

$$z = 0 \qquad \partial \rho_1 / \partial z = \partial \rho_2 / \partial z = 0 \tag{19}$$

$$= L(t) - D_{11}\partial \rho_1 / \partial z - D_{12}\partial \rho_2 / \partial_z$$

= $k_1 (\rho_{1g}^i - \rho_{1g}^{\infty})$
 $- D_2 \partial \rho_2 / \partial z = k_2 (\rho_{2g}^i - \rho_{2g}^{\infty})$ (20)

 \boldsymbol{z}

where L(t) is the membrane thickness at time tand k_i is the gas-side mass transfer coefficient of component i. ρ_{i0} , ρ_{ig}^i , ρ_{ig}^∞ are the initial mass density in the cast solution, the mass density in the gas phase at the air-film interface and that in the gas bulk phase, respectively. Provided that ideal gas behavior on vapor side and gas-liquid equilibrium at the air-film interface are assumed, ρ_{ig}^i can be related with activity a_i in the polymer solution as follows:

$$\rho_{ig}^{i} = a_{i} P_{i}^{0} / (V_{ig} P_{t}) \quad (i = 1, 2)$$
(21)

where P_t and P_i^0 are the total pressure and the saturated vapor pressure for pure component *i*, respectively. V_{ig} is the partial specific volume of component *i* in the gas phase. The activity a_i is related to the chemical potential as follows.

$$a_i = \exp\{\Delta \mu_i / (RT)\}$$
 $(i = 1, 2)$ (22)

The conservation equation of the polymer is given by

$$\int_{0}^{L(t)} \rho_3 \, dz = L_0 \rho_{30} \tag{23}$$

where subscript 0 denotes the initial value.

The membrane thickness L(t) changes with time t due to the evaporation of solvent and the penetration of nonsolvent. If the out-flow of solvent from the film is larger than the in-flow of nonsolvent, the membrane thickness decreases, whereas it increases in the opposite situation. In order to immobilize the interface position, the following coordination transformation was used.

$$\eta = z/L(t) \tag{24}$$

This coordination transformation and the substitution of the volume fraction ϕ_i by the mass density ρ_i give the following equations.

$$\frac{\partial \phi_1}{\partial t} = \frac{\eta}{L(t)} \frac{dL(t)}{dt} \frac{\partial \phi_1}{\partial \eta} + \frac{1}{L(t)^2} \frac{\partial}{\partial \eta} \left[D_{11} \frac{\partial \phi_1}{\partial \eta} + D_{12} \frac{V_1}{V_2} \frac{\partial \phi_2}{\partial \eta} \right]$$
(25)

$$\frac{\partial \phi_2}{\partial t} = \frac{\eta}{L(t)} \frac{dL(t)}{dt} \frac{\partial \phi_2}{\partial \eta} + \frac{1}{L(t)^2} \frac{\partial}{\partial \eta} \left[D_2 \frac{\partial \phi_2}{\partial \eta} \right]$$
(26)

$$t = 0; \ \phi_1 = \phi_{10}, \ \phi_2 = \phi_{20} \tag{27}$$

$$\eta = 0; \ \partial \phi_1 / \partial \eta = \partial \phi_2 / \partial \eta = 0 \tag{28}$$

$$\eta = 1; -D_{11}\partial \phi_1 / \partial \eta$$

- $D_{12}(V_1 / V_2) \partial \phi_2 / \partial \eta = k_1 L(t) V_1(\rho_{1g}^i - \rho_{1g}^{\infty})$
- $D_2 \partial \phi_2 / \partial \eta = k_2 L(t) V_2(\rho_{2g}^i - \rho_{2g}^{\infty})$ (29)

$$L(t) = L_0 \phi_{30} / \int_0^1 \phi_3 d\eta$$
 (30)

Here, V_i is the partial specific volume of component i in the film phase.

Determination of Model Parameters

The mutual diffusion coefficient of solvent in quasi-binary system $D_{\rm 2}$ was estimated based on the free volume theory by Vrentas and Duda.^{29,30} The self-diffusion coefficient of the solvent D_2^* is expressed as the following equation.

$$D_{2}^{*} = D_{20} \exp(-E/RT) \\ \times \exp\left\{-\frac{w_{2}V_{2}^{*} + w_{3}\xi V_{3}^{*}}{w_{2}(K_{22}/\gamma)(K_{32} + T - T_{g2})} \\ + w_{3}(K_{23}/\gamma)(K_{33} + T - T_{g3})\right\}$$
(31)

Here, D_{20} is the pre-exponential factor of the solvent, E is the energy per mole that a molecule needs to overcome attractive forces which constrain it to its neighbors, V_i^* and w_i are the specific critical hole free volume required for a jump and the weight fraction of component i, ξ is the ratio of molar volumes for the solvent and polymer jumping units. $K_{\rm 22}$ and $K_{\rm 32}$ are free-volume parameters for the solvent, while K_{23} and K_{33} are those for the polymer. γ is the overlap factor and $T_{\sigma i}$ is the glass transition temperature of component *i*. The relation between D_2^* and D_2 is given by eq. (32).^{31,32}

$$D_2 = D_2^* (1 - \phi_2)^2 (1 - 2g_{23}\phi_2) \tag{32}$$

The parameters in eq. (31) were estimated according to Zielinski and Duda's method.³² Those are summarized in Table II.

 D_{11} and D_{12} in eq. (25) are given by the following equations. 6,28

$$D_{11} = -\frac{V_1}{N_A^2 E_0} \left(E_{22} \frac{\partial \mu_1}{\partial \phi_1} - E_{12} \frac{\partial \mu_2}{\partial \phi_1} \right) \quad (33)$$

$$D_{12} = -\frac{V_2}{N_A^2 E_0} \left(E_{22} \frac{\partial \mu_1}{\partial \phi_2} - E_{12} \frac{\partial \mu_2}{\partial \phi_2} \right) \qquad (34)$$

Here, N_A is Avogadro's number and E_{ij} and E_0 are defined as

$$E_{12} = \frac{(1 - \phi_1)\zeta_{12}}{M_2\phi_3} - \frac{RTV_2}{N_A^2 D_{T1}\phi_3}$$
(35)

$$E_{22} = \frac{V_2 \phi_1 \zeta_{12}}{\nu_1 \phi_3} - \frac{RT V_2 (1 - \phi_1)}{N_A^2 D_{T2} \phi_2 \phi_3}$$
(36)

$$E_{0} = -\frac{\zeta_{12}^{2}}{M_{1}M_{2}\phi_{3}} + \frac{R^{2}T^{2}V_{1}V_{2}}{N_{A}^{4}D_{T1}D_{T2}\phi_{1}\phi_{2}\phi_{3}} \quad (37)$$

$$D_{T1} = \frac{RT}{N_A^2(\phi_2\zeta_{12}/\nu_2 + \phi_3\zeta_{13}/\nu_3)}$$
(38)

Table II Parameters in Eq. (31)

$V_{2}^{*} ({ m cm}^{3}/{ m g})^{ m a}$	0.926
$V_{3}^{*} (\text{cm}^{3}/\text{g})^{a}$	0.565
ξ ^b	1.10
$D_{20} \ ({\rm cm}^2/{\rm s})^{\rm c}$	$8.48 imes10^{-4}$
$K_{22}/\gamma \;({\rm cm}^3/({\rm g~K}))^{ m c}$	$9.76 imes10^{-4}$
$K_{32} - T_{g2} ({ m K})^{ m c}$	-43.8
$E (J/mol)^{d}$	0
$K_{23}/\gamma \;({ m cm}^3/({ m g~K}))^{ m e}$	$2.73 imes10^{-4}$
$K_{33} ({ m K})^{ m e}$	111
$T_{g3} \ (\mathrm{K})^{\mathrm{f}}$	238

^a V_2^* and V_3^* were estimated as the specific volumes of the diluent and polymer at 0 K, which can be obtained using group contribution methods.^{32,33}

^b $\xi = M_2 V_2^* / V_{2j}^{32}$ (M_2 : molecular weight of solvent, V_{2j} : molar volume of polymer jumping unit). V_{2j} was estimated by the equation of $V_{2j} = 0.6224T_{g3} - 86.95^{-32}$ ^c These values were determined by Dullien's equation³² based on viscosity Data^{34,35} for the pure diluent in the as-

sumption of negligible energy effects (E = 0).

¹ Ref. 32.

^e These values were determined by WLF equations.³² The polymer WLF parameters at 298 K were estimated from average values at glass transition temperature available in the reference.36

^f Ref. 37.

$$D_{T2} = \frac{RT}{N_A^2(\phi_1\zeta_{12}/\nu_1 + \phi_3\zeta_{23}/\nu_3)}$$
(39)

Here, M_i is the molecular weight of component i and ζ_{ij} is the friction coefficient between component i and j.

In order to obtain D_{11} and D_{12} , three friction parameters ζ_{12} , ζ_{23} , and ζ_{13} must be determined. ζ_{12} is related to the mutual diffusion coefficient in solvent-nonsolvent system D_{12} as³⁸

$$\zeta_{12} = \frac{\nu_2 \phi_1}{N_A^2 D^{12}} \left(\frac{d\mu_1}{d\phi_1} \right)$$
(40)

If ζ_{12} is assumed to be independent of $\phi_1/(\phi_1 + \phi_2)$ and to be equal to $\zeta_{12}(\phi_1 = 1)^4$, eq. (41) is derived from eq. (40).

$$\zeta_{12} = \frac{\nu_1 R T}{N_A^2 D^{12}(\phi_1 = 1)} \tag{41}$$

 $D^{12}(\phi_1 = 1)$ is estimated as 1.12×10^{-5} cm²/s by Wilke–Chang equation.³⁹ ζ_{23} is also related to the mutual diffusion coefficient in solvent-polymer system D_2 .

$$\zeta_{23} = \frac{\nu_3 \phi_2}{N_A^2 D_2} \left(\frac{d\mu_2}{d\phi_2} \right) \tag{42}$$

The following equation can be used to relate the mutual diffusion coefficient D_2 and self diffusion coefficient D_2^* .^{31,40}

$$D_2 = D_2^* \phi_3 \phi_2 \frac{d(\mu_2/RT)}{d\phi_2}$$
(43)

Substituting eq. (43) into eq. (42) yields the following equation:

$$\zeta_{23} = \frac{\nu_3 R T}{D_2^* \phi_3 N_A^2} \tag{44}$$

 ζ_{12} is empirically related to ζ_{23} by the following equation:^{4,6,8}

$$\zeta_{13} = C(\nu_1/\nu_2)\zeta_{23} \tag{45}$$

Here, C is the constant parameter. The value of 0.5 was chosen in this work, which is the same as that used by Reuvers and Smolders.⁴

The gas-side mass transfer coefficient k_i (i = 1, 2) was estimated by eq. (46) because the process

Table IIIParameters Used in the Estimationof k and Used in the Analysis ofMass Transfer Process

$D_{1g} \ ({\rm cm}^2/{\rm s})^{\rm a}$	0.267
$D_{2g}^{'} (\text{cm}^{2}/\text{s})^{\text{b}}$	0.023
μ_{g} (Pa s) ^c	$1.85 imes10^{-5}$
$\rho_g^{(c)}$ (g/cm ³) ^c	$1.18 imes10^{-3}$
$ au_1^{\mathrm{d}}$	0.413
$ au_2^{ m ~d}$	-1.65
$L_c \ (\mathrm{cm})^{\mathrm{e}}$	1.0
$P_1^0 (\text{atm})^{\text{f}}$	0.0313
$P_2^0 (\text{atm})^{\text{a}}$	$4.97 imes10^{-3}$
$V_{1g} \ ({\rm cm}^3/{\rm g})^{\rm d}$	1358
$V_{2g}^{}~(\mathrm{cm^{3}/g})^{\mathrm{d}}$	335

^a Ref. 42.

^b Estimated from Chapman-Enskog equation.⁴³

^c Value for air.⁴⁴

 $^{\rm d}$ Calculated by assuming the ideal gas.

^e Hydraulic diameter of cast film.

^f Ref. 45.

was carried out under almost free convection condition.⁴¹

$$k_i L_c y_{\rm air}^{lm} / D_{ig} = 0.54 (G_r S_c)^{0.25}$$
 (46)

$$G_r = L_c^3 \rho_g^2 g \left| \tau_i (y_{ig}^i - y_{ig}^\infty) \right| \tag{47}$$

$$S_c = \mu_g / (\rho_g D_{2g}) \tag{48}$$

Here, L_c and y_{air}^{lm} denote the characteristic length of the cast film surface and the logarithm mean mole fraction difference of air. D_{ig} , ρ_g and μ_g are the mutual diffusion coefficient of component i in the gas phase, total mass density of the gas phase and viscosity of the gas, respectively. y_{ig}^i and y_{ig}^{∞} are the mole fraction of component i at air-film interface and that in the gas bulk phase. g is the gravity constant and coefficient τ_i is given by $-(1/\rho_g)(\partial \rho_g/\partial y_{ig})_{P,T}$. The parameters used for the calculation of k_i are summarized in Table III along with other parameters.

EXPERIMENTAL

Polymer and solvent used were poly(vinylidene fluoride) (Aldrich Chemical Co., M_w : 534000) and dimethyl formamide (Nacalai Tesque Inc.). Nonsolvent was water vapor. The solvent of analytical grade was used without further purification.

Mixture of polymer and solvent was cast on the glass plate with the thickness of 256 μ m and the cast film was put on the balance placed in the

chamber in which temperature and humidity were set at 298 K and the prescribed value (10%, 20%, and 40%), respectively. The humidity was controlled by a condenser and a supersonic waves humidifier (Matsushita Electric Co., FE-05KYC). Changes of the film weight accompanied with the evaporation of DMF and the penetration of water vapor were monitored.

To determine the cloud point curve, the polymer solutions (polymer concentration: 3, 5, 10 and 15 wt %) were prepared at 298 K. Under the constant polymer weight fraction, a series of solutions with the different nonsolvent weight fractions were prepared. The cloud point was determined by measuring the turbidity of the solution at 500 nm by a spectrophotometer (Hitachi Co., Ltd., U-2000). For every cases, turbidity occurred immediately. Because the polymer crystallization needs the induced time, turbidity caused by solidliquid phase separation is usually observed after long times such as several hours.¹³ The immediate occurrence of turbidity in this case indicates that it is caused by liquid-liquid phase separation rather than solid-liquid phase separation. Actually, as shown in Figure 2, the crystallization line lies in the fairly higher polymer concentration region, compared with the region of the cloud point experiments.

Crystallization temperature was measured by a Perkin–Elmer DSC-7. 3–5 mg samples were prepared by weighing the appropriate amount of PVDF and solvent/nonsolvent mixture directly into an aluminum DSC pan. Homogeneous solution was prepared by heating the sealed pan at 120° C for 10 min, followed by cooling into -10° C with the rate of 10° C/min to induce crystallization. The onset of the exothermic peak during the cooling was taken as the dynamic crystallization temperature.

RESULTS AND DISCUSSION

Phase Diagram

The calculated binodal, spinodal and crystallization line are shown in Figure 2. This figure is a part of the enlarged triangle coordinate. The binodal is roughly parallel with the polymer-solvent axis and close to the axis. This means that even in the addition of small amount of water, liquid-liquid phase separation occurs. The circles in Figure 2 are the experimental data for the cloud point. These data are approximately in agreement with the binodal. Soh et al. calculated the phase diagram for PVDF/DMF/octanol system.⁴⁶ Their binodal is located farther from the polymer-solvent axis than our binodal. The difference in the kind of nonsolvent will lead to the difference in the locations of the binodals. Also included in this figure are the calculated spinodal and tie line when the binodal crosses over the crystallization line.

Figure 3 shows dynamic crystallization temperature T_c measured by DSC for various polymer composition ϕ_3 . Pure DMF and mixture of DMF and water (96:4) were used in Figure 3(a)and Fig. 3(b), respectively. Similar plots have been done in the systems cellulose acetate/dioxane/water⁴⁷ and poly(2,6-dimethyl-1,4-phenyleneoxide)/trichloroethylene/ethanol48 although the melting temperatures were plotted instead of the crystallization temperatures. As can be seen in Figure 3, the crystallization temperature increased almost linearly with the increase of ϕ_3 . This tendency is in agreement with relations between the melting temperature and ϕ_3 in the previous works.^{47,48} The polymer volume fractions at the crystallization temperature of 25°C can be estimated by extrapolating the lines shown in Figure 3(a) and (b). The obtained compositions in the crystallization are plotted in Figure 2 as open squares. The crystallization line calculated



Figure 2 Phase diagram for three component system. (\bigcirc) observed cloud point, (\square) estimated crystalline temperature from Figure 3, (\blacksquare) calculated critical point. Tie line in this figure is the line when the binodal crosses over the crystallization line.



Figure 3 Dynamic crystallization temperature measured by DSC.

by eq. (8) shows the equilibrium condition, whereas it is well known that polymer crystallization is a highly nonequilibrium process. Although the experimental crystallization temperatures are the kinetic data, these do not deviate so much from the calculated line.

Calculation Results of Mass Transfer Process

Figure 4 shows the changes of the cast film weights during the precipitation process from the vapor phase. The ordinate is a dimensionless cast film weight, which is defined as the film weight at certain time divided by the initial film weight. For all cases in different polymer concentrations, the film weight decreases slower as the humidity in the vapor phase increases. This is because the amount of water penetration into the film increases. Especially in the case of the polymer concentration of 20 wt % and the humidity of 40%, the dimensionless weight increased over unity in



Figure 4 Changes of the cast film weights during the precipitation process.



Figure 5 Calculated concentration profiles of PVDF, DMF and water. Initial polymer concentration: 10 wt %, humidity: 20%.

the initial stage of the process. This means that the inflow of water vapor into the film is larger than the outflow (evaporation) of the solvent in the initial stage. In the constant humidity conditions, the decrease in the film weight becomes faster with the decrease of the polymer concentration. This is due to both the larger amount of the solvent in the film and the lower viscosity of the solution which leads to the higher diffusivity. The solid lines in this figure are the calculated results and are approximately in agreement with the experimental data. This agreement demonstrates the validity of the assumption introduced in the calculation of the mass transfer process. However, the film weight versus time predictions are relatively worse as the polymer concentration increases. Generally, it becomes more difficult to predict physical and chemical properties of polymer solutions as the polymer concentration in the solution becomes higher. This may be the reason for the worse prediction in the higher polymer concentration cases.

Figure 5 shows the calculated concentration profiles of PVDF, DMF, and water. The abscissa in this figure is the dimensionless film thickness and right side and left side of this figure correspond to the air-facing (top) surface and glassfacing (bottom) surface, respectively. The solvent fraction decreases at the top surface because of the evaporation into the gas phase, whereas the penetration of water vapor into the film leads to the increase of the water fraction at the top surface. The water volume fractions are fairly low compared with the DMF or polymer volume fractions.

The calculated results on the relation of the polymer volume fraction and the film thickness are shown in Figure 6. In all cases, similar tendency was obtained as follows. At the initial stage of the process, only the polymer volume fraction near top surface increases, while that at the bottom surface remains unaltered. Then, the polymer volume fraction near the bottom surface starts to increase accompanying the decrease in the film thickness. Finally, the flat concentration profile is formed and then whole polymer concentration increases with the time. As the humidity increases, the film weight decreased slowly as shown in Figure 4, which takes longer time to become the flat concentration profile (Figs. 6(a), (b), and (c)). The flat profile was obtained relatively faster when the initial polymer concentra-



Figure 6 Calculated results on the relation of the polymer volume fraction and the film thickness.

tion is higher (Figs. 6(b) and (d)). Figure 6(c)shows that the polymer volume fraction at the certain position inside the film becomes lower than the initial polymer concentration in the case of humidity of 40%. This means that the water flux at that point is higher than the solvent flux. As the humidity increases, a driving force for the water flux increases. This may bring about the higher water flux than the solvent flux at that point. In all cases, because the polymer concentration at the top surface is not so high, compared with the initial concentration even at the initial stage. Thus, isotropic structure rather than asymmetric structure is expected in this experimental condition. The obtained membrane morphology will be discussed in the second part of this study.

CONCLUSIONS

Formation of porous structure via phase separation induced by the penetration of nonsolvent for the vapor phase was investigated in PVDF/DMF/ water system. The isothermal phase diagram for this three component system was derived. The binodal and spinodal were calculated based on the Flory–Huggins theory. It was found that the liquid–liquid phase separation can occur by the addition of small amount of nonsolvent. The calculated binodal was approximately in agreement with the experimental data of the cloud point. The isothermal crystallization line was also obtained according to the theory of melting point depression. The dynamic crystallization temperature measured by DSC was found not to deviate so much from the calculated equilibrium crystallization line.

Mass transfer of the three components during membrane formation by the precipitation from the vapor phase has been studied. The experimental data on the changes of the cast film weights were well analyzed by this calculation. The calculated polymer concentration profiles showed that only the polymer volume fraction near the top surface increases at the initial stage, then the flat profiles is formed and the whole polymer concentration increases with time. Because the polymer concentration at the top surface is not so high compared with the initial concentration even at the initial stage, isotropic structure is expected in this experimental condition.

NOMENCLATURE

- activity of component i a_i
- Ċ constant defined in eq. (45)
- D_{ig} mutual diffusion coefficient of component i in gas phase (m^2/s)
- appropriate phenomenological diffusion D_{ii} coefficient for ternary system (m^2/s)
- mutual diffusion coefficient of solvent in D_2 the binary system (m^2/s)
- D_2^* self diffusion coefficient of solvent in the binary system (m^2/s)
- $D_{20} \\ D^{12}$ pre-exponential factor of solvent (m^2/s)
- mutual diffusion coefficient in solventnonsolvent system (m^2/s)
- Eenergy required to overcome attractive forces from neighboring molecules (J/mol)
- E_0 variable defined in eq. (37)
- E_{ii} variable defined in eqs. (35) and (36)
- G_{ij} differential equation defined in eq. (4)
- ΔG_m Gibbs free energy of mixing (J)

 G_r Grashof number

- gravity constant (m/s^2) g
- thermodynamic interaction parameter be g_{ij} tween component i and j
- ΔH_u heat of fusion of polymer repeating unit (J/mol)
- j_i^{\ddagger} mass flux with respect to the volume average velocity $(g/(sm^2))$
- solvent free volume parameter $(m^3/(gK))$ K_{22}
- K_{32} solvent free volume parameter (K)
- K_{23} polymer free volume parameter (m³/(gK))
- K_{33} polymer free volume parameter (K)
- k_i gas-side mass transfer coefficient of component i (m/s)
- L_c characteristic length of cast film (m)
- L_0 initial membrane thickness (m)
- L(t)membrane thickness at time t (m)
- M_{i} molecular weight of component i (g/mol)
- N_A Avogadro's number
- $n_i \\ P_i^0$ number of moles of component $i \pmod{i}$
- saturated vapor pressure for pure component *i* (atm)
- P_t total pressure (atm)
- R gas constant (J/(mol K))
- r v_1 / v_3
- S_c Schmidt number
- v_1 / v_2 s

- Т temperature (K)
- T_{c} dynamic crystallization temperature (K)
- T_{gi} glass transition temperature of component i (K)

melting point of polymer solution (K)

 $T_m T_m^0$ melting point of pure polymer (K)

 $\phi_2/(\phi_1 + \phi_2)$ u_2

- V_i partial specific volume of component i in film phase (m^3/g)
- V_i^* specific critical hole free volume required for a jump of component i (m³/g)
- V_{ig} partial specific volume of component i in gas phase (m^3/g)
- V_{2i} molar volume of polymer jumping unit (m^3/mol)
- $w_i y_{air}^{lm}$ weight fraction of component i
 - logarithm mean mole fraction difference of air
 - mole fraction of component *i* in gas phase
 - vertical position coordinate relative to casting surface (m)
- overlap parameter γ

 y_{ig}

 δ_i

 ν_i

 ρ_g

z

- solubility parameter of component i $(MPa^{1/2})$
- friction coefficient between component iζ_{ii} and $j (\text{gm}^3/\text{s})$
- dimensionless position coordinate defined η in eq. (24)
- chemical potential of component i in mix- μ_i ture state (J/mol)
- viscosity of gas phase (Pa s) μ_g
- chemical potential of polymer repeating μ_{u} unit in polymer solution (J/mol)
- μ_u^c chemical potential of polymer repeating unit in crystalline state (J/mol)
- μ_u^0 chemical potential of polymer repeating unit in standard state (J/mol)
- $\Delta \mu_i$ difference between chemical potential of component i in mixture and pure state (J/mol)
 - molar volume of component i (m³/mol)
- molar volume per repeating unit in the ν_u polymer (m³/mol)
- ratio of molar volumes for solvent and ξ polymer jumping unit
 - total mass density of gas phase (g/m³)
- mass density of component i (g/m³) ρ_i
- mass density of component i in gas phase ρ_{ig} (g/m^3)
- parameter accounting for effect of concen au_i tration profile on gas phase density of component *i*

 ϕ_i volume fraction of component *i*

Subscript

- 0 initail value
- 1 nonsolvent
- 2 solvent
- 3 polymer

Superscript

- *i* air-film interface
- α polymer-lean phase
- β polymer-rich phase
- ∞ gas bulk phase

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