

Enhancement of Impurity Removal from Polymer Films

J. S. VRENTAS, J. L. DUDA, and H.-C. LING, *Department of Chemical Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802*

Synopsis

The problem of the enhancement of the removal of a volatile impurity in a polymer film by the addition of a second solvent is analyzed. The introduction of a second solvent that diffuses faster than the impurity can increase the free volume of the system and can thus facilitate removal of the volatile impurity. Solution of the ternary diffusion problem indicates the role of the properties of the second solvent and of processing conditions on the devolatilization effectiveness. It is shown that more than a 10-fold decrease in the devolatilization time can be achieved using a second solvent and appropriate processing conditions.

INTRODUCTION

After the formation of a polymer in a polymerization reactor, volatile residues, such as monomers, solvents, condensation by-products, and other impurities, have to be removed before the polymer can be processed further. Thus, a devolatilization process, which essentially involves molecular diffusion in a concentrated polymer solution, is often included after the polymerization reactor. The optimum design of such devolatilizers has assumed increased importance in recent years because of the necessity of meeting tighter health and environmental standards. The purpose of this paper is to present an analysis of a devolatilization scheme that can lead to enhanced removal of the volatile impurity.

The analysis of industrial devolatilizers should include determination of the relative contributions of diffusive and foam devolatilization and of the importance of film evaporation, pool evaporation, and surface renewal.¹ In this paper, we concentrate on the analysis of the removal of a volatile impurity in a diffusing film configuration by the addition of a second solvent. The introduction of this second solvent, which is chosen so that it diffuses faster than the impurity, can increase the free volume of the system and can thus facilitate removal of the volatile impurity. In effect, the diffusion rate of the impurity is increased by using an increased total solvent concentration to loosen the polymer matrix and promote more rapid transport of small-molecule contaminants. The same type of effect can be achieved by increasing the temperature of the devolatilization process but with increased risk of polymer degradation.

Carrà et al.² have previously noted that the addition of solvents can facilitate the removal of small amounts of volatile residues from polymeric materials, and they examined one example of this effect by conducting experiments in which the solvent acetone was used to enhance the removal

of carbon tetrachloride from chlorinated rubber. They also formulated a mathematical model of the purification units used in their experiments. In this paper, we conduct a detailed examination of the nature of the effects that result when a second solvent is used to enhance the removal of an impurity from a polymer film. Equations describing the self-diffusion and mutual diffusion processes in the ternary system are presented in the second and third sections of this paper, respectively. The mass transfer problem in the polymer film is described in the fourth section, and appropriate equations used to determine the concentration fields for this problem are presented in this section. Pertinent results from the solution of this equation set are presented and discussed in the final section of the paper.

SELF-DIFFUSION IN TERNARY SYSTEMS

The free-volume theory of transport can be used to derive expressions for the self-diffusion coefficients of the two solvents in a polymer-solvent-solvent system at sufficiently high polymer concentrations.³ In this paper, the subscript 1 will generally refer to the impurity originally in the polymer film, the subscript 2 will generally denote a second solvent added to enhance the removal of the impurity, and the subscript 3 will refer to the polymer. The self-diffusion coefficients D_1 and D_2 of the two penetrants can be expressed as follows if it is assumed that the concentration dependence of the partial specific volumes of all components is negligible:

$$D_1 = D_{01} \exp\left(-\frac{(\omega_1 \hat{V}_1^* + \omega_2 \hat{V}_2^* \xi_{13}/\xi_{23} + \omega_3 \hat{V}_3^* \xi_{13})}{\hat{V}_{FH}/\gamma}\right) \quad (1)$$

$$D_2 = D_{02} \exp\left(-\frac{(\omega_1 \hat{V}_1^* \xi_{23}/\xi_{13} + \omega_2 \hat{V}_2^* + \omega_3 \hat{V}_3^* \xi_{23})}{\hat{V}_{FH}/\gamma}\right) \quad (2)$$

$$\frac{\hat{V}_{FH}}{\gamma} = \frac{K_{11}}{\gamma} (K_{21} + T - T_{g1})\omega_1 + \frac{K_{12}}{\gamma} (K_{22} + T - T_{g2})\omega_2 + \frac{K_{13}}{\gamma} (K_{23} + T - T_{g3})\omega_3 \quad (3)$$

Here, D_{0i} is the pre-exponential factor for component I, ω_i is the mass fraction of component I and \hat{V}_i^* is the specific critical hole free volume of component I required for a jump. Also, \hat{V}_{FH} is the average hole free volume per gram of mixture, γ is an overlap factor introduced because the same free volume is available to more than one molecule, and the parameter ξ_{13} represents the ratio of the critical molar volume of a jumping unit of component I to the critical molar volume of the jumping unit of the polymer. Finally, K_{11} and K_{21} are free-volume parameters for component I, and T_{g1} is the glass transition temperature of component I. The definitions of the free-volume parameters K_{1i}/γ and K_{2i} are given elsewhere.^{4,5} For a particular component (the polymer or either of the solvents), these two constants are simply related to the WLF constants for that component.^{5,6}

The parameters in the free-volume expressions for D_1 and D_2 can be determined from volumetric, viscosity, and diffusivity data collected using single-component or binary systems. An estimate of \hat{V}_I^* for each of the three components can be computed by equating this quantity to the equilibrium liquid volume at 0 K.⁷ The parameters K_{11}/γ and $K_{21} - T_{g1}$ for each of the components can be determined using viscosity data for that component. Finally, D_{01} and ξ_{13} and D_{02} and ξ_{23} can be determined using diffusivity data for the binary systems solvent 1-polymer and solvent 2-polymer, respectively. The procedures for determining these free-volume parameters are described in detail elsewhere.⁸

Equations that relate the self-diffusion coefficients to the friction coefficients for the ternary system are also of interest here since friction coefficients provide a link between the self-diffusion and mutual diffusion processes. It can be shown, in the usual way,⁹ that the self-diffusion coefficients D_1 and D_2 are related to the friction coefficients ζ_{1j} by the following equations:

$$D_1 = \frac{RT}{N_A^2 (\rho_1 \zeta_{11}/M_1 + \rho_2 \zeta_{12}/M_2 + \rho_3 \zeta_{13}/M_3)} \quad (4)$$

$$D_2 = \frac{RT}{N_A^2 (\rho_1 \zeta_{22}/M_1 + \rho_2 \zeta_{22}/M_2 + \rho_3 \zeta_{23}/M_3)} \quad (5)$$

Here, ρ_i is the mass density of component I, M_i is the molecular weight of component I, T is temperature, and N_A is Avogadro's number. The two self-diffusion coefficients D_1 and D_2 are thus related to five friction coefficients: ζ_{11} , ζ_{12} , ζ_{13} , ζ_{22} , and ζ_{23} . It will prove useful to define the following quantities:

$$D_1^* = \frac{RTM_1}{\rho_1 \zeta_{11} N_A^2} \quad (6)$$

$$D_2^* = \frac{RTM_2}{\rho_2 \zeta_{22} N_A^2} \quad (7)$$

$$D_{T1} = \frac{D_1}{1 - \frac{D_1}{D_1^*}} \quad (8)$$

$$D_{T2} = \frac{D_2}{1 - \frac{D_2}{D_2^*}} \quad (9)$$

The following equations can then be derived from eqs. (4) through (9):

$$\zeta_{13} = \frac{M_3}{\rho_3} \left(\frac{RT}{N_A^2 D_{T1}} - \frac{\rho_2 \zeta_{12}}{M_2} \right) \quad (10)$$

$$\zeta_{23} = \frac{M_3}{\rho_3} \left(\frac{RT}{N_A^2 D_{T2}} - \frac{\rho_1 \zeta_{12}}{M_1} \right) \quad (11)$$

and these expressions can be used to eliminate ζ_{13} and ζ_{23} in later derivations.

In the limit of small solvent concentrations ($\rho_1 \rightarrow 0$, $\rho_2 \rightarrow 0$), it can be shown using eqs. (4) through (7) that $D_1/D_1^* \rightarrow 0$ and $D_2/D_2^* \rightarrow 0$ if it is assumed that the friction coefficients are bounded near the pure polymer limit. Hence, from eqs. (8) and (9), it follows that

$$D_{T1} \approx D_1 \quad (12)$$

$$D_{T2} \approx D_2 \quad (13)$$

in some concentration interval near $\rho_1 = 0$, $\rho_2 = 0$ where D_1/D_1^* and D_2/D_2^* are sufficiently small. Experimental data¹⁰ for the toluene-polystyrene system show that approximations of the form of eqs. (12) and (13) are acceptable for an appreciable part of the concentration range for a typical polymer-solvent system. Hence, it will be assumed that these equations are satisfactory for this investigation since only concentrations close to the pure polymer limit are considered.

MUTUAL DIFFUSION IN TERNARY SYSTEMS

In the analysis of a one-dimensional mutual diffusion process in a ternary system, it is convenient to once again introduce a friction coefficient formulation. The chemical potential gradient of component I in the x direction can be expressed as⁹

$$\frac{\partial \bar{\mu}_1}{\partial x} = - \sum_{j=1}^3 \bar{C}_j \zeta_{1j} (u_1 - u_j) \quad (14)$$

where $\bar{\mu}_1$ is the chemical potential per molecule of component I, \bar{C}_1 is the concentration of component I in units of molecules per unit volume, and u_1 is the x component of the velocity of component I with respect to a laboratory frame of reference. Introduction of j_1^\neq , the x component of the mass diffusion flux of component I with respect to the volume-average velocity,¹¹ into eq. (14) and utilization of the equations

$$\sum_{i=1}^3 j_i^\neq \hat{V}_i = 0 \quad (15)$$

$$\sum_{i=1}^3 \rho_i \hat{V}_i = 1 \quad (16)$$

yield the flowing expressions for the chemical potential gradients of the two solvents:

$$\frac{\partial \bar{\mu}_1}{\partial x} = N_A \left(- \frac{\rho_2 \zeta_{12}}{\rho_1 M_2} - \frac{(1 - \rho_2 \hat{V}_2) \zeta_{13}}{\rho_1 \hat{V}_3 M_3} \right) j_1^\neq + N_A \left(\frac{\zeta_{12}}{M_2} - \frac{\hat{V}_2 \zeta_{13}}{\hat{V}_3 M_3} \right) j_2^\neq \quad (17)$$

$$\frac{\partial \bar{\mu}_2}{\partial x} = N_A \left(\frac{\zeta_{12}}{M_1} - \frac{\hat{V}_1 \zeta_{23}}{\hat{V}_3 M_3} \right) j_1^\neq + N_A \left(-\frac{\rho_1 \zeta_{12}}{\rho_2 M_1} - \frac{(1 - \rho_1 \hat{V}_1) \zeta_{23}}{\rho_2 \hat{V}_3 M_3} \right) j_2^\neq \quad (18)$$

Here, \hat{V}_I is the partial specific volume of component I, which is equal to the specific volume of pure component I in this study because of the assumption of negligible concentration dependence of the \hat{V}_I .

Inversion of eqs. (17) and (18) and utilization of eqs. (10) and (11) lead to the following expressions for the diffusion fluxes of the two solvents.

$$j_1^\neq = -D_{11} \frac{\partial \rho_1}{\partial x} - D_{12} \frac{\partial \rho_2}{\partial x} \quad (19)$$

$$j_2^\neq = -D_{21} \frac{\partial \rho_1}{\partial x} - D_{22} \frac{\partial \rho_2}{\partial x} \quad (20)$$

$$D_{11} = -\frac{\phi_{22} \frac{\partial \mu_1}{\partial \rho_1} - \phi_{12} \frac{\partial \mu_2}{\partial \rho_1}}{N_A^2 |\phi|} \quad (21)$$

$$D_{12} = -\frac{\phi_{22} \frac{\partial \mu_1}{\partial \rho_2} - \phi_{12} \frac{\partial \mu_2}{\partial \rho_2}}{N_A^2 |\phi|} \quad (22)$$

$$D_{21} = -\frac{\phi_{11} \frac{\partial \mu_2}{\partial \rho_1} - \phi_{21} \frac{\partial \mu_1}{\partial \rho_1}}{N_A^2 |\phi|} \quad (23)$$

$$D_{22} = -\frac{\phi_{11} \frac{\partial \mu_2}{\partial \rho_2} - \phi_{21} \frac{\partial \mu_1}{\partial \rho_2}}{N_A^2 |\phi|} \quad (24)$$

Here, μ_I is the chemical potential of component I per mole and the ϕ_{IJ} and $|\phi|$ are defined as

$$\phi_{11} = \frac{\rho_2 \hat{V}_1 \zeta_{12}}{\rho_3 \hat{V}_3 M_2} - \frac{(1 - \rho_2 \hat{V}_2) RT}{\rho_1 \rho_3 \hat{V}_3 N_A^2 D_{T1}} \quad (25)$$

$$\phi_{12} = \frac{\zeta_{12}(1 - \rho_1 \hat{V}_1)}{\rho_3 \hat{V}_3 M_2} - \frac{\hat{V}_2 RT}{\rho_3 \hat{V}_3 N_A^2 D_{T1}} \quad (26)$$

$$\phi_{21} = \frac{\zeta_{12}(1 - \rho_2 \hat{V}_2)}{\rho_3 \hat{V}_3 M_1} - \frac{\hat{V}_1 RT}{\rho_3 \hat{V}_3 N_A^2 D_{T2}} \quad (27)$$

$$\phi_{22} = \frac{\rho_1 \hat{V}_2 \zeta_{12}}{\rho_3 \hat{V}_3 M_1} - \frac{(1 - \rho_1 \hat{V}_1) RT}{\rho_2 \rho_3 \hat{V}_3 N_A^2 D_{T2}} \quad (28)$$

$$|\phi| = -\frac{\zeta_{12}^2}{\rho_3 \hat{V}_3 M_1 M_2} + \frac{R^2 T^2}{\rho_1 \rho_2 \rho_3 \hat{V}_3 N_A^4 D_{T1} D_{T2}} \quad (29)$$

The solvent chemical potentials in the expressions for the four diffusion coefficients can be conveniently calculated using the Flory-Huggins theory of polymer solutions.¹² More general thermodynamic theories² can easily be incorporated into the analysis if necessary. For solvent 1, we can write

$$\frac{\mu_1 - \mu_1^0}{RT} = \ln\phi_1 + (1 - \phi_1) - \phi_2 + (\chi_{12}\phi_2 + \chi_{13}\phi_3)(\phi_2 + \phi_3) - \chi_{23}\phi_2\phi_3 \quad (30)$$

$$\phi_1 = \rho_1 \hat{V}_1 \quad (31)$$

where μ_1^0 is the chemical potential of pure component I, ϕ_1 is the volume fraction of component I, and the χ_{IJ} are pair interaction parameters. The equation for the chemical potential of component 2 can be deduced from eq. (30) by interchanging the subscripts 1 and 2.

If all four of the mutual diffusion coefficients for the ternary system (D_{11} , D_{12} , D_{21} , and D_{22}) could be expressed solely in terms of the two solvent self-diffusion coefficients (D_1 and D_2), then the mutual diffusion process could be analyzed using only the free-volume theory of transport and a convenient thermodynamic theory for the ternary polymer solution. Unfortunately, it is easy to show that this cannot generally be done over the complete concentration range. Since theoretical expressions for D_1 and D_2 are available from free-volume theory, it is clear that eqs. (4) and (5) constitute a set of two equations for five friction coefficients. Hence, it is not in general possible to derive equations for the D_{IJ} which contain D_1 and D_2 and none of the friction coefficients. Additional equations for the friction coefficients are needed. The friction coefficients ζ_{11} and ζ_{22} can be removed from the equations for the D_{IJ} if eqs. (12) and (13) are utilized, but the friction coefficient ζ_{12} remains and another equation is needed before the D_{IJ} can be computed. Since it is not obvious how an equation for the concentration dependence of ζ_{12} can be derived, we attempt to formulate expressions for the D_{IJ} that are valid at sufficiently small mass fractions of the two solvents.

It can be easily shown from the above equations that the following limits are obtained as $\rho_1 \rightarrow 0$, and $\rho_2 \rightarrow 0$:

$$D_{11} \rightarrow D_1 \quad (32)$$

$$D_{12} \rightarrow 0 \quad (33)$$

$$D_{21} \rightarrow 0 \quad (34)$$

$$D_{22} \rightarrow D_2 \quad (35)$$

Hence, in a sufficiently small neighborhood of the pure polymer limit, the principal diffusion coefficients (D_{11} and D_{22}) are significantly larger than the cross-diffusion coefficients (D_{12} and D_{21}). Since the present analysis is limited to relatively small concentrations of the two solvents, we shall assume that the cross-diffusion coefficients are sufficiently smaller than the principal diffusion coefficients so that they have a negligible effect on

the mass transfer process over the entire concentration region under consideration. This assumption has been introduced in other studies of diffusion in polymer-solvent-solvent systems.^{13,14} Furthermore, in the determination of D_{11} and D_{22} , eqs. (12) and (13) are utilized, and the equations for these coefficients are reduced to forms valid for small ρ_1 and ρ_2 . Finally, it is assumed that the volumetric and thermodynamic effects on the concentration dependences of D_{11} and D_{22} are very small compared with the concentration effects introduced by the concentration dependences of D_1 and D_2 . Hence, in the analysis of the ternary diffusion process in the polymer film, it is assumed that ρ_1 and ρ_2 are sufficiently small so that the above equations yield the following expressions for the solvent diffusion fluxes:

$$j_1^{\neq} = - D_1 \frac{\partial \rho_1}{\partial x} \quad (36)$$

$$j_2^{\neq} = - D_2 \frac{\partial \rho_2}{\partial x} \quad (37)$$

More general equations for the diffusion fluxes could be derived from the equations presented in this section if more information on friction coefficients were available. Although the general equations presented above are not utilized below, they are included here because they form the basis of a more general analysis of the diffusion process.

FORMULATION OF MASS TRANSFER PROBLEM

To conduct a comprehensive study of the effect of solvent addition on impurity devolatilization, we consider unsteady diffusion in a thin polymer film sitting on a flat plate, as depicted in Figure 1. Initially, the polymer film has a thickness L , and it contains a small amount of the impurity, solvent 1, with initial mass density $\rho_1 = \rho_{10}$. At time $t = 0$, the film is suddenly exposed to a gas stream containing solvent 2 that maintains the concentration of solvent 2 at the gas-liquid interface at $\rho_2 = \rho_{2E}$. Also, this gas stream sweeps away any solvent 1 that has desorbed from the polymer film so that the concentration of solvent 1 at the gas-liquid interface is maintained at $\rho_1 = 0$. At $t = t_1$, the gas stream containing solvent 2 is replaced by an inert gas stream so that desorption of solvent 2 can also take place, and hence, $\rho_1 = 0$ and $\rho_2 = 0$ at the surface for $t > t_1$. We wish to determine the effects of the properties of the second solvent and the parameters t_1 and ρ_{2E} on the removal rate of the impurity, solvent 1.

Since the thickness of the film $X(t)$ is small compared with its other dimensions, it is assumed that the mass transfer process is essentially one dimensional. In addition, there are no chemical reactions, and it is further

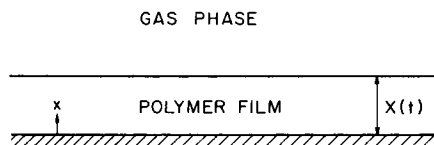


Fig. 1. Geometry for mass transfer problem.

assumed that the process is effectively isothermal. Under usual devolatilization conditions, the relaxation and rearrangement of polymer molecules are very fast compared with the rate of diffusion. Consequently, it is reasonable to assume that the diffusion process is Fickian and that there is instantaneous establishment of equilibrium at the phase interface. Finally, the effect of the pressure field on the diffusion flux and on the density is considered negligible, and as noted above, it is assumed that the partial specific volumes are all independent of composition so that there is no volume change on mixing.

With these assumptions, the one-dimensional mass transfer process is described by the following set of equations:

$$\frac{\partial \rho_1}{\partial t} = \frac{\partial}{\partial x} \left(D_1 \frac{\partial \rho_1}{\partial x} \right) \quad (38)$$

$$\frac{\partial \rho_2}{\partial t} = \frac{\partial}{\partial x} \left(D_2 \frac{\partial \rho_2}{\partial x} \right) \quad (39)$$

$$\rho_1(x, 0) = \rho_{10} \quad (40)$$

$$\rho_2(x, 0) = 0 \quad (41)$$

$$\rho_1[X(t), t] = 0 \quad (42)$$

$$\rho_2[X(t), t] = \rho_{2E}, \quad 0 < t < t_1 \quad (43)$$

$$\rho_2[X(t), t] = 0, \quad t > t_1 \quad (44)$$

$$\frac{\partial \rho_1}{\partial x} = \frac{\partial \rho_2}{\partial x} = 0, \quad x = 0 \quad (45)$$

$$\frac{dX}{dt} = \left(\frac{\hat{V}_1 D_1 \frac{\partial \rho_1}{\partial x} + \hat{V}_2 D_2 \frac{\partial \rho_2}{\partial x}}{1 - \rho_2(t) \hat{V}_2} \right)_{x=X(t)} \quad (46)$$

$$X(0) = L \quad (47)$$

The derivation of these equations is based on using the result that the volume-average velocity is zero everywhere in the polymer film and on introducing the assumption that the solvent diffusion fluxes are adequately represented by eqs. (36) and (37) for the concentration levels under consideration. The variation of the film thickness with time is described by eq. (46), and this equation is derived by application of a jump mass balance at the phase boundary.

Numerical solution of the above moving boundary problem is facilitated if the following transformation is used to immobilize the phase interface:

$$\eta = \frac{x}{X(t)} \quad (48)$$

In addition, it is convenient to introduce the following dimensionless variables:

$$\rho_1^* = \frac{\rho_1}{\rho_{10}} \tag{49}$$

$$\rho_2^* = \frac{\rho_{2E} - \rho_2}{\rho_{2E}} \tag{50}$$

$$X^* = \frac{X}{L} \tag{51}$$

$$t^* = \frac{D_1^0 t}{L^2} \tag{52}$$

$$D_1^0 = D_1(\rho_1 = 0, \rho_2 = 0) \tag{53}$$

Thus, the above equations can be written in the following dimensionless form, if the asterisks are dropped for convenience:

$$\frac{\partial \rho_1}{\partial t} - \frac{\eta}{X} \frac{dX}{dt} \frac{\partial \rho_1}{\partial \eta} = \frac{1}{X^2} \frac{\partial}{\partial \eta} \left(\frac{D_1}{D_1^0} \frac{\partial \rho_1}{\partial \eta} \right) \tag{54}$$

$$\frac{\partial \rho_2}{\partial t} - \frac{\eta}{X} \frac{dX}{dt} \frac{\partial \rho_2}{\partial \eta} = \frac{\beta}{X^2} \frac{\partial}{\partial \eta} \left(\frac{D_2}{D_2^0} \frac{\partial \rho_2}{\partial \eta} \right) \tag{55}$$

$$D_2^0 = D_2(\rho_1 = 0, \rho_2 = 0) \tag{56}$$

$$\beta = \frac{D_2^0}{D_1^0} \tag{57}$$

$$\rho_1(\eta, 0) = 1 \tag{58}$$

$$\rho_2(\eta, 0) = 1 \tag{59}$$

$$\rho_1(1, t) = 0 \tag{60}$$

$$\rho_2(1, t) = 0, \quad 0 < t < \alpha \tag{61}$$

$$\rho_2(1, t) = 1, \quad t > \alpha \tag{62}$$

$$\alpha = \frac{D_1^0 t_1}{L^2} \tag{63}$$

$$\frac{\partial \rho_1}{\partial \eta} = \frac{\partial \rho_2}{\partial \eta} = 0, \quad \eta = 0 \tag{64}$$

$$X \frac{dX}{dt} = \left(\frac{\hat{V}_1 \rho_{10} \frac{D_1}{D_1^0} \frac{\partial \rho_1}{\partial \eta} - \hat{V}_2 \rho_{2E} \beta \frac{D_2}{D_2^0} \frac{\partial \rho_2}{\partial \eta}}{1 - \rho_{2E} \hat{V}_2 (1 - \rho_2)} \right)_{\eta=1} \tag{65}$$

$$X(0) = 1 \tag{66}$$

These equations were solved for the spatial and time variations of ρ_1 and ρ_2 using an implicit finite-difference technique applied in conjunction with an iterative method for solving the coupled equations at each time step. A transformation in the spatial coordinate was used to expand the region near the surface where sharp concentration gradients exist initially. The transformation introduced for this purpose is

$$\xi = \frac{\tanh^{-1}(\eta \tanh m)}{m} \quad (67)$$

where m is an adjustable parameter. The emphasis that the new variable ξ gives to the region near the phase interface is illustrated in Figure 2.

RESULTS AND DISCUSSION

It is evident from eqs. (54) through (66) that the concentration fields for the two solvents ρ_1 and ρ_2 depend on α , β , D_1/D_1^0 , D_2/D_2^0 , the initial volume fraction of impurity ($\hat{V}_1\rho_{10}$), and the equilibrium volume fraction of the second solvent ($\hat{V}_2\rho_{2E}$). The ratios D_1/D_1^0 and D_2/D_2^0 depend on the volumetric and free-volume properties of the three components, as can be readily deduced from eqs. (1) and (2). Hence, solutions of the mass transfer problem can be obtained once the following parameters are designated: α , β , ρ_{10} , ρ_{2E} , three values of \hat{V}_1 , three values of \hat{V}_1^* , three values of K_{11}/γ ($K_{21} + T - T_{g1}$), ξ_{13} , and ξ_{23} . In practice, the initial mass fraction of solvent 1 in the film, ω_{10} , and the equilibrium mass fraction of solvent 2 at the gas-liquid interface, ω_{2E} , were set, and ρ_{10} and ρ_{2E} were calculated by using the following equations:

$$\rho_{10} = \frac{\omega_{10}}{\omega_{10}\hat{V}_1 + (1 - \omega_{10})\hat{V}_3} \quad (68)$$

$$\rho_{2E} = \frac{\omega_{2E}}{\omega_{2E}\hat{V}_2 + (1 - \omega_{2E})\hat{V}_3} \quad (69)$$

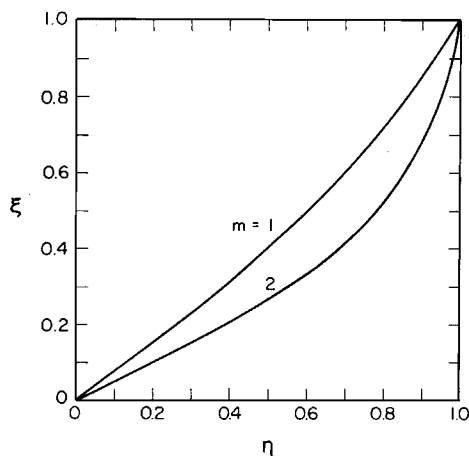


Fig. 2. Illustration of $\xi - \eta$ coordinate transformation with an adjustable parameter m .

The effectiveness of the devolatilization process can conveniently be ascertained by computing the following three quantities: \bar{M}_1 , \bar{M}_2 , and t_R . The quantities \bar{M}_1 and \bar{M}_2 are defined by the following equations in terms of dimensionless variables:

$$\bar{M}_1 = X \int_0^1 \rho_1 d\eta \quad (70)$$

$$\bar{M}_2 = X \frac{\rho_{2E}}{\rho_{10}} \int_0^1 (1 - \rho_2) d\eta \quad (71)$$

The quantity \bar{M}_1 is the fraction of the initial amount of solvent 1 present in the film at the time t ; it decreases monotonically from $\bar{M}_1 = 1$ to $\bar{M}_1 = 0$ as t increases. The quantity \bar{M}_2 is the ratio of the mass of solvent 2 present in the film at time t to the initial mass of solvent 1. It is zero initially, assumes a maximum value at some intermediate time, and then decreases monotonically to zero after solvent 2 is removed from the gas phase. The quantity t_R is defined as the ratio of the time required to have the total amount of impurities (both solvents 1 and 2) drop to 1% of the original amount of solvent 1 if solvent 2 is added to the time required to reach the same criterion without adding a second solvent. The quantity \bar{M}_1 provides a useful measure of the effectiveness of the devolatilization process if the presence of solvent 2 in the polymer film in reasonably small amounts is not viewed as detrimental to the utilization of the polymer. In this case, a harmless solvent (solvent 2) is used to facilitate the removal of a harmful impurity (solvent 1). On the other hand, if the goal is to minimize the amounts of all impurities, then t_R is a more useful indication of the efficiency of the enhanced devolatilization scheme.

There is of course considerable freedom in choosing solvent 2, and it is crucial to select the second solvent so that it possesses the following two characteristics. First, the second solvent should supply substantial additional free volume to the polymer film so that it will lead to a significant acceleration of the devolatilization process for the first solvent. Second, solvent 2 should diffuse at a considerably faster rate than solvent 1. This property will lead to a rapid absorption of solvent 2 relative to the desorption of solvent 1, thus assuring that the additional free volume created by the introduction of the second solvent will be effective in enhancing the diffusion rate of solvent 1 throughout the entire polymer film. In addition, the subsequent desorption of solvent 2 will proceed at a much faster rate than the desorption of solvent 1.

It is evident from eqs. (1) and (3) that large values of the parameter $(K_{12}/\gamma)(K_{22} + T - T_{g2})$ will lead to increased free volume, increased values of D_1/D_1^0 , and, hence, to enhanced removal of solvent 1. The pronounced influence of increasing the value of $(K_{12}/\gamma)(K_{22} + T - T_{g2})$ is illustrated in Figure 3. In this diagram, the effect of $(K_{12}/\gamma)(K_{22} + T - T_{g2})$ on the time dependence of \bar{M}_1 is illustrated by holding all the other parameters constant. Clearly, a second solvent with as large a value of $(K_{12}/\gamma)(K_{22} + T - T_{g2})$ as is possible should be used to enhance the devolatilization of the first solvent. In practice, however, there is not generally a great variation of the values of $(K_{12}/\gamma)(K_{22} + T - T_{g2})$ among typical solvents. This

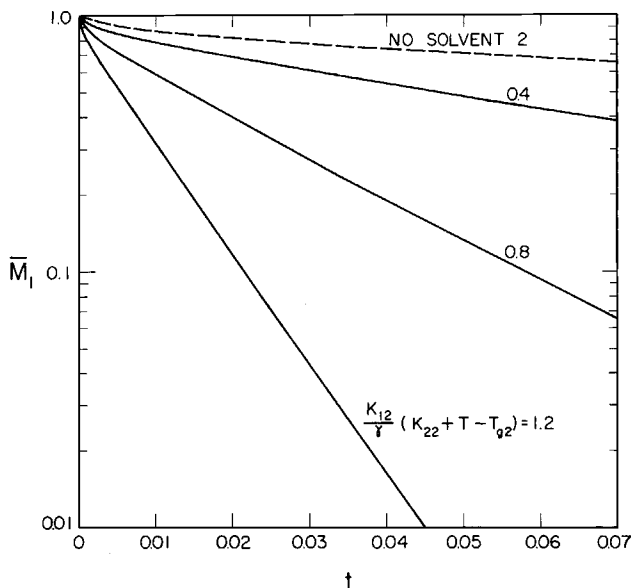


Fig. 3. Effect of free-volume properties of solvent 2 on removal rate of solvent 1 with $\omega_{10} = 0.01$, $\omega_{2E} = 0.02$, $\beta = 10$, and $\alpha = \infty$ (no desorption of solvent 2).

point is illustrated in Table I, where values of this parameter for five common solvents are presented. Consequently, although the utilization of solvents with large values of $(K_{12}/\gamma)(K_{22} + T - T_{g2})$ is of course desirable, in practice it may be difficult to find such solvents. Hence, in this study, we do not take advantage of this possibility and choose identical volumetric and free-volume properties for solvents 1 and 2. Furthermore, polymer properties for a typical amorphous polymer are utilized. The volumetric and free-volume properties of the three components used in all further calculations are presented in Table II. Finally, all but one of the computations are carried out using a single initial impurity mass fraction, $\omega_{10} = 0.01$. Hence, except for this single case, only the parameters α , β , and ω_{2E} are varied in the remainder of this paper. The parameter β can be varied by choosing solvent 2 appropriately, whereas parameters α and ω_{2E} can be changed by varying the processing conditions.

If the volumetric and free-volume parameters for solvents 1 and 2 are identical, then $D_1/D_1^0 = D_2/D_2^0$. However, the quantity $\beta = D_2^0/D_1^0$ generally need not be close to unity since the self-diffusion coefficients of solvents in the same polymer at zero solvent concentration can be considerably differ-

TABLE I
Values of $K_{12}/\gamma (K_{22} + T - T_{g2})$ at 100°C for Five Typical Solvents

Solvent	$K_{12}/\gamma (K_{22} + T - T_{g2})$
Chloroform	0.304
Ethylbenzene	0.430
Methanol	0.381
Methyl acetate	0.422
Toluene	0.443

TABLE II
 Free-Volume and Volumetric Properties

Property	Solvent 1	Solvent 2	Polymer
\hat{V}_1^* (cm ³ /g)	0.90	0.90	0.80
\hat{V}_1 (cm ³ /g)	1.20	1.20	0.90
$K_{11}/\gamma (K_{21} + T \cdot T_{g1})$ (cm ³ /g)	0.40	0.40	0.05
ξ_{13}	0.75	0.75	—

ent from one solvent to another. For example, self-diffusion coefficients of 10 solvents in poly(vinyl acetate) at 40°C and zero solvent concentration¹⁵ are presented in Table III. It is evident that values of the parameter β larger than 10^8 are possible. Hence, it is reasonable to assume that solvents that yield large values of β are available for utilization as a second solvent in the devolatilization process. Large values of the parameter β will lead to enhanced removal of the impurity in the polymer film and to a more rapid subsequent desorption of the second solvent.

The basic features of the devolatilization process, with and without a second solvent, are illustrated in Figure 4, where the time dependences of \bar{M}_1 and \bar{M}_2 are presented for $\alpha = 0.40$, $\beta = 10$, and $\omega_{2E} = 0.02$. For large β , there is a rapid increase of \bar{M}_2 , after solvent 2 is introduced at $t = 0$, to a nearly constant value and a subsequent rapid decrease of \bar{M}_2 , after solvent 2 is removed from the gas phase at $t = 0.4$. The dependence of \bar{M}_1 on β is illustrated in Figure 5 for $\omega_{2E} = 0.02$ and $\alpha = \infty$ (no desorption of solvent 2). The addition of the second solvent has a very pronounced effect on the devolatilization rate of solvent 1, and additional enhancement of the removal rate of the impurity can be obtained by choosing second solvents with increasingly larger values of β . However, \bar{M}_1 versus time curves for $\beta \geq 100$ are virtually identical, so that it suffices to choose a second solvent that diffuses 100 times faster than the impurity.

Since additional free volume can be generated by introducing higher amounts of the second solvent in the polymer film, the equilibrium concentration of solvent 2 will also be an important factor in the devolatilization process. The substantial influence of ω_{2E} on the time dependence of \bar{M}_1 is

 TABLE III
 Self-Diffusion Coefficients of Solvents in Poly(vinyl Acetate) at 40°C and Zero Solvent Concentration

Solvent	Self-diffusion coefficient (cm ² /s)
Water	1.2×10^{-7}
Methanol	1.4×10^{-9}
Acetone	1.3×10^{-11}
Allyl chloride	1.3×10^{-11}
Propylamine	5.1×10^{-12}
Isopropylamine	1.7×10^{-12}
Propyl chloride	1.3×10^{-12}
Propyl alcohol	1.1×10^{-12}
Benzene	4.8×10^{-13}
Carbon tetrachloride	3.0×10^{-16}

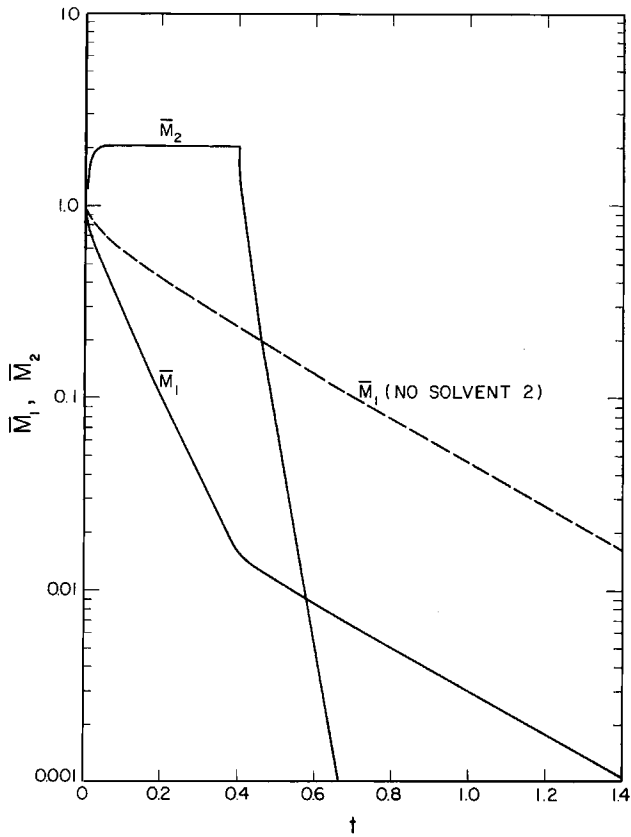


Fig. 4. Typical devolatilization process with and without solvent 2. Calculations are based on the following parameters: $\alpha = 0.4$, $\beta = 10$, $\omega_{10} = 0.01$, and $\omega_{2E} = 0.02$.

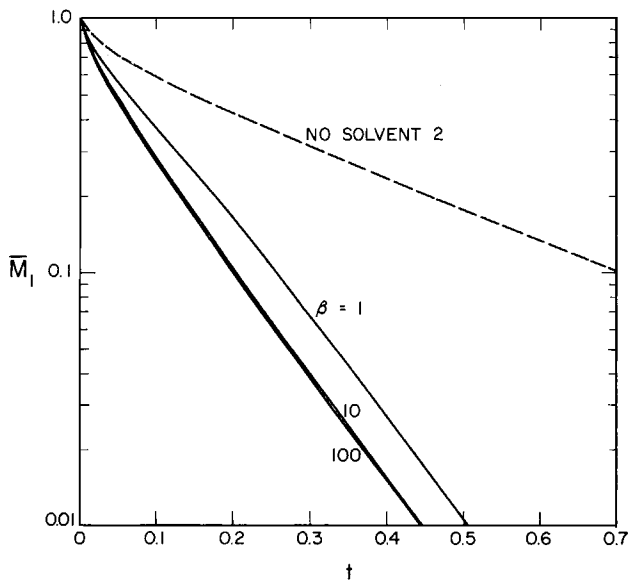


Fig. 5. Effect of β on \bar{M}_1 with $\omega_{10} = 0.01$, $\omega_{2E} = 0.02$, and $\alpha = \infty$.

illustrated in Figure 6 with $\beta = 10$ and $\alpha = \infty$. Although increasing the value of ω_{2E} can significantly decrease the fraction of solvent 1 remaining at a particular time, there is also an increased amount of solvent 2 that must ultimately be removed. Consequently, as noted above, if the total solvent concentration in the polymer film is to be minimized, then a better assessment of the efficiency of the devolatilization process can be obtained by comparing values of t_R rather than \bar{M}_1 versus time curves.

With fixed ω_{10} , the quantity t_R will of course depend on α , β , and ω_{2E} . The effect of α , which represents the duration that the second solvent is in the gas phase, is particularly important. If α is too small, then the second solvent is present in the polymer film for too short a time interval to have the desired effect in enhancing the removal of the impurity. If α is too large, then solvent 2 will remain in the polymer film after it has achieved its maximum effectiveness. Hence, there is an optimum value of α that will lead to a minimum value of t_R for fixed β and ω_{2E} . The dependence of t_R on α is illustrated in Figure 7 for $\beta = 10$ and for four values of ω_{2E} . For all values of ω_{2E} , it is evident that addition of the second solvent has led to a substantial reduction in the time needed for the total impurities to drop to 1% of their initial value. Values of the minimum value of t_R (denoted as t_R^*) for each value of ω_{2E} were determined from Figure 7 and plotted in Figure 8 along with corresponding t_R^* values for $\beta = 100$. The values of α needed to achieve the minimum values of t_R are denoted as α^* and are plotted versus ω_{2E} in Figure 9 for $\beta = 100$. It is evident from Figure 8 that t_R^* values decrease with increasing β and increasing ω_{2E} . However, there are relatively small changes in t_R^* with increasing ω_{2E} and fixed β for $\omega_{2E} > 0.08$. In addition, calculations show that there are insignificant changes in t_R^* with increasing β and fixed ω_{2E} for $\beta > 100$. It can also be shown

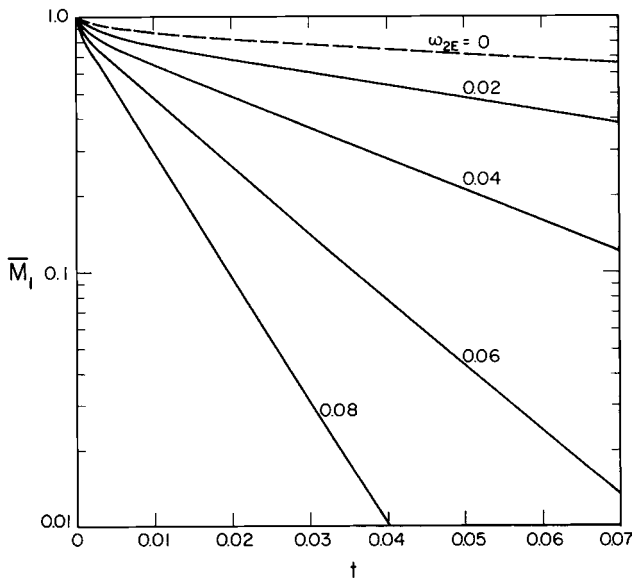


Fig. 6. Effect of ω_{2E} on \bar{M}_1 with $\omega_{10} = 0.01$, $\beta = 10$, and $\alpha = \infty$.

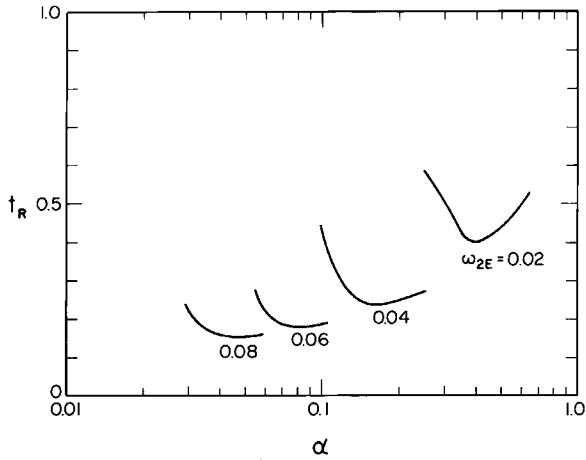


Fig. 7. Dependence of t_R on α for four values of ω_{2E} . Calculations are based on $\omega_{10} = 0.01$ and $\beta = 10$.

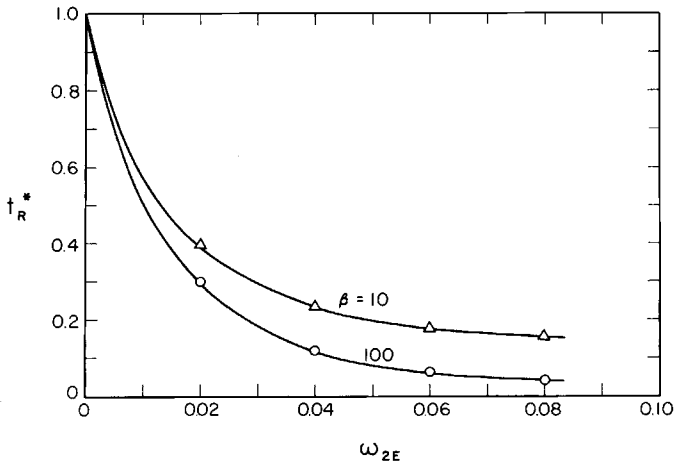


Fig. 8. Dependence of t_R^* on β and ω_{2E} with $\omega_{10} = 0.01$.

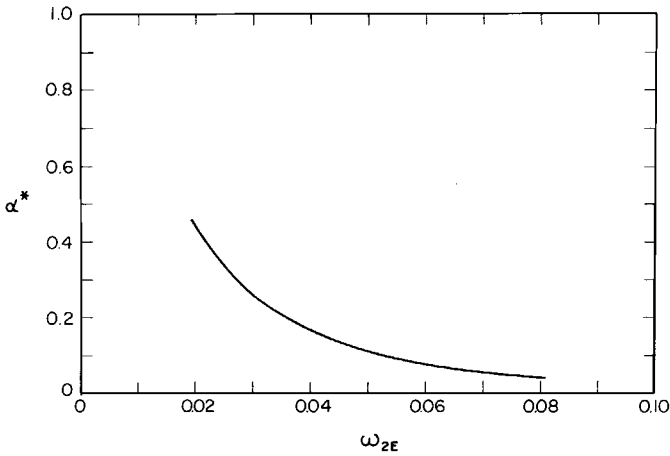


Fig. 9. Dependence of α^* on ω_{2E} for $\beta = 100$ and $\omega_{10} = 0.01$.

that α^* is negligibly dependent on ω_{2E} and β for $\omega_{2E} > 0.08$ and $\beta > 100$.

In all the previous calculations, we have set $\omega_{10} = 0.01$ since the most difficult part of a devolatilization process is removing small amounts of solvent because of the smaller values of diffusion coefficients near the pure polymer limit. It is thus reasonable to expect that the devolatilization time for a higher value of ω_{10} should be only slightly greater than that for $\omega_{10} = 0.01$. This is illustrated in Figure 10, where the devolatilization time is plotted as a function of ω_{2E} for $\omega_{10} = 0.01$ and for $\omega_{10} = 0.05$ with $\beta = 100$ and $\alpha = \infty$. The devolatilization time for this figure is defined as the time needed to reduce the ratio of the mass of solvent 1 in the film to the mass of polymer to 1.01×10^{-4} .

It is fair to conclude from the above results that the addition of a second solvent can lead to a substantial reduction in the time needed to decrease the total impurities in the polymer film to 1% of their initial value. The devolatilization process time can be reduced by a factor of 10 by utilizing $\omega_{2E} = 0.05$ for a second solvent that diffuses 100 times faster than the original solvent. A 20-fold reduction of the process time can be achieved with $\omega_{2E} = 0.08$. Calculations for higher values of ω_{2E} must be viewed with caution because the theoretical analysis is limited to small values of ρ_1 and ρ_2 . The above results indicate that appropriate choices of the parameters α , β , and ω_{2E} (α determined from Fig. 9, $\beta \geq 100$, $\omega_{2E} \approx 0.05-0.08$) will lead to at least an order of magnitude decrease of the process time for devolatilization in polymer films. It thus is reasonable to suggest that the strategy of adding a second solvent should receive serious consideration in the design and improvement of devolatilization units.

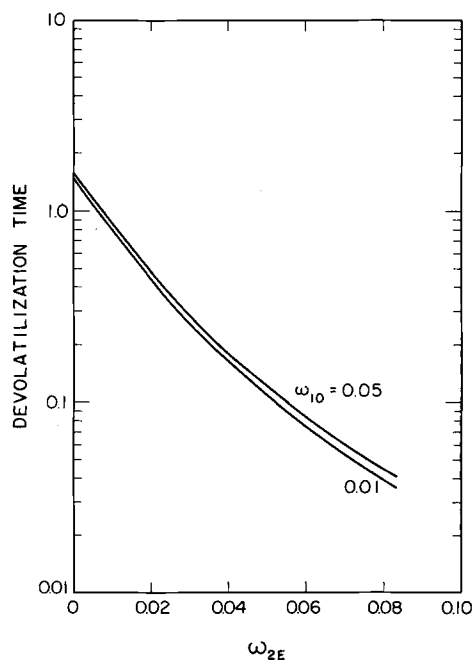


Fig. 10. Dependence of devolatilization time on ω_{2E} for two values of ω_{10} and for $\beta = 100$ and $\alpha = \infty$.

This work was supported by the National Science Foundation Grant CPE-8207401.

References

1. J. A. Biesenberger and D. H. Sebastian, *Principles of Polymerization Engineering*, Wiley, New York, 1983.
2. S. Carrà, M. Morbidelli, E. Santacesaria, and G. Niederjaufer, *J. Appl. Polym. Sci.*, **26**, 1497 (1981).
3. J. S. Vrentas, J. L. Duda, and H.-C. Ling, *J. Polym. Sci., Polym. Phys. Ed.*, **22**, 459 (1984).
4. J. S. Vrentas and J. L. Duda, *J. Appl. Polym. Sci.*, **21**, 1715 (1977).
5. J. S. Vrentas and J. L. Duda, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 417 (1977).
6. J. S. Vrentas and J. L. Duda, *J. Polym. Sci., Polym. Phys. Ed.*, **17**, 1085 (1979).
7. R. N. Haward, *J. Macromol. Sci. Rev. Macromol. Chem.*, **C4**, 191 (1970).
8. J. S. Vrentas, J. L. Duda, and H.-C. Ling, *J. Polym. Sci., Polym. Phys. Ed.*, **23**, 275 (1985).
9. R. J. Bearman, *J. Phys. Chem.*, **65**, 1961 (1961).
10. J. L. Duda, Y. C. Ni, and J. S. Vrentas, *Macromolecules*, **12**, 459 (1979).
11. S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics*, North-Holland, Amsterdam, 1962.
12. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953.
13. H. L. Frisch, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 1651 (1978).
14. F. H. L. Wang, J. L. Duda, and J. S. Vrentas, *Polym. Eng. Sci.*, **20**, 120 (1980).
15. R. J. Kokes and F. A. Long, *J. Amer. Chem. Soc.*, **75**, 6142 (1953).