

Diffusion of Dioctyl Phthalate into Poly(vinyl Chloride)

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Synopsis

Diffusion coefficients were determined gravimetrically for the diffusion of dioctyl phthalate into disks of suspension-polymerized poly(vinyl chloride) in the temperature range of 65–85°C. After an initial induction period, values of D were obtained which ranged from 10^{-10} to 10^{-8} cm.²/sec. and which gave an activation energy of 60 kcal./mole. The diffusion rates showed an inverse dependence on the number-average molecular weight of the poly(vinyl chloride), indicating that the chain ends are the primary point of attack in the diffusion process below the glass transition temperature.

Introduction

The importance of the rate of diffusion of plasticizers into poly(vinyl chloride) to the ease and speed by which plasticized articles can be made has prompted a study of the factors which affect the rate of diffusion of plasticizers into unplasticized polyvinyl chloride. Studies have been made by Knappe^{1,2} and by Kikkawa^{3,4} of the diffusion rate between two disks of plasticized poly(vinyl chloride) of different plasticizer content, but only the studies of Dannis^{5,6} seem to have been made on unplasticized poly(vinyl chloride). Diffusion coefficients of 10^{-6} – 10^{-9} cm.²/sec. and activation energies of 6–30 kcal./mole were obtained for the pre-plasticized polymers, depending upon the concentration of plasticizer in the system. Dannis, by following the change in dielectric constant of plasticizer-polymer systems and treating his results as a first-order chemical reaction, obtained values of 70–110 kcal./mole for the unplasticized polymers. Dannis reported different results for different samples of suspension-polymerized poly(vinyl chloride), but offered no reason for the cause of these observations.

Experimental

The diffusion measurements were made on disks of suspension-polymerized poly(vinyl chloride) which were prepared from the poly(vinyl chloride) granules in a metallurgical press at a pressure of 10,000 psi and a temperature of 85°C. Samples of 5 g. polymer were used in a cylindrical mold of 1.25 in. diameter. The disks were suspended in test tubes containing the plasticizer in a constant temperature oil bath controlled to 0.05°C. The disks were removed at intervals and weighed on an analytical balance

to obtain the amount of plasticizer which had diffused into the disks. This procedure was found to be effective for the suspension polymerized polymers. The disk surface could be readily wiped dry of excess plasticizer and no detectable solution of the polymer occurred during the course of the measurements. The results for a given polymer sample were reproducible to within 8%.

The samples of poly(vinyl chloride) employed were kindly furnished by the B. F. Goodrich Chemical Company. The number-average molecular weights of the polymers were determined from intrinsic viscosity measurements in purified cyclohexanone in a Ubbelohde viscometer which was calibrated with National Bureau of Standards standard viscosity oils. The intrinsic viscosities were converted to number-average molecular weights by the relationship of Danusso, Moraglio, and Gazzera.⁷

$$[\eta] = 2.4 \times 10^{-5} \bar{M}_n^{0.77} \quad (1)$$

The plasticizer used was Matheson, Coleman, and Bell practical grade di-2-ethylhexyl phthalate (dioctyl phthalate). No attempt was made to purify this material before use.

The uniform dispersion of additives to the polymer samples was effected by adding them in a suitable solvent and then slowly evaporating the solvent. Benzene was used as the solvent for benzoyl and lauroyl peroxides, and water was used as the solvent for sodium stearate, sodium lauryl sulfate, poly(vinyl alcohol) (DuPont Elvanol 50-42), and methyl cellulose (Dow Methocel, 4000 cpoise). The final traces of the solvent were removed by heating in a vacuum oven for 4 hr. at 70°C.

Results

A convenient solution^{8a} of Fick's second law of diffusion for a constant concentration, C_0 , of diffusing substance maintained at both ends of an infinite cylinder is

$$C = C_0[1 - \operatorname{erf}(x/2\sqrt{Dt})] \quad (2)$$

where C is the concentration at distance x from the surface and at time t , D is the diffusion coefficient, and $\operatorname{erf}(x)$ is the Gauss error function

$$\operatorname{erf}(x) = (2/\sqrt{\pi}) \int_0^x \exp\{-\eta^2\} d\eta \quad (3)$$

The total weight, s , of substance that diffuses across a total cross-sectional area of q in time t is given by

$$s = q \int_0^t J dt = 2qC_0(Dt/\pi)^{1/2} \quad (4)$$

where

$$J = -D(\partial C/\partial x)_{x=0} \quad (5)$$

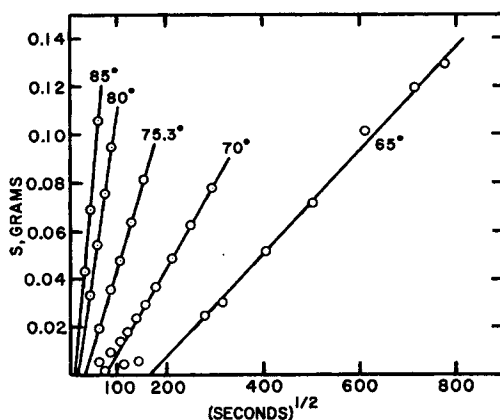


Fig. 1. Plot of the increase in weight of the poly(vinyl chloride) disks vs. the square root of time.

When this relationship is obeyed a plot of s versus $t^{1/2}$ will be linear with a slope of $2qC_0(D/\pi)^{1/2}$. The value of the diffusion coefficient is then given by

$$D = \pi(\text{slope})^2/4q^2C_0^2 \quad (6)$$

Plots of the diffusion data obtained according to this relationship gave results as illustrated in Figure 1. After an initial induction period which was time- and temperature-dependent, linear plots were obtained.

To determine if the induction period was associated with a fortuitous difference at the disk surface or if it was associated with the diffusion process, 1/2 mm. was slowly sanded off of both sides of two disks. Diffusion measurements on these disks also showed induction periods as illustrated in Figure 1, followed by a linear dependence of s on the square root of t .

To calculate values for D , C_0 was taken to be the density of the plasticizer at the temperature of measurement. The values obtained for D varied from 9.6×10^{-11} cm.²/sec. at 65°C. to 3.0×10^{-8} at 85°C. and were found to depend on the sample of polymer employed. The simplest diffusion theory^{8b} predicts the temperature dependence of D to be

$$D = A \exp\{-Q/RT\} \quad (7)$$

where A is a frequency factor and Q is an activation energy. Diffusion measurements were made on two samples of poly(vinyl chloride) at 65, 70, 75.3, 80, and 85°C. The values of $\log D$ are plotted against $1/T$ in Figure 2. For one of the polymer samples, values of 57 kcal./mole and 6.9×10^{26} cm.²/sec. were obtained for Q and A , respectively, and for the other sample, values of 63 kcal./mole and 3.5×10^{31} cm.²/sec. were obtained.

A series of diffusion measurements were made at 80°C. in an effort to determine the cause of the difference in diffusion rate for different samples of poly(vinyl chloride). The polymer samples could differ in the amount of residual peroxides and suspending agents from the polymerization process

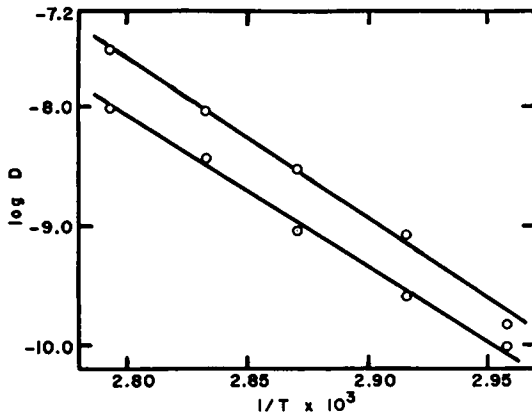


Fig. 2. Plot of the logarithm of the diffusion coefficients for two samples of poly(vinyl chloride) vs. the reciprocal of the absolute temperature.

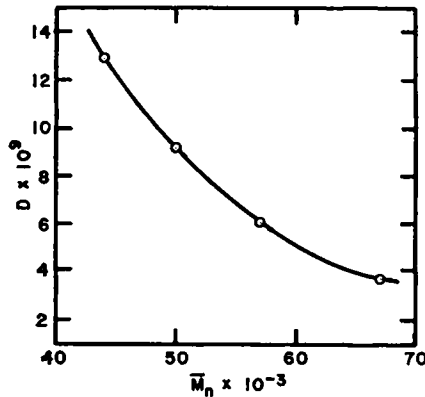


Fig. 3. Plot of the diffusion coefficients at 80°C. vs. the number-average molecular weights of the samples of poly(vinyl chloride).

and in the molecular weight and molecular structure of the polymer molecules. To determine if small amounts of residual substances from the polymerization process could alter the diffusion rates, disks were prepared with added benzoyl peroxide, lauroyl peroxide, sodium stearate, sodium lauryl sulfate, poly(vinyl alcohol), and methyl cellulose. No significant change in diffusion rate was observed when the amounts of the additives were at a level that might be expected to be left from the polymerization process. Relatively large amounts, 1% or more by weight of the polymer, of the peroxides or of sodium lauryl sulfate or sodium stearate acted as a plasticizer and increased the rate of diffusion of dioctyl phthalate into the disks. Relatively large amounts of poly(vinyl alcohol) or of methyl cellulose caused a decrease in the rate of diffusion of dioctyl phthalate into the disks.

Diffusion measurements were made on two more samples of suspension poly(vinyl chloride) at 80°C. and the number-average molecular weights of the polymers were determined. A plot of the diffusion coefficient against number-average molecular weight is given in Figure 3. The results show a continuous decrease in diffusion coefficient with increase in number-average molecular weight.

Discussion

The appearance of an induction period and the apparent independence of the diffusion rate on the swelling of the plasticized system both imply that the rate-determining process in the diffusion is the movement of segments of the polymer chain. The rate of diffusion is slow until a portion of the surface polymer molecules have been solvated by the plasticizer. The induction period would be expected to disappear at temperatures somewhere above the glass transition temperature of the poly(vinyl chloride) (78–82°C.). This trend is shown by the data in Figure 1.

The apparent dependence of diffusion rate on polymer molecular weight indicates that the chain ends make a greater contribution to the rate than the centers of the polymer chains. The lack of a linear dependence on the number average molecular weight might be ascribed to an increase in the degree of branching with the temperature of polymerization of the vinyl chloride. Cotman⁹ concluded from his studies that poly(vinyl chloride) is a significantly branched polymer. The increase in branching with an increase in polymerization temperature has been well established for a number of polymers.¹⁰

This study gives an activation energy which is intermediate between the values reported in the literature. Knappe,¹ however, showed that the activation energy increased with decreasing concentration of plasticizer in his pre-plasticized samples of poly(vinyl chloride). The still higher values of the activation energy which were obtained by Dannis by following the change in dielectric constant indicate that there is a higher energy barrier for dipole orientation of the polymer segments than for the movement of the segments to accommodate the diffusing plasticizer molecules.

Dannis⁵ treated his data as a first-order chemical reaction after stating that the results did not conform to the mathematical treatment of diffusion of a substance into spherical particles. His results, however, are consistent with the mathematical treatment of diffusion into spheres since the relationship that he observed was

$$\ln[(\epsilon_2 - \epsilon_1)/(\epsilon_2 - \epsilon_t)] = mt \quad (8)$$

where ϵ_2 and ϵ_1 are the final and initial dielectric constants and ϵ_t is the dielectric constant at time t . This agrees with the solution to Fick's second law of diffusion for diffusion into a sphere of radius r_0

$$\ln[(C_2 - C_1)/(C_2 - C_t)] = (t/\tau) - \ln(6/\pi^2) \quad (9)$$

for sufficiently large values of t .^{8c}

In eq. (9) $\tau = r_0^2/\pi^2 D$. It is of interest to compare the data of Dannis with the results of this study to obtain the average diameter of the poly(vinyl chloride) granules used by Dannis. Suspension-polymerized poly(vinyl chloride) particles have average diameters in the range of 75–200 μ , but they are somewhat porous and are believed to be an agglomeration of smaller particles of perhaps 1–3 μ in diameter. τ was calculated from the curve at 70°C. from Figure 5 of reference 5 and combined with the diffusion coefficients obtained in this study to calculate the diameters of the particles employed by Dannis. This gave values between 126 and 226 μ (depending on the value of D used), which is in excellent agreement with the external dimensions of suspension poly(vinyl chloride) granules, but which, unfortunately, does not provide any information about the internal structure of the granules.

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Résumé

On a déterminé par gravimétrie les coefficients de diffusion du phtalate de dioctyle dans des disques de chlorure de polyvinyle polymérisés en suspension. Les mesures ont été effectuées entre 65 et 85°. On trouve, après une période d'induction initiale, des valeurs de D variant entre 10^{-10} et 10^{-8} $\text{cm}^2 \text{sec}^{-1}$, ce qui donne une énergie d'activation de 60 Kcal. mole⁻¹. Les vitesses de diffusion varient en fonction inverse du poids moléculaire exprimé en nombre, ce qui indique que les fins de chaîne sont attaquées en premier lieu pendant le processus de diffusion, ceci en-dessous du point de transition vitreuse.

Zusammenfassung

Für die Diffusion von Dioctylphthalat in Scheiben von Suspensionspolymerisiertem Polyvinylchlorid im Temperaturbereich von 65–85° wurden die Diffusionskoeffizienten gravimetrisch bestimmt. Nach einer anfänglichen Induktionsperiode wurden D -Werte, die im Bereich von 10^{-10} bis 10^{-8} $\text{cm}^2 \text{sec}^{-1}$ liegen und eine Aktivierungsenergie von 60 Kcal mol⁻¹ ergeben, erhalten. Die Diffusionsgeschwindigkeit zeigt eine reziproke Abhängigkeit vom Zahlenmittel des Molekulargewicht des Polyvinylchlorids, was zeigt, dass die Kettenenden der primäre Angriffspunkt im Diffusionsprozess unterhalb der Glasstemperatur sind.

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