

MUTUAL DIFFUSIVITY OF VOLATILE MATERIALS IN MOLTEN POLYSTYRENE

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A new method is developed for the determination of mutual diffusivity of low-molecular weight materials in concentrated polymer solution far above the glass transition temperature. The most important feature of the present method is that the diffusivity of the monomer can be determined by consideration of the simultaneous diffusion and polymerization of the monomer. This method can be easily applied to systems containing non-reactive diffusant as well.

The diffusivities of styrene monomer and ethylbenzene in molten polystyrene and their temperature dependency are determined over a temperature range from 423 to 523 K and a concentration range up to 3 wt% of diffusant. Treating the diffusivities as constant regardless of concentration over the experimental range of concentration, we correlate the diffusivities as

$$D = 6.97 \times 10^{-2} \exp(-42400/RT)$$

for styrene and

$$D = 1.17 \times 10^{-2} \exp(-72600/RT)$$

for ethylbenzene, where the units of D , R and T are $\text{cm}^2 \cdot \text{s}^{-1}$, $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ and K, respectively.

Introduction

Recently, the regulations for residual volatile content in a final polymer product have been tightened up due to the requirements of hygiene and the prevention of environmental pollution. Devolatilization processes, in which unreacted monomers and solvents are removed from reactor effluent, have therefore become very important in polymer manufacturing plants. If the volatiles are removed effectively and the residual volatile content in a product is reduced sufficiently to meet the require-

ments through the devolatilization process, it is economically competitive and the polymer product becomes superior in quality.

In polystyrene manufacturing plants, these volatiles are removed by flashing under reduced pressure, or by evaporation from a renewed surface in a film evaporator or an extruder. These operations involve a diffusion process of low-molecular weight components in molten polymer. The optimal design of the devolatilization process requires knowledge of the values of the diffusivities of these components.

The diffusivity of styrene monomer in molten polystyrene above the glass transition temperature was measured by Latinen.⁵⁾ The mutual diffusivities of

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ethylbenzene and toluene in polystyrene were measured by Duda *et al.*^{3,4)} over a wide range of concentration, using the well-known sorption method.^{1,2)} However, data at an elevated temperature are not available.

The sorption method is not suitable for measuring the diffusivity of polymerizable diffusants such as styrene monomer. In this method, the amount of diffusant taken up by polymer film is measured till equilibrium is reached. The ratio of the amount of diffusant to that at equilibrium sorption is used to calculate the diffusivity. The method cannot be used for a diffusant such as styrene monomer because the styrene polymerizes in a film during diffusion and then equilibrium sorption cannot be attained. It is also quite difficult to sustain a polymer film at such an elevated temperature as in an actual devolatilization process, because of the deformation of the polymer film.

In the present paper, we develop a new method for measuring the diffusivity of a monomer or organic solvent in molten polymer. The method proposed here is an unsteady-state technique, and its principle is simple. The method allows polymerization of monomer during a diffusion.

Using this method, we determine the mutual diffusivities of styrene monomer and ethylbenzene and their temperature dependencies in concentrated molten polystyrene at the elevated temperature far above the glass transition temperature. To confirm the soundness of our method, we compare the diffusivity of ethylbenzene with the values of Duda *et al.*³⁾

1. Experimental Apparatus and Procedure

Figure 1 shows schematic diagrams of the experimental apparatus and a diffusion cell. The experiment consists of two steps, a polymerization step and a diffusion step. The former polymerizes the styrene monomer isothermally to prepare the diffusion cell and the latter, which is then carried out, diffuses monomer or solvent in the resultant polymer. In this step, evaporation occurs from the polymer surface under reduced pressure.

In the polymerization step, styrene monomer polymerizes in liquid phase by thermal initiation without catalyst. Styrene monomer is washed with sodium hydroxide and dehydrated with anhydrous calcium chloride, and the approx. 2 g of the monomer is charged into a glass tube, the inner diameter of which is accurately measured in advance. The washed monomer in the glass tube is degassed sufficiently and sealed off under vacuum. Eight to ten sealed glass tubes are placed in an aluminum block heater maintained at the polymerization temperature of 413K. The polymerization is carried out for 24 hours. At the end of the polymerization step, the glass tube

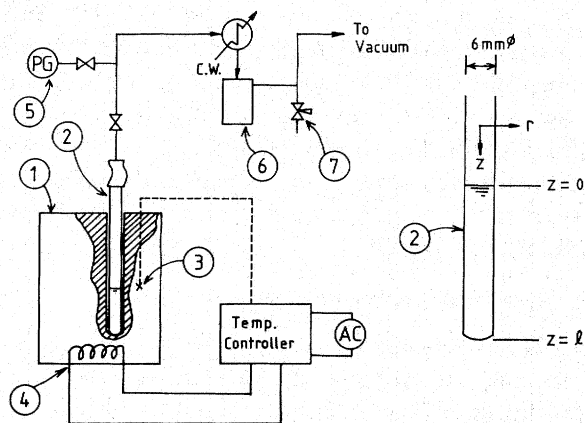


Fig. 1. Schematic diagram of the experimental apparatus and cell: 1, Aluminum block; 2, Cell; 3, Thermocouple; 4, Rod heaters; 5, Manometer; 6, Vacuum trap; 7, Precise needle valve

is taken out to check the molecular weight of polymer. The conversion of styrene monomer was 97–98%. The viscosity averaged molecular weight of polystyrene obtained was 169,000. This molecular weight is of nearly the same order as that of commercially available polystyrene.

For the ethylbenzene system, a mixture of about 3 wt% ethylbenzene with the washed and dried monomer is prepared and sealed off in the same way as for the styrene monomer. The polymerization is carried out at 413 K for 24 hours and continually at 498 K for 72 hours to achieve a final conversion of approximately 100%. The viscosity averaged molecular weight of polystyrene was 140,000.

At the end of the polymerization step, the top of the sealed tubes are opened and the temperature of the aluminum block is changed to the diffusion temperature. Then the diffusion step begins.

After the diffusion temperature is stabilized, the diffusion cells are connected to the vacuum line and evacuation begins. The diffusant vaporizes from the polymer surface and a concentration gradient arises in the polymer layer, i.e., diffusion of the volatile material commences in the polymer layer. The diffusion time is counted from the start of evacuation. The pressure of the system is adjusted at 5300 Pa to regulate the precise needle valve by leaking air into the vacuum system. Under the experimental conditions, the diffusant did not form bubbles in the polymer layer. Each cell is removed from the aluminum block according to the time schedule. The cell is cooled by blowing nitrogen onto the evaporation surface of the polymer. The solidified polymer is removed from the cell and sliced into six to eight cylinders. The cylinders are dissolved completely in dimethylformamide and this solution is analyzed to obtain the diffusant concentration by FID gas chromatograph. Thus the average concentration of the diffusant in the cylinder is determined.

The height of the cylinder is calculated by dividing the weight of the cylinder by the density at the diffusion temperature and the sectional area of the cell. The distance from the evaporation surface is determined as the sum of the cylinder heights.

The temperature range for measuring the diffusivity was from 423 to 523K for styrene and from 423 to 498K for ethylbenzene.

2. Numerical Analysis of Diffusion

2.1 Diffusion equation

Assuming no volume change with polymerization and diffusion, the one-dimensional unsteady-state diffusion equation with chemical reaction is

$$\frac{\partial C}{\partial t} = D \frac{\partial}{\partial z} \left(D \frac{\partial C}{\partial z} \right) - r_e M_w \quad (1)$$

where z is the distance from the evaporation surface, C the mass concentration of diffusant, r_e the molar reaction rate of styrene, M_w the molecular weight of styrene, and D the mutual diffusivity. The initial and boundary conditions are set at follows:

$$C = C_0(z) \quad \text{at } t = 0 \quad (2)$$

$$D \frac{\partial C}{\partial z} = k(C_s - C^*) \quad \text{at } z = 0 \quad (3)$$

$$\frac{\partial C}{\partial z} = 0 \quad \text{at } z = l \quad (4)$$

where $C_0(z)$ is the initial concentration distribution of diffusant, k the film coefficient at the evaporation surface⁵⁾, C_s the surface concentration of diffusant, C^* the equilibrium concentration of diffusant, and l the depth of polymer layer.

The concentration of diffusant during the experiments is less than 3 wt% for both styrene and ethylbenzene. In polymer-organic solvent systems, diffusivity reveals a strong concentration dependency in general. However, in the present study we treat the diffusivity as constant regardless of the diffusant concentration over the experimental range of concentration. Thereby, the system to be solved can be simplified extremely.

In almost the entire experimental period the evaporation rate of diffusant is quite slow, and thus we consider that the partial pressure of the diffusant in gas phase is extremely lower than that of the air throughout the run. Therefore, we assume that the equilibrium concentration C^* is zero.

2.2 Reaction rate

As mentioned in the previous section, the concentration of styrene monomer is sufficiently low. We assume that the molar reaction rate of styrene can be expressed empirically as

$$r_e = k_e C_M^n \quad (5)$$

where k_e is the reaction rate constant, n the reaction order, and C_M the molar concentration of styrene. Equation (5) indicates the substantial rate of decrease of styrene due to both polymerization and depolymerization. As described later (see Fig. 2), the measured concentration distribution of styrene monomer is flat far from the surface. The decrease of concentration with time in this part is due only to the reaction of styrene. This implies that the rate of diffusion of styrene monomer is smaller than the rate of polymerization. Therefore, we determined the rate constant k_e and reaction order n with the least squares method, using the flat concentration distributions which vary with time. For the diffusion of the ethylbenzene system, we may neglect the term of the reaction of styrene in Eq. (1) because the concentration of styrene is up to about 1000 wt ppm during the whole experimental period.

2.3 Determination of D and k

Substitution of Eq. (5) into Eq. (1) gives the following equation.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - k_e C_M^n \cdot M_w \quad (1')$$

This equation cannot be solved by analytical methods but it can be solved by a numerical method under the conditions shown in Eqs. (2)–(4). When the diffusivity D and the film coefficient k are once assigned, the Crank-Nicolson method is useful. To determine optimal values of D and k , let an object function be

$$\text{Obj}(D, k) = \sum \left\{ \frac{\bar{C}_{exp} - \bar{C}_{cal}}{\bar{C}_{exp}} \right\}^2 \rightarrow \text{Min}. \quad (6)$$

where \bar{C}_{exp} and \bar{C}_{cal} are respectively the average concentrations determined experimentally and numerically. The summation in Eq. (6) is carried out over the average concentration of each cylinder obtained during the experiment. For the styrene system, however, data in the vicinity of the evaporation surface are only used to reject systematic errors due to the unfitness of the reaction rate.

For the determination of \bar{C}_{cal} , the discrete concentrations obtained by the Crank-Nicolson method are fitted to the third-order polynomials of the distance z , using four neighboring points of concentration, and the polynomials are integrated over the specified distance ranges to give the average concentration of the cylinder.

Then the optimum variables D and k are determined simultaneously by the simplex optimization method.

3. Results and Discussion

Figures 2 and 3 show a typical observed concentration distribution of styrene for the styrene-

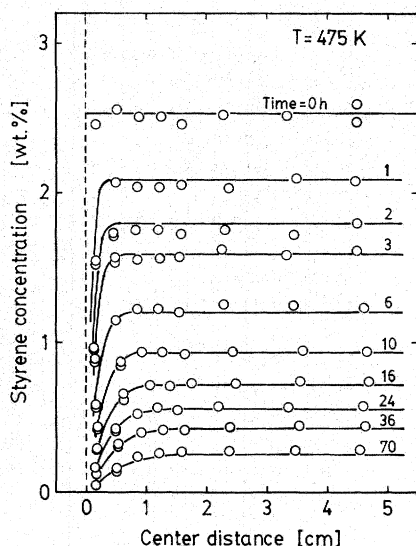


Fig. 2. Concentration distributions with time for styrene-polystyrene system at 475K: Solid lines indicate the optimized distribution.

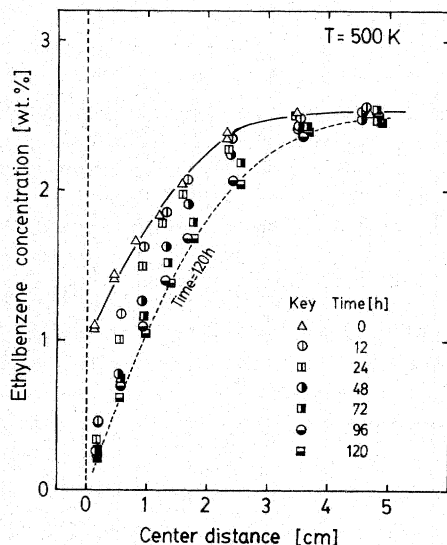


Fig. 3. Concentration distributions with time for ethylbenzene-polystyrene system at 500K: Solid line shows initial concentration distribution, drawn smoothly, and dotted line shows the optimized distribution.

polystyrene system and that of ethylbenzene for the ethylbenzene-polystyrene system, respectively. The keys indicate the observed concentration of diffusant in a sliced cylinder. The abscissa, a center distance, means the distance from the polymer surface to an arithmetic average position between top and bottom of the sliced cylinder. Figure 2 indicates that polymerization exclusively occurred far from the surface and simultaneously occurred with diffusion in the vicinity of the surface. The solid line in Fig. 2 shows the optimized concentration distribution calculated from optimal D and k .

The initial concentration distribution for styrene in Fig. 2 is flat, whereas that for ethylbenzene in

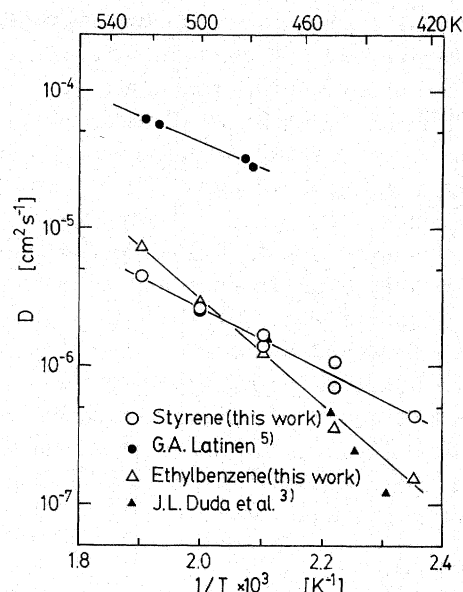


Fig. 4. Temperature dependency of diffusivity for styrene-polystyrene and ethylbenzene-polystyrene systems: Data by Latinen⁵⁾ are for styrene and those by Duda *et al.*³⁾ are zero-concentration diffusivity values for ethylbenzene.

Fig. 3 is a curve. Therefore, we consider the initial concentration distribution $C_0(z)$ is constant, independent of the distance z , for the styrene-polystyrene system. For the ethylbenzene-polystyrene system we approximate it with third-order spline functions.

Figure 4 shows the dependency of the observed diffusivities of styrene and ethylbenzene on temperature, and the observed data by other investigators are also plotted for comparison. Fitting of our experimental results to an Arrhenius-type equation, by using the least squares method, gives

$$D = 6.97 \times 10^{-2} \exp(-42400/RT)$$

for styrene and

$$D = 1.17 \times 10^2 \exp(-72600/RT)$$

for ethylbenzene.

The diffusivity for styrene by Latinen⁵⁾ is larger by one order than ours, but the 37.7 kJ/mole value of activation energy of diffusion reported by Latinen is almost the same as our value of 42.4 kJ/mole. Latinen determined the mass transfer volumetric coefficient by solving the eddy diffusion model from inlet and outlet styrene concentrations. From the volumetric coefficient he derived the diffusivity of styrene assuming a smooth evaporation surface in the extruder and estimating the surface area from the screw geometry. He mentioned that the actual evaporation surface in the extruder was not smooth as assumed. This method causes overestimation of the diffusivity.

Figure 4 also shows that our experiments have high reproducibility, because the diffusivities obtained

separately under almost the same operating conditions such as temperature, pressure and concentration range of diffusant agree well with each other.

The diffusivity values for ethylbenzene obtained by Duda *et al.*³⁾ extrapolated to zero concentration are also shown in Fig. 4. At temperatures above 448 K our experimental data agree well with theirs, whereas at lower temperatures the former deviate extremely from the latter. This deviation may come from the concentration dependency of the diffusivity as mentioned by Duda and Vrentas.^{6,7)}

We confirm that the proposed method for measuring the diffusivity of styrene and ethylbenzene in polystyrene gives satisfactorily sound results, especially at temperatures far above the glass transition temperature of the polymer.

Conclusion

We have developed a new method of measuring mutual diffusivity of low-molecular weight materials including monomer in concentrated molten polymer far above the glass transition temperature. The principle of the method is simple, and the measuring procedures are easy. The most important feature of this method is that the diffusivity of monomer can be measured by considering the polymerization of monomer in the calculation.

Using this method, we measured the diffusivity and its temperature dependency for styrene and ethylbenzene in polystyrene over a wide temperature range. Comparison of these values with the observed data by Duda *et al.*³⁾ indicates that our method gives sound results. It can be easily extended to other monomer-polymer systems in which monomer polymerizes in a liquid phase.

Nomenclature

C	= mass concentration of diffusant	$[\text{g} \cdot \text{cm}^{-3}]$
\bar{C}	= average concentration	$[\text{g} \cdot \text{cm}^{-3}]$
C_M	= molar concentration of styrene	$[\text{mol} \cdot \text{cm}^{-3}]$
C_s	= surface concentration	$[\text{g} \cdot \text{cm}^{-3}]$
C^*	= concentration equilibrium to gas phase pressure	$[\text{g} \cdot \text{cm}^{-3}]$
$C_0(z)$	= initial concentration distribution	$[\text{g} \cdot \text{cm}^{-3}]$
D	= mutual diffusivity	$[\text{cm}^2 \cdot \text{s}^{-1}]$
k	= film coefficient	$[\text{cm} \cdot \text{s}^{-1}]$
k_e	= reaction rate constant defined in Eq. (5)	$[\text{mol} \cdot \text{cm}^{-3} \cdot \text{s}^{-1}]$
l	= depth of polymer	$[\text{cm}]$
M_w	= molecular weight of styrene	$[-]$
n	= reaction order defined in Eq. (5)	$[-]$
R	= gas constant	$[\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}]$
r_e	= molar reaction rate of styrene	$[\text{mol} \cdot \text{cm}^{-3} \cdot \text{s}^{-1}]$
T	= temperature	$[\text{K}]$
t	= time	$[\text{s}]$
z	= distance from evaporation surface	$[\text{cm}]$

<Subscript>

<i>cal</i>	= calculated
<i>exp</i>	= experimental

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