# NOTES

## Diffusion of Dissolved Gases in Molten Condensation Polymers

Diffusion of dissolved gases in molten condensation polymers is of considerable importance to the chemical industry. In particular, the diffusion rate for the condensation product in these polymers is required for adequate design of process equipment, since the equilibrium molecular weight depends upon the concentration of condensation product in the polymer melt.

Several papers[1-5] have been published on the diffusion of nitrogen, argon, helium, and carbon dioxide, in molten polyethylene, polystyrene, polyisobutylene, and polypropylene. However, no data have been published on the diffusion of condensation products through their respective polymer melts. The apparent reason is that in the techniques[5] developed to date for measurement of these diffusion coefficients the chemical kinetics of the condensation reaction must be accurately known. This paper describes a technique of measuring the Fick diffusion coefficient for a condensation product in its respective polymer melt without previous knowledge of the chemical kinetics controlling the polymerization reaction.

A system that could be used for the measurement of the Fick diffusion coefficient for a condensation product in its respective polymer melt is shown in Fig. 1 for a typical condensation polymer, a polyamide. The diffusion cell is cylindrical in shape. A concentration gradient is imposed on the system in the vertical direction $z$ by passing an inert gas over the polymer melt and maintaining saturated steam at the porous plate.

By applying the law of conservation of mass for the condensation product $i$ in the volume element $r\Delta\theta\Delta r\Delta z$ in the polymer melt the following differential equation results:

$$\partial\rho_i/\partial t + \nabla\cdot n_i = r_i \tag{1}$$

Assuming unidirectional diffusion and steady state, eq. (1) reduces to

$$dn_i/dz = 0 \tag{2}$$

since $r_i$ is also zero. For this system

$$n = n_i + n_j \tag{3}$$

$$n_j = 0 \tag{4}$$

Therefore, by definition of the mass flux

$$n = \rho v \tag{5}$$

and the fact that for unidirectional transport

$$n_i = \rho_i v - D_{ij}\rho(dw_i/dz) \tag{6}$$

the final equation results for transport of the condensation product in the vertical direction,

$$n_i = - [D_{ij}\rho/(1 - w_i)](dw_i/dz) \tag{7}$$

From eqs. (2) and (7) we see

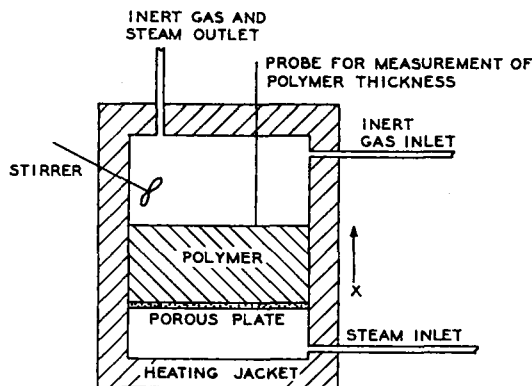$$n_i \int_0^h dz = - \int_{w_{io}}^{w_{ih}} D_{ij}\rho dw_i/(1 - w_i) \tag{8}$$

Fig. 1. Schematic of cell for diffusion studies of vapors through polymer melts.

or

$$n_i h = \int_{w_{ih}}^{w_{io}} \rho D_{ij} dw_i / (1 - w_i)$$ (9)

The boundary conditions on the integral in eq. (9) and the density can be measured easily in ordinary laboratory glassware and through the use of standard analytical techniques.

The Fick diffusion coefficient may be a function of the weight fraction of water at equilibrium (degree of polymerization). To describe the fact that

$$D_{ij} = f(w_i)$$ (10)

various forms of equations both theoretical and empirical can be tested for their applicability. The constants in these expressions can be obtained by measuring $n_i$ as a function of the polymer layer thickness and the boundary condition $w_{ih}$ in eq. (9).

Two aspects of the technique described require further discussion. One might expect that the porous plate would provide an added resistance to diffusion. However, for the high molecular weight polymers used in the diffusion studies a porous material with large pore diameters could be used. Porous material having a pore size sufficient to maintain both sides of the plate at essentially the same partial pressure of condensation product would be required. Bubble formation may occur in the polymer melt. That phenomenon would be minimized, if small gradients were imposed across the polymer melt. Even if bubble formation did occur, information on the affect of that phenomenon on the diffusion coefficient would be valuable, since industrial reactors operate under conditions favorable for bubble formation.

In the production of many condensation polymers continuous tank reactors with inert gas blanketing are employed. The residence time needed for the polymer in the reactor to attain the required degree of polymerization is a function of the polymerization kinetics and the diffusion coefficient for the condensation product in the melt. The design of polymerization reactors could be more easily completed, if data and theory were available to describe the variance and magnitude of these coefficients. The technique described above would yield these data in a straightforward and accurate manner.

### Nomenclature

$D_{ij}$    Fick diffusion coefficient for $i$ through $j$, cm.$^2$/sec.
$h$    Thickness of polymer melt in diffusion cell, cm.
$n$    Mass flux, g./cm.$^2$ sec.
$r_i$    Production rate of $i$ by chemical reaction, g./cm.$^3$-sec.

$r, \theta, z$   Cylindrical coordinate system
$v$         Mass average velocity, cm./sec.
$w_i$       Mass fraction, $\rho_i/\rho$
$\rho$      Density, g./cm.$^3$
$\rho_i$    Mass concentration of component i, g. of $i$ per cm.$^3$

Subscripts:
$i$         Condensation product
$j$         Condensation polymer
$0$         At porous plate
$h$         At upper surface of polymer melt

### References

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