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Equilibrium Thermodynamics of a Quaternary Membrane-Forming System with Two Polymers. 2. Experiments

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ABSTRACT: Concentration-dependent binary Flory–Huggins interaction parameters belonging to the quaternary system poly(ether sulfone) (PES)–poly(vinylpyrrolidone) (PVP)–*N*-methylpyrrolidone (NMP)–water are determined by means of high-pressure osmometry. The interaction parameter between PVP and water was in accordance with literature values. The interaction parameters between PES and NMP and between PVP and NMP were found to be slightly concentration dependent; the values indicate near-Θ conditions for both polymers in the solvent. The binary interaction parameter between the polymers PES and PVP is estimated from ternary osmotic measurements and found to be quite low: between −0.5 and −1.0. This is in accordance with earlier findings. Cloud point curves were evaluated experimentally and theoretically.[1] The agreement between theory and experiment was qualitative.

Introduction

The thermodynamics of a polymeric system are determined by its parameters: the molecular weights of the components and the interaction parameters between the components.[2] The interaction parameters are a measure of the enthalpic interaction between the components; moreover, they contain a nonideality term. Their determination can be performed in a number of ways. Well known are static light scattering[3] and osmometry.[4] Especially the latter method is also suitable for measuring concentrated polymer solutions.

Studied here is the quaternary system poly(ether sulfone)–poly(vinylpyrrolidone)–*N*-methylpyrrolidone–water. Solutions prepared from these components are used to prepare microfiltration and ultrafiltration membranes with outstanding properties.[5–9]

It is known that PES and PVP blend homogeneously.[5] Further, glass transition measurements on homogeneous blends indicate a strong interaction between the polymers.[5] These determinations were all done on the binary system PES–PVP. For the study of the formation of membranes by immersion precipitation, it is, however, essential that at least an estimate of the interaction between the two polymers can be made in the presence of a solvent. Measurements of the interaction of the pure polymeric blend (e.g., by X-ray scattering experiments[10]) do not yield information that can be extrapolated to a solution of 30 wt % of total polymer in a solvent.

The method that was chosen is as follows. First the binary systems PES–NMP and PVP–NMP are measured by osmometry by a procedure that is similar to the one originally developed by Altena.[4] Then the ternary system PES–PVP–NMP is measured by the same method. Using the Flory–Huggins theory, one is able to describe the ternary situation from binary interactions. With the use of the binary interaction parameters for PES–NMP and PVP–NMP, we can obtain an estimate of the interaction between PES and PVP in a solution of NMP.

Altena[4] used high-pressure osmometry to study ternary systems consisting of polymer, solvent, and nonsolvent at high polymer concentrations. In these systems, nonsolvent and solvent are in both compartments. In our case, we use two polymers that are present in only the high-pressure side of the cell. Therefore, the theory involved is different from Altena's treatment.

To maintain consistency with earlier work,[1] the following substance indices are used: 1, water (nonsolvent); 2, NMP (solvent); 3, poly(ether sulfone); 4, poly(vinylpyrrolidone). For this system, six binary interaction parameters should be determined: g_{12}, g_{13}, g_{23}, g_{34}, g_{14}, and g_{24}. In this work the latter four will be determined or estimated. The first two are known already from Tkacik and Zeman.[18]

Theory of Osmotic Measurements

Binary Systems. The modified Flory–Huggins theory gives the following relation for the chemical potential of mixing of the solvent in a polymeric solution:

$$\frac{\Delta\mu_2}{RT} = \ln \varphi_2 + (1-\varphi_2)\left(\frac{\bar{v}_3 M_3 - \bar{v}_2 M_2}{\bar{v}_3 M_3}\right) + (1-\varphi_2)^2\left(\frac{\partial \varphi_2 g_{23}}{\partial \varphi_2}\right) \tag{1}$$

in which φ_i is the volume fraction of component i, $\bar{v}_i$ is the specific volume, M_i is the molar mass of component i, and g_{23} is the (concentration dependent) interaction parameter between components 2 and 3. The chemical potential of mixing of the solvent given by eq 1 is related to the osmotic pressure relative to the pure solvent $\Delta\pi$:

$$\frac{\Delta\mu_2}{RT} = -\Delta\pi\frac{\bar{v}_2 M_2}{RT} \tag{2}$$

The osmotic pressure is measured; all other parameters in eqs 1 and 2, except the interaction parameter, g_{23}, are known. Hence the value of g_{23} can be found from relations 1 and 2.

Ternary Systems. Analogous to the binary situation, the chemical potential of mixing of the solvent can be derived for the situation in which two polymers (3 and 4) are dissolved (relation analogous to Reuvers[11]):

$$\frac{s\Delta\mu_2}{RT} = \ln \varphi_2 - \varphi_4 - r\varphi_3 + (s + g_{24}\varphi_4 + s g_{22\varphi 3})(1-\varphi_2) - g_{34}\varphi_3\varphi_4 + \varphi_4 w_2(1-w_2)\frac{\partial g_{24}}{\partial w_2} + s\varphi_3 v_2(1-v_2)\frac{\partial g_{23}}{\partial v_2} \tag{3}$$

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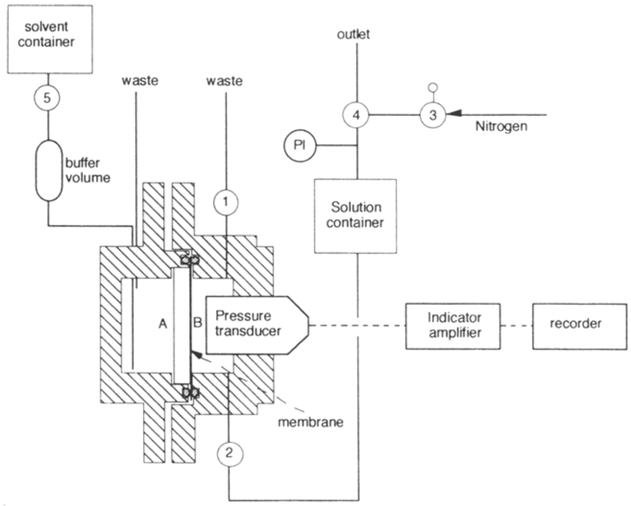

Figure 1. Experimental setup of the osmometer. Circles represent valves. Side A is the low (atmospheric)-pressure side, and side B is the high-pressure side. The expected pressure was preset with valve 3 before each measurement. The complete setup was immersed in a thermostated bath kept at 298 K.

The symbols are[1,12]

$$s = \frac{\bar{v}_4 M_4}{\bar{v}_2 M_2}; \qquad r = \frac{\bar{v}_4 M_4}{\bar{v}_3 M_3} \tag{4}$$

and

$$v_2 = \frac{\varphi_2}{\varphi_2 + \varphi_3}; \qquad w_2 = \frac{\varphi_2}{\varphi_2 + \varphi_4} \tag{5}$$

It is assumed that the interaction parameters are purely binary, i.e., that g_{23} is solely dependent on v_2 and that g_{24} is solely dependent on w_2.

The value of the chemical potential difference (as given by relation 3) is obtained by measuring the osmotic pressure difference of a solution containing polymers 3 and 4 compared to the pure solvent. By using relations 2 and 3 together, the value of g_{34} can be found.

Interactions that are ternary in nature (a so-called ternary interaction parameter g_{234}) are neglected in relation 3. The results may be influenced by this assumption.

Experimental Section

The Osmometer. As was shown by Staverman,[12] special care should be taken to ensure that measurements are performed under equilibrium conditions instead of under conditions of a constant (small) flux through the membrane. A membrane was selected that only swells a few percent in the solvent used (NMP). It was found that Cuprophan membranes fulfill the requirements, while being resistant enough to enable long-term experiments.

The experimental setup is represented in Figure 1. Before the measurement, valves 1, 2, and 3 are opened (valve 4 is set into the position allowing transport to the solution container). A pressure is applied on the polymer solution in the solution container (up to 8 bar). The solution is pushed into the cell. Valve 1 is closed, and with valve 3 the pressure is brought to the osmotic pressure as found from previous measurements. Then valve 2 is closed. Side A of the cell and the buffer container are filled with solvent. The pressure is followed (resolution of 1 mbar) as a function of time. The pressure will converge to the osmotic pressure. The solvent at the solvent side (A) of the cell is refreshed repeatedly to check for any polymer permeating through the membrane. Any permeability at all for the polymer should result in a slightly higher osmotic pressure after the refreshment. This was, however, never observed. The procedure is repeated several times to check for reproducibility, which was typically around a few tens of millibars.

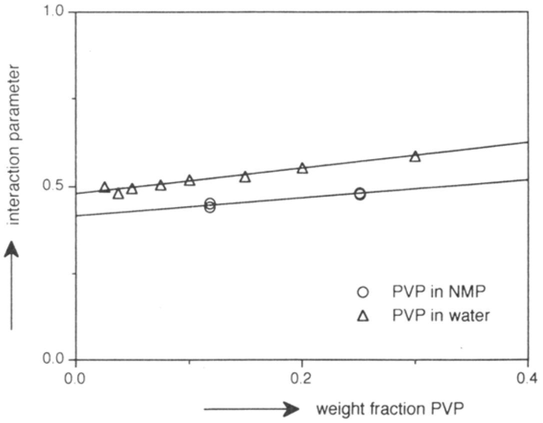

Figure 2. Interaction parameter of PVP in water and NMP. The results for PVP in water are in excellent agreement with literature values.[16,17] All measurements were performed at least in triplicate. Especially at higher polymer concentrations, the value for g_{ij} was quite accurate; only one point could be drawn.

Materials Used. Poly(ether sulfone), Victrex 5200 P (ICI Ltd.) (M_w = 43 800 g/mol, M_n = 22 300 g/mol), was dried for at least 12 h at 80 °C before use. No further purification was applied. Poly(vinylpyrrolidone)s, grade K30 (M_w = 18 100 g/mol, M_n = 8700 g/mol) and grade K90 (M_w = 228 200 g/mol, M_n = 99 800 g/mol) (Jansen Chimica), were used without further purification (the molecular weights mentioned were determined by GPC). Special care was taken to avoid water sorption. *N*-Methyl-2-pyrrolidone (NMP; Merck), synthesis grade, was used as received. The solutions were not filtered before use. A Cuprophan (Enka, Wuppertal, FRG) membrane with a dry thickness of 8 μm was applied. The membrane was allowed to equilibrate in pure solvent (NMP) before application in the cell.

Cloud Point Measurements. The cloud points were determined by a simple titration measurement. Thermostated flasks were filled with an amount of the polymer solution. With a syringe water was added very slowly. The cloud point was defined as the composition at which the solution did not become clear again after 12 h of homogenation. All cloud point measurements were performed at 298 K. Although some authors use temporary heating of the solution to accelerate the homogenation process,[13] this was not done, since this can lead to loss of water from the solution. For details on the calculation procedure for the cloud point curves, we refer to other work;[1] it was assumed that the molecular weight of PVP had no influence on the value of the interaction parameters.

Results

Osmotic Pressure Measurements. During the measurements, the osmotic pressure did not show any decrease with time: even after 2 weeks the pressure was still within 10 mbar of the initial equilibrium value during a single measurement. Refreshing the solvent after some time should result in an increase of the pressure difference whenever polymer molecules would have diffused into the solvent compartment. Since this was never observed, we could be reasonably sure that the measured pressure difference is indeed the actual osmotic pressure difference.

Since in the literature[3,14,15] linear dependencies of the interaction parameters on the composition are often found, we assumed a linear dependence of the interaction parameters on the concentration. Figure 2 gives the values found for PVP in water and NMP. The PVP–water measurements are used as a check for the accuracy of the setup. A value of 0.48 for g_{14} at $\varphi_4 = 0$ is reported in the literature.[16,17] Our measurement of 0.475 is in excellent agreement. Figure 3 gives the values found for the binary systems PES–NMP and PVP–NMP (included for comparison). Reproducibility of the measurements was within a few percent.

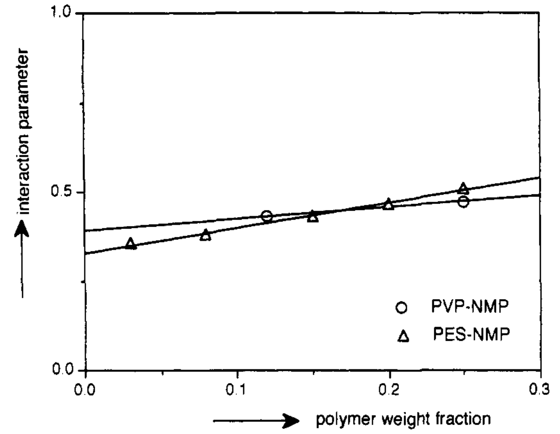

Figure 3. Concentration-dependent interaction parameters for the system PES–NMP; the system PVP–NMP is included for comparison.

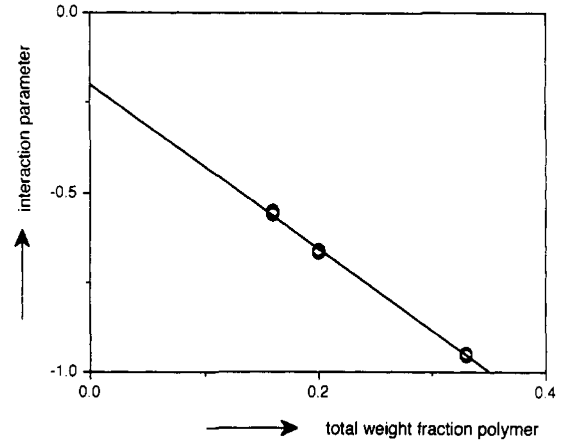

Figure 4. Interaction parameter between PES and PVP as determined with high-pressure osmometry, measured with a ratio between PES and PVP of 2.03:1.

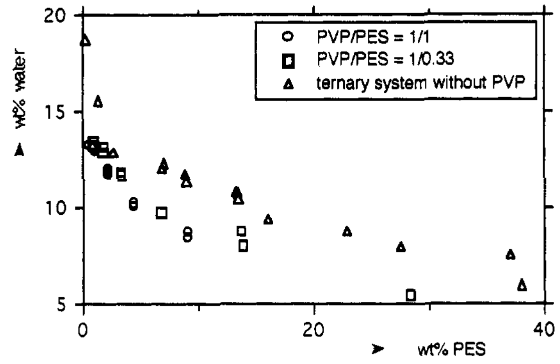

Figure 5. Experimental cloud points at 298 K for three different weight ratios of PVP to PES.

The interaction of PES with NMP is not very strong: the value of somewhat lower than 0.5 suggests near-Θ conditions. This is in agreement with the results obtained by Tkacik and Zeman from static light scattering.[18]

Ternary experiments were done with a fixed weight ratio between PES and PVP of 2.03:1. From the measurements, the interaction between PES and PVP turns out to be quite strong: measurements give a value of −0.5 to −1.0 (Figure 4).

Cloud Point Measurements. Figure 5 shows experimentally determined cloud points for the system water–NMP–PES–PVP for different ratios between the two polymers. The presence of PVP reduces the water content at the cloud point curve, which was predicted from calculations.[1]

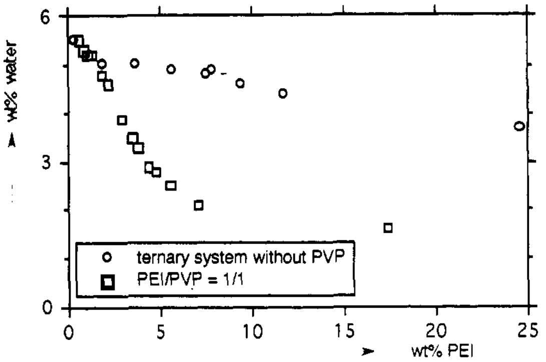

Figure 6. Experimental cloud point compositions for the system water–NMP–PEI–PVP (the same type of PVP as used with PES). Measurements were performed at 20.1–21.5 °C. After Roesink.[5]

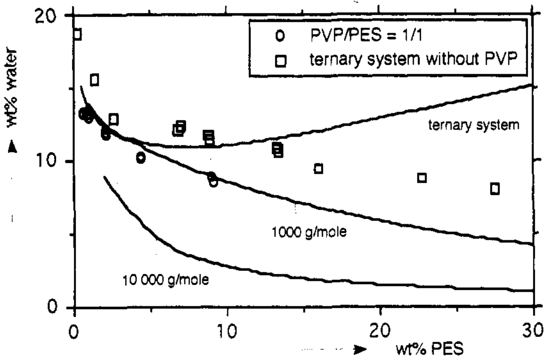

Figure 7. Comparison of experimental cloud points with calculations[1] for the ternary system water–NMP–PES (□) and the quaternary system water–NMP–PES–PVP (○) in which the ratio of PVP to PES is kept at 1/1 (wt %/wt %). Indicated molecular weight is for PVP in the calculations.

Roesink[5] measured cloud points of the system water–NMP–PEI–PVP (PEI stands for poly(ether imide)); see Figure 6. Also in this system a large influence of the addition of PVP is seen. Addition of PVP to the solution again results in a decrease of the water content at the cloud point compositions.

In Figure 7 the experimental data are compared with some calculated cloud point curves.[1] It appears that, to obtain a reasonable fit of the experimental data, one has to assume a molecular weight of the additive that is a 100-fold lower than the real number-average molecular weight of the additive (1000 g/mol instead of 100 kg/mol). The large discrepancy between theory and experiment will be mostly due to the fact that any polar and hydrogen-bonding effects have been neglected in the calculations, which play a large role here. Also, since the measurements are all near the critical point, a large influence of polydispersity can be expected, as was clearly shown by Koningsveld.[20]

Discussion

Osmotic Pressure Measurements. The results from PVP in water indicate that the experimental setup is quite reliable. PVP seems to have only a weak interaction with either water or NMP (interaction with NMP is somewhat stronger). It is to be expected that PVP should not have a strong interaction with NMP, since the structure of NMP resembles a segment of the PVP molecule.

PES has approximately the same interaction with NMP as PVP has. The results are in agreement with light scattering experiments.[18] The present authors were not able to carry out accurate static light scattering experiments, since the solutions of PES in NMP always appeared to be slightly turbid. Wijmans and Smolders[19] found that this type of turbidity (in their case of polysulfone) was due to crystallization of oligomeric fractions of the polymer. GPC measurements indeed indicate that also in the case of PES a significant amount of oligomers in the polymer is present. Earlier efforts by the authors to separate the oligomeric fraction from the polymer were, however, not successful.

The measurement of ternary solutions is only carried out for one fixed ratio between the two polymers. For a more complete picture of the interaction between the polymers more mixing ratios should be evaluated. With the available results we can conclude that the interaction between the two polymers is strong. Roesink[5] found that a blend of PES and PVP gave only one glass transition temperature, indicating that homogenous blends were prepared. From the dependency of the glass transition on the composition it could be seen that the interaction parameter should be negative. He found that many polymers show a strong interaction with PVP.

It should be noted that in our eq 3 we neglected any ternary parameters resulting from ternary interactions.[4] Any of these effects are lumped together in the PES–PVP interaction parameter. Therefore, although the reproducibility was always within a few percent, the values measured for PES–PVP should not be seen as highly exact.

Cloud Point Measurements. It is clear that addition of PVP K90 reduces the amount of water than can be added to both PES–NMP and PEI–NMP solutions. This conclusion followed also from calculations.[1] Figure 7 shows, however, that the agreement is at most qualitative.

For this range of concentrations, even the predicted binodal for the basic *ternary* system is inaccurate. This may be caused by the polydispersity of the polymer, and, e.g., by an incorrect value of g_{13} (the value that was used, 1.5, was estimated by Zeman and Tkacik[18]).

In the quaternary systems, the effect of PVP is exaggerated by the calculations, compared to the experiments, concerning the molecular weight of the PVP. This is caused by the fact that in the calculations based on the Flory–Huggins theory any effects from polarity and hydrogen bonding are neglected. These effects will greatly influence the behavior of the system. It may also partly be caused by the polydispersity of the polymer. Since all measurements were performed near the critical point, strong effects of polydispersity are present, as was shown by Koningsveld.[20]

Conclusions

High-pressure osmometry appears to be a reliable tool to determine interaction parameters in binary solutions of polymers: the results were in close agreement with literature values, and all data showed an experimental scatter of only a few percent.

The results show that NMP is more or less a Θ solvent for PES and PVP. The interaction between PVP and PES appears to be strong. The measured values of the interaction parameter lie between −0.5 and −1.0. Since only one fixed ratio between the concentrations of the polymers were measured so far, more measurements need to be carried out to obtain a complete impression.

It appears that the value suggested by Tkacik and Zeman for PES–NMP ($g_{23} = 0.5$) is reasonable; for qualitative evaluation, the interaction parameter for PVP–NMP can also be assumed to be 0.5. For the PES–PVP couple a low value has to be assumed: between −0.5 and −1.0.

Addition of PVP reduces the concentration of water at the cloud point curve. A larger amount of PVP (relative to the amount of the other polymer) results in a larger effect on the cloud point composition. It was suggested in the literature[5] that PVP therefore must act as a nonsolvent for PES, which is in contradiction with the strong interaction between the two polymers. It appears, however, that the reduced compatibility with water is intrinsic to such a quaternary system.[1]

The experimental findings show a large deviation from theory, although the trends are well predicted. For adequate quantitative description of the cloud point curve of a quaternary system, polar and hydrogen-bonding effects have to be considered. The polydispersity of both polymers should also be taken into account.

List of Symbols

Indices indicate the four components of the system: 1, nonsolvent (water); 2, solvent (*N*-methylpyrrolidone (NMP)); 3, membrane-forming polymer (poly(ether sulfone) (PES)); 4, polymeric additive (poly(vinylpyrrolidone (PVP)).

g_{ij}	interaction parameter between components i and j
M_i	molecular weight of component i (kg/mol)
n_i	number of moles of component i (mol)
s	$\bar{v}_1 M_1/\bar{v}_2 M_2$
r	$\bar{v}_1 M_1/\bar{v}_3 M_3$
R	gas constant ((J/mol) K)
T	temperature (K)
$\bar{v}_i$	specific volume of component i (m^3/kg)
v_2	$\varphi_2/(\varphi_2 + \varphi_3)$
w_2	$\varphi_2/(\varphi_2 + \varphi_4)$
ΔG_m	free enthalpy of mixing (J)
$\Delta\mu_i$	chemical potential of mixing
φ_i	volume fraction of component i

References and Notes

(1) Boom, R. M.; van den Boomgaard, Th.; Smolders, C. A. *Macromolecules*, preceding paper in this issue.
(2) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(3) Scholte, Th. G. *Eur. Polym. J.* **1970**, *6*, 1063.
(4) Altena, F. W. Thesis, University of Twente, The Netherlands, 1982.
(5) Roesink, H. D. W. Thesis, University of Twente, The Netherlands, 1989.
(6) Aptel, P.; Abidine, N.; Ivaldi, F.; LaFaille, J. P. *J. Membr. Sci.* **1985**, *22*, 199.
(7) Tweddle, T. A.; Kutowy, O.; Thayer, W. L.; Sourirajan, S. *Ind. Eng. Chem. Res.* **1983**, *22*, 320.
(8) Lafreniere, L. Y.; Talbot, F. D. F.; Matsuura, T.; Sourirajan, S. *Ind. Eng. Chem. Res.* **1987**, *26*, 2385.
(9) Nguyen, Q. T.; Blanc, L. L.; Neel, J. *J. Membr. Sci.* **1985**, *22*, 245.
(10) Koch, T.; Strobl, G. R. *J. Polym. Sci., Poly. Phys. Ed.* **1990**, *28*, 343.
(11) Reuvers, A. J.; van den Berg, J. W. A.; Smolders, C. A. *J. Membr. Sci.* **1987**, *34*, 45.
(12) Staverman, A. J. *Recl. Trav. Chim. Pays-Bas* **1951**, *70*, 344.
(13) Lau, W. W. Y.; Guiver, M. D.; Matsuura, T. *J. Membr. Sci.* **1991**, *59*, 219.
(14) Reuvers, A. J.; Smolders, C. A. *J. Membr. Sci.* **1987**, *34*, 67.
(15) Radovanovic, Ph.; Thiel, S. W.; Hwang, S.-T. *J. Membr. Sci.* **1992**, *65*, 213.
(16) Franks, F. In *Chemistry and Technology of Water-Soluble Polymers*; French, C. A.; Ed.; Plenum: New York, 1983; p 157.
(17) Cerny, L. C.; Helminiak, T. E.; Meier, J. F. *J. Polym. Sci.* **1960**, *44*, 539.
(18) Tkacik, G.; Zeman, L. *J. Membr. Sci.* **1987**, *31*, 273.
(19) Wijmans, J. G.; Smolders, C. A. *Eur. Polym. J.* **1983**, *13*, 1143.
(20) Koningsveld, R.; Staverman, A. J. *J. Polym. Sci., Part A-2* **1968**, *6*, 305.