Diffusion of Benzene through Poly(γ-benzyl L-glutamate)

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ABSTRACT: Permeability of benzene through poly(γ-benzyl L-glutamate) (PBLG) film was found to be dependent on the solvent used for casting the membrane. Thin films of PBLG were cast from methylene chloride and benzene solutions. Permeability of benzene (liquid) through these membranes was measured at different concentrations of benzene, using heptane as diluent. Although the solubility coefficient of the film cast from benzene was only ~18% higher than that of the film cast from methylene chloride (densities being identical), the diffusion coefficient of benzene at infinite dilution, $\bar{D}_0$, of the former film exceeded that of the latter one by ~550%. These data indicate differences in the morphology of the membranes. The origin of these differences has been related to the different lyotropic solutions (cholesteric in the case of PBLG in methylene chloride and probably smectic in the other case) from which these films were cast.

The diffusion rate of a penetrant in a membrane is governed by a number of factors, including the chemical nature, molecular size, and molecular shape of the diffusing species as well as physiochemical properties of the polymer. The dependence of the diffusion rate on the morphological features of the polymer is of particular interest to polymer scientists. Studies by Samulski and Tobolsky[2] showed that solid films of PBLG cast from solvents such as chloroform or methylene chloride retain the cholesteric liquid-crystal structure found in the fluid liquid crystalline solutions of PBLG.[3–5] Powers and Peticolas[6,7] have recently shown evidence for the presence of the smectic phase in concentrated solutions of PBLG in benzene and dioxane and, therefore, it could be expected that solid films of PBLG cast from benzene should also maintain reminiscent characteristics of the smectic phase. We would like to present, therefore, in this paper some preliminary results of diffusion of an organic molecule, benzene, in two PBLG films which possess different morphological characteristics as a result of film preparation from methylene chloride and benzene, respectively.

Experimental Section

Materials. PBLG with a molecular weight of 3.1×10^5 (Lot No. G-152) was obtained from Pilot Chemical, Inc. Methylene chloride (ACS grade, Matheson Coleman and Bell) and benzene (ACS grade, Allied Chemicals) were used without any further purification. Heptane (ACS grade, Matheson Coleman and Bell) was purified by continuously extracting it with three portions of concentrated sulfuric acid at 60° over a period of 24 hr. It was then stored over sodium hydroxide pellets before use.

Film Preparation. PBLG films were prepared by casting 2–3% solutions (by weight) on a mercury surface. Evaporation of the solvent while casting films from methylene chloride was completed in 4 days, while that from benzene took 7 days. The solid films, 10 × 8 cm, were then placed in a vacuum oven at 25° for a period of 2 weeks. Both films have glass-transition temperatures of about 25°.

Swelling Experiments. Strips of PBLG films, 1–2 mils thick and 0.15–0.20 g in weight, were cut and dried *in vacuo* at room temperature. The films were weighed and then immersed in benzene–heptane mixtures of varying proportions. Heptane was chosen as an inert diluent for benzene in order to vary the chemical potential of benzene. After several days, the films were removed from the solutions, surface dried with filter paper, and immediately weighed. Correction was made for the small amount of heptane absorbed by the film. This procedure was repeated until swelling equilibrium was reached. The swelling data are used to calculate solubility S in eq 1.

Permeation Studies. Liquid permeation fluxes were measured by using the permeation cell illustrated in Figure 1. A membrane of a suitable size, 6 × 6 cm, was cut from those portions of the film which did not vary in thickness by more than 0.05 mil. It was then placed in position as shown in Figure 1, and the two half-cells were clamped together. Each chamber of the cell was filled with an accurately measured quantity of purified heptane. The cell was tightly capped and allowed to stand overnight to check for possible leakages and at the same time to allow the system to come to equilibrium. The next day, a portion of the heptane from the right side (side A) was pipetted out and replaced by the same volume of benzene. Aliquots were taken from side B at given time intervals and were replaced by equal volumes of heptane. The quantity, Q, of benzene permeated through the membrane at any time was determined from the concentration of benzene in the aliquot by measuring the intensity of the absorption with the use of a Cary 14 spectrophotometer. The amount diffused never exceeded 2% of the total concentration of benzene; as a first approximation, constant concentrations are maintained at both sides of the film. The steady-state permeation rate gives the permeability, P, from which the average diffusion coefficient, $\bar{D}$, may be obtained by using the relation

$$P = \bar{D}S \tag{1}$$

where S is the solubility coefficient. No correction was made for the increase in the thickness of the film during the permeation experiment because the increase did not exceed 10% even at the highest benzene concentration for either films.

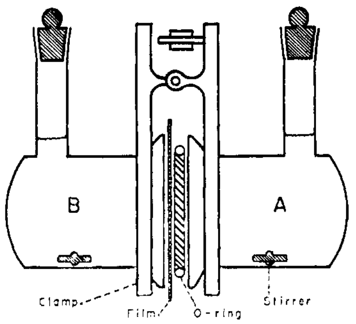

Figure 1. Permeation apparatus.

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[1] (a) Princeton University; (b) Bell Laboratories.

[2] (a) E. T. Samulski and A. V. Tobolsky, *Nature (London)*, **216**, 997 (1967); (b) *Mol. Cryst. Liq. Cryst.*, **7**, 433 (1969).

[3] A. Elliot and E. J. Ambrose, *Discuss. Faraday Soc.*, **No. 9**, 246 (1950).

[4] C. Robinson, *Trans. Faraday Soc.*, **52**, 571 (1956).

[5] C. Robinson, *Tetrahedron*, **13**, 219 (1961).

[6] J. C. Powers, Jr., and W. L. Peticolas, *Biopolymers*, **9**, 195 (1970).

[7] J. C. Powers, Jr., and W. L. Peticolas, *Advan. Chem. Ser.*, **No. 63**, 217 (1967).

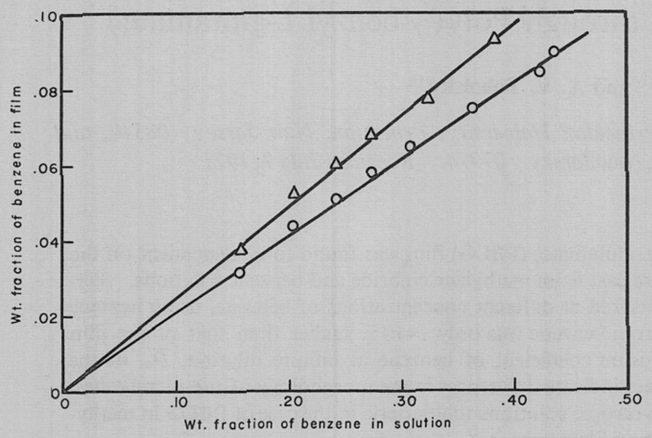

Figure 2. Solubility of benzene in PBLG films, cast from benzene (△) and methylene chloride (○).

X-Ray. X-Ray diffractions were taken with a Weisenberg camera with a Cu Kα, Ni-filtered source.

Results and Discussion

Both PBLG films absorb small quantities of heptane at room temperature; the equilibrium absorption is 0.5% by weight for the methylene chloride film and 2.5% for the benzene film.

The results of the swelling experiments are plotted in Figure 2. It is interesting to point out that linear solubility isotherms, exemplified by Henry's law, are obtained. The solubility S is 0.203 (calculated as weight fraction of benzene in the polymer divided by its weight fraction in solution) for the film cast from methylene chloride and 0.240 for the film cast from benzene.

In Figure 3 we have presented a comparison of the permeation rates of benzene through the PBLG films cast from methylene chloride and benzene. Figure 4 is a plot of log $\bar{D}$ *vs.* concentration of benzene. The relationship between $\bar{D}$ and concentration can be expressed as follows

$$\bar{D} = \bar{D}_0 e^{\alpha c} \quad (2)$$

where $\bar{D}_0$ is the average diffusion coefficient at infinite dilution, obtained from the intercept of Figure 4, α is the slope of the graph, and c is the molar concentration of benzene in solution at the upstream side of the permeation cell. This type of concentration dependence is known to be indicative of a strong interaction between the penetrant and the film. The values of D_0 are 1.1×10^{-10} cm² sec⁻¹ for the CH_2Cl_2 film and 6.9×10^{-10} cm² sec⁻¹ for the benzene film. On the other hand, the α values are similar in magnitude, 1.21 for the former film and 1.12 for the latter.

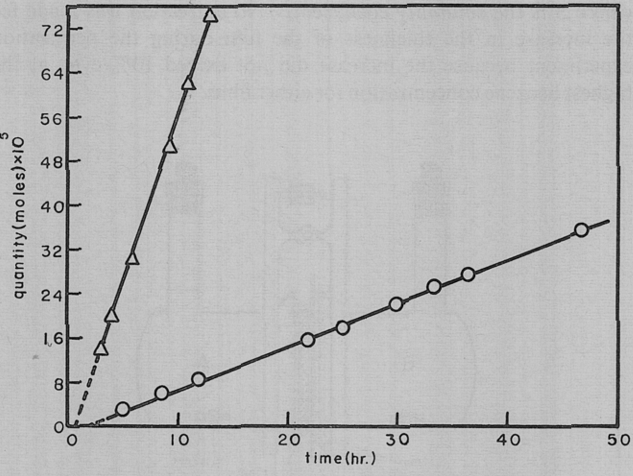

Figure 3. Comparison of permeation of benzene through PBLG films cast from benzene (△) and methylene chloride (○) ; c = 1.7 *M*.

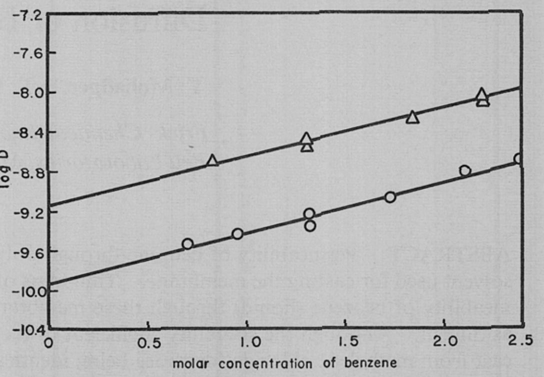

Figure 4. Dependence of diffusion coefficient of benzene on concentration of benzene; films cast from benzene (△) and methylene chloride (○).

Clearly the films cast from benzene exhibit greater permeability than films prepared from methylene chloride. For example, permeability of benzene through the benzene cast film is 650% higher than that through the methylene chloride cast film (see Figure 3), and the diffusion coefficient at infinite dilution, $\bar{D}_0$, of the former film exceeds that of the latter by ~550%. On the other hand, the increase in solubility coefficient of the PBLG film cast from benzene relative to the film cast from methylene chloride is only 18%. This indicates that morphological changes affect the diffusion coefficient of the membrane to a higher degree than does the solubility coefficient. Similar results have been reported for other systems.

Roberts and Kammermayer[8] studied permeation rates of gases through various solution cast ethyl cellulose films; however, the change of permeation rate, approximately 10–12% for N_2, O_2, and CO_2 at 25°, is small compared to the variations that we have observed in our systems. Michaels, *et al.*,[9] have studied the transport of different organic liquids through polypropylene membranes prepared and treated in a

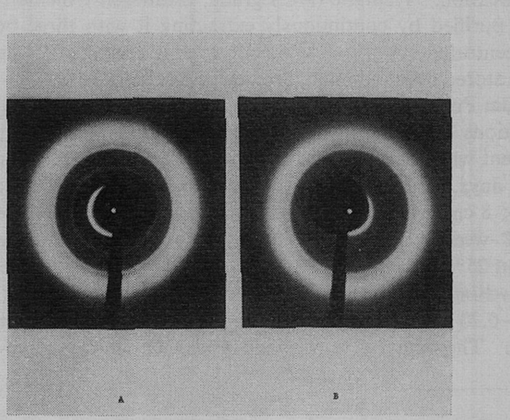

Figure 5. PBLG X-ray diffraction patterns from thin-film sandwich; X-ray normal to film surface. Films cast from methylene chloride (A) and benzene (B).

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[8] R. S. Roberts and K. Kammermeyer, *J. Appl. Polym. Sci.*, 7, 2183 (1963).

[9] A. S. Michaels, W. Vieth, A. S. Hoffman, and H. A. Alcalay, *ibid.*, 13, 577 (1969).

variety of conditions. Films annealed in various organic solvents exhibited enhanced permeability relative to untreated membranes. They postulate that this enhancement is caused by formation of more open or coarser spherulitic structures as a result of recrystallization during annealing. However, the same explanation is inapplicable to the PBLG films, since the formation of spherulites has been reported to occur only in aged solutions of PBLG.

To check whether the enhanced permeability of the benzene cast films was due to lower density of this film relative to the film cast from methylene chloride, densities of the membranes were measured at 25°. It was found that the densities were identical, 1.265 g cm^{-3}. This finding eliminates the possibilities of the "voids" left behind by the benzene molecule during casting, since if that were the case, one would expect a lower density for this film.

X-Ray scattering diagrams were taken from a sandwich of thin films with the incident beam normal to the surface (Figure 5). Films cast from methylene chloride show a more ordered pattern than the films cast from benzene, and this could account, in part, for the lower permeation rate of the former films. It appears that the two different morphological structures are reflected in the different path lengths of diffusion and therefore in the values of diffusion constants.

Pressure Coefficients for Newtonian Viscosity of Polymeric Liquids[1]

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ABSTRACT: Mathematical relationships between Newtonian viscosity and equilibrium p–v–T properties are reviewed and applied to published η–p–T data on polymeric liquids. It is shown empirically that at constant (*i.e.*, atmospheric) pressure the ratio of the compressibility, βv, and the isoviscosity term, $(\partial T/\partial p)_\eta$, is quite insensitive to temperature over a broad range down to the glass-transition temperature, *i.e.*, $\beta v/(\partial T/\partial p)_\eta = K$. From this, the variation of the viscosity–pressure coefficient, $(\partial \ln \eta/\partial p)_T$, with temperature can be predicted. For seven nonpolar polymeric liquids for which experimental data are available, $-10^4 K = 17(\pm 1)$ cm^3/(g deg), apparently a "universal" constant for such liquids.

Relatively few measurements of pressure effects on the Newtonian viscosity of polymeric liquids have been reported. Somewhat more data are available on the pressure dependence of the glass-transition temperature, T_g, measured by a number of techniques. This paper discusses relationships between effects of pressure on T_g and viscosity, leading to methods for predicting the pressure coefficient of viscosity at various temperatures.

Although these relationships are focused on viscosity, it will become apparent that they should apply equally well to other relaxation processes which involve segmental mobility of the main polymer chain, such as the α process in dielectric relaxation.

Thermodynamic Equations

The following are exact relationships between the variables viscosity, volume, pressure, and temperature.

$$(\partial \ln \eta/\partial T)_v = (\partial \ln \eta/\partial T)_p + \alpha_0 \gamma \qquad (1)$$

where $\gamma = (\partial p/\partial T)_v$, the thermal pressure coefficient, and $\alpha_0 = (\partial \ln \eta/\partial p)_T$, the pressure coefficient of viscosity. (The latter symbol is attributed to Hellwege and coworkers[2] and is not to be confused with α, the thermal expansion coefficient). Since

$$\alpha_0 = -(\partial \ln \eta/\partial T)_p(\partial T/\partial p)_\eta \qquad (2)$$

eq 1 can be rearranged to

$$(\partial \ln \eta/\partial T)_v/(\partial \ln \eta/\partial T)_p = E_v/E_p = 1 - \gamma(\partial T/\partial p)_\eta \qquad (3)$$

in which E_v and E_p are the flow "activation energies" at constant volume and pressure, respectively. The "activation volume" is given by

$$\Delta V^* = RT\alpha_0 = -RT(\partial \ln \eta/\partial T)_p(\partial T/\partial p)_\eta \qquad (4)$$

The following equation, explicit in volume, has already been reported[3] in an altered form

$$[(\partial v/\partial T)_\eta - (\partial v/\partial T)_p] = (\partial v/\partial p)_T/(\partial T/\partial p)_\eta \qquad (5)$$

$$= (\partial \ln \eta/\partial T)_p/(\partial \ln \eta/\partial v)_T \qquad (5a)$$

Henceforth in this paper, the term in the brackets will be designated as K. It will be shown that for a given liquid at constant (*i.e.*, atmospheric) pressure, K appears to be independent of temperature.

The temperature dependence of liquid viscosity at atmospheric pressure may be expressed by the Vogel equation

$$\ln \eta = A + 2.3B/(T - T_0)$$

from which

$$(\partial \ln \eta/\partial T)_p = -2.3B/(T - T_0)^2 \qquad (6)$$

Substitution of eq 6 in eq 4 gives

$$\Delta V^* = 2.3RTB/(T - T_0)^2(\partial T/\partial p)_\eta \qquad (7)$$

The preceding equations do not invoke any molecular model for viscous flow or the glass transition. By comparing the Vogel and the Adam–Gibbs viscosity equations at T_g for linear vinyl polymers, it was shown[4] that Z_g^*, the "co-

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(1) Presented in part at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971; see *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, 12, 517 (1971).

(2) K. H. Hellwege, W. Knappe, F. Paul, and V. Semjenow, *Rheol. Acta*, 6, 165 (1967).

(3) A. A. Miller, *J. Polym. Sci., Part A-2*, 6, 1161 (1968).

(4) A. A. Miller, *J. Chem. Phys.*, 49, 1393 (1968).