

NOTES

Solubility of Vinyl Chloride in Poly(vinyl Chloride) from Plant Data

INTRODUCTION

It has long been known that poly(vinyl chloride) is practically insoluble in its monomer as is evidenced by the precipitation of the polymer during the bulk polymerization of vinyl chloride. On the other hand, the solubility and diffusion characteristics of vinyl chloride in poly(vinyl chloride) has long been considered no more than scientific curiosity. For example, about 20 to 25 years ago, the precipitated polymer particles were qualitatively noticed by several workers¹⁻³ to be swollen with monomer to a certain extent, but no quantitative measurements were reported.

In recent years it has become very important to make poly(vinyl chloride) free of vinyl chloride monomer. To do this, poly(vinyl chloride) producers need accurate quantitative data on the solubility and diffusion behavior of vinyl chloride in poly(vinyl chloride) so that they can design adequate facilities for the removal of the monomer.

THEORY

Typically, for a system such as vinyl chloride/poly(vinyl chloride), solubility at a given temperature can be measured by mixing known quantities of the polymer and monomer in a pressure vessel of known volume and measuring the pressure at equilibrium. At low pressures, higher accuracy can be achieved by using an electrobalance. Both techniques were recently utilized by Berens^{4,5} to measure the solubility of vinyl chloride in poly(vinyl chloride). Berens fitted his data to the Flory-Huggins equation⁶:

$$\ln a_1 = \ln \phi_1 + \phi_2 + \chi \phi_2^2 \quad (1)$$

where a_1 = solute (vinyl chloride) activity = P/P_0 , P being the equilibrium partial pressure and P_0 the vapor pressure at the given temperature; ϕ_1 = volume fraction of the monomer; ϕ_2 = volume fraction of the polymer = $(1 - \phi_1)$; and, χ = Flory-Huggins interaction parameter.

He found that a value of $\chi = 0.98$ represented the best fit of the data above 1 atmosphere. This value was found to be independent of temperature.

In this paper actual plant data were used to measure the solubility of vinyl chloride in poly(vinyl chloride) at pressures above 1 atmosphere. In suspension polymerization of vinyl chloride, the pressure in the reactor is the vapor pressure of monomer at reaction temperature. The pressure remains constant until about 70%–80% conversion, and then it starts to drop continuously until the reaction is terminated (for example, by adding a chain stopper). The theory behind this is that the polymerization of vinyl chloride in suspension or bulk takes place in two phases.^{7,8} The composition of each phase is given by the saturation solubilities of the monomer and the polymer in each other. The monomer-rich phase is essentially pure monomer since poly(vinyl chloride) is insoluble in vinyl chloride. The polymer-rich phase is a mixture of polymer and monomer given by the saturation solubility of vinyl chloride in poly(vinyl chloride). As the reaction proceeds and the monomer is converted into polymer, the mass of the monomer-rich phase decreases while that of the polymer-rich phase increases, but the composition of each phase remains unchanged. As long as vinyl chloride exists as a separate phase, it will exert its own vapor pressure and the pressure in the reactor will assume a constant value. Classical homogeneous kinetics apply to the specific reaction rates in each phase, and the apparent rate is the weighted sum of the two with a variable weighing factor. At the point when the free monomer phase is completely depleted the reaction continues, but in one phase only, namely, the polymer-rich phase. The conversion at this point is identical to the polymer content of this phase. At higher conversions the composition of the reaction mixture changes and the monomer content continually decreases. The equilibrium partial pressure of vinyl chloride also decreases, following the composition of the monomer/polymer mixture. If the reaction is stopped during the pressure drop period at any specified pressure, the composition of the monomer/polymer

mixture in equilibrium with vapor phase at this pressure can be calculated by determining the polymer yield (y) and calculating the conversion (c) from the yield as shown in the next section.

RESULTS AND DISCUSSION

Results from a series of actual plant polymerizations terminated at different pressures are given in Table I. The yield y is defined as follows:

$$y = \frac{\text{mass of polymer produced}}{\text{mass of monomer charged}} \quad (2)$$

Conversion c can be calculated from the yield by allowing for the inaccessible monomer. This is the monomer in the vapor space of the reactor and the monomer dissolved in the suspending medium, usually water. At the pressure drop point, the inaccessible monomer $(M_{in})_{P_0}$ is given by

$$(M_{in})_{P_0} = M_v + M_w \quad (3)$$

where M_v is the mass of monomer in the vapor space. This can be calculated from the volume of vapour space (V), the pressure in the reactor (P_0), and reaction temperature (T):

$$M_v = 62.5P_0V/RT \quad (4)$$

where R is the gas constant and 62.5 is the molecular weight of vinyl chloride. M_w is the mass of monomer dissolved in the water; it can be calculated from the mass of water in the reactor (W) using an expression derived from the data of Berens⁴ of vinyl chloride solubility in water at various temperatures. The solubility is given by

$$\frac{\text{grams vinyl chloride}}{\text{grams water}} = 0.01 \left(\frac{P}{P_0} \right) \quad (5)$$

where P is the pressure and P_0 is the vapor pressure. At pressure drop point the pressure is the vapor pressure, and hence M_w is given by

$$M_w = 0.01W \quad (6)$$

Since M_v and M_w are linear functions of the pressure, the inaccessible monomer at any termination pressure is given by

$$(M_{in})_P = (M_{in})_{P_0} \frac{P}{P_0} \quad (7)$$

The inaccessible monomer does not take part in the reaction, and this results in the apparent yield (y) being lower than the actual conversion (c).

If M_0 is the mass of the monomer charged to the reactor, the actual conversion at termination is calculated from the yield as follows:

$$c = y / \left(1 - \frac{M_{in}}{M_0} \right) \quad (8)$$

If ρ_m and ρ_p are the densities of monomer and polymer, respectively, the volume fraction of the polymer in the mixture (ϕ_2) is given by

$$\phi_2 = \frac{c\rho_m}{c\rho_m + (1-c)\rho_p} \quad (9)$$

The Flory-Huggins equation can be rewritten as

$$\ln \left(\frac{a_1}{\phi_1} \right) - \phi_2 = \chi\phi_2^2 \quad (10)$$

If $[\ln(a_1/\phi_1) - \phi_2]$ is plotted versus ϕ_2^2 , a straight line passing through the origin should result. The slope of the line is the interaction parameter χ . Such a plot is shown in Figure 1. The slope χ of the best-fit line passing through the origin is estimated as 0.985. This estimate of χ is in excellent agreement with Berens' estimate^{4,5} of $\chi = 0.98$ and also in fair agreement with $\chi = 0.88$ as estimated by Gerrens et al.⁹ from data on emulsion polymerization of vinyl chloride.

The good agreement with Berens' estimate suggests that the presence of water does not influence the solubility of vinyl chloride in PVC, since Berens carried out his experiments in the absence of water.

TABLE I
Yield and Conversion Results at Various Termination Pressures^a

Reaction temperature, °C	Reaction pressure P_0 , psia	Termination pressure P , psia	Monomer activity $a_1 = P/P_0$	Observed yield y	Calculated conversion c , eq. (8)	Polymer volume fraction ϕ_2 , eq. (9)	Monomer volume fraction $\phi_1 = 1 - \phi_2$	$\ln \left(\frac{c_1}{\phi_1} \right) - \phi_2$
57	139.7	134.7	0.964	0.775	0.801	0.707	0.293	0.484
57	139.7	129.7	0.928	0.801	0.826	0.740	0.260	0.532
57	139.7	105.7	0.757	0.869	0.893	0.834	0.166	0.683
57	139.7	99.7	0.714	0.880	0.902	0.847	0.153	0.693
57	139.7	84.7	0.606	0.910	0.930	0.889	0.111	0.808
65	163.8	134.7	0.822	0.866	0.880	0.811	0.189	0.659
65	163.8	104.7	0.639	0.908	0.920	0.871	0.129	0.758

^a Density of polymer = 1.403 g/cm³; density of monomer = 0.9479 - 0.00189T g/cm³, T in °C.

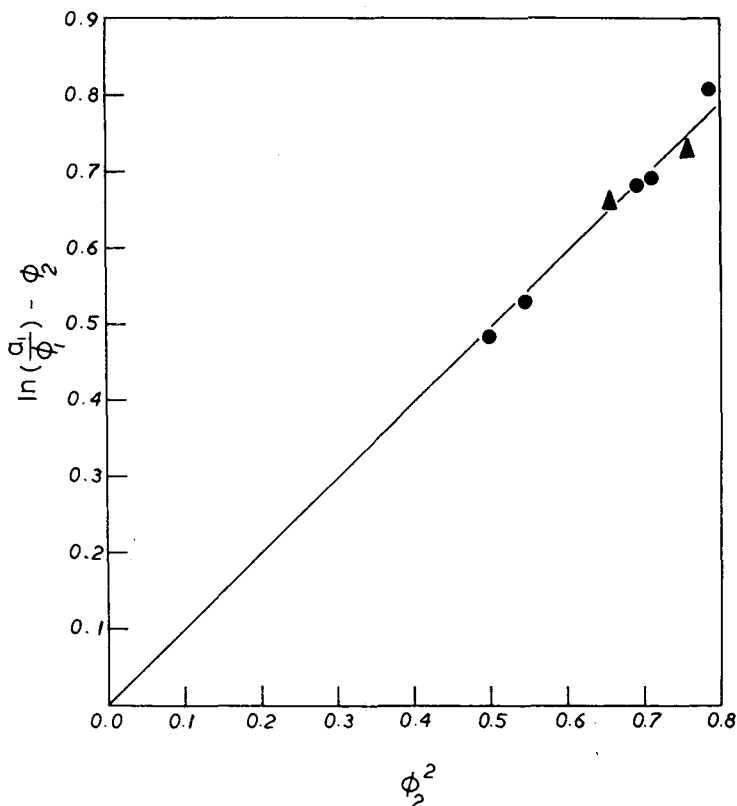


Fig. 1. Flory-Huggins plot of plant data: (▲) 65°C; (●) 57°C.

The conversion c at the pressure drop point can be obtained by solving eq. (1) for ϕ_2 at $a_1 = 1$. Rearranging eq. (9) to yield conversion from polymer volume fraction ϕ_2 ,

$$c = \frac{\phi_2 \rho_p}{\phi_2 \rho_p + (1 - \phi_2) \rho_m} \quad (11)$$

For $a_1 = 1$, eq. (1) yields $\phi_2 = 0.675$. Substituting this value in eq. (11) yields the conversion at the pressure drop point as 77.6% at 57°C and 77.9% at 65°C.

It is also noted from Figure 1 that points from runs at different temperatures lie on the same line, indicating that χ is independent of temperature in the range studied. This conclusion is also in agreement with Berens' conclusions.

The correlation between the pressure in the reactor and conversion during the pressure drop period can be very useful in determining the yield of the reaction at termination. Conversely, the correlation could also be used to terminate the reaction at any desired conversion.

CONCLUSIONS

Quantitative description of the solubility behavior of vinyl chloride in poly(vinyl chloride) could be obtained by utilizing actual plant data to estimate the Flory-Huggins interaction parameter χ . Although this method is equivalent to and in excellent agreement with the one carried out in the laboratory by mixing known quantities of monomer and polymer, it offers two distinct advantages. First, the data are usually available from reactors since the pressure is recorded and the yield is measured routinely. Secondly, the system is at equilibrium all the time since the changes involved are gradual and small, unlike the large step change associated with mixing pure polymer and pure monomer.

Solubilities in other systems where the polymer has partial solubility in the monomer can be determined by applying the method described in this article. Examples of such systems are polyacrylonitrile and poly(vinylidene chloride).

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