Transport of hydrogen in poly(vinylidene chloride-ethyl acrylate)

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The time-lag technique has been used to measure the diffusion, permeability and solubility coefficients of hydrogen in poly(vinylidene chloride–ethyl acrylate) containing 0.864 mole fraction of vinylidene chloride between 25° and 45°C. The low permeability of hydrogen in this material can be accounted for by the high activation energy of diffusion.

INTRODUCTION

Polymers containing vinylidene chloride have been recognized as having good barrier properties for many years. The permeation of nitrogen, oxygen and carbon dioxide in poly (vinylidene chloride–acrylonitrile)[1] has been reported by Bennett *et al.* and that of water vapour in poly(vinylidene chloride–acrylonitrile) by Hauser and McLaren[2]. The permeability of oxygen, nitrogen, carbon dioxide and water in vinylidene chloride copolymers has been compared with other polymers by Woodford[3]. In a review by Kammermeyer *et al.*[4], the permeability coefficients of hydrogen in a large number of polymers are compared, and from this comparison the low permeability of hydrogen in Saran 925 (a vinylidene chloride copolymer) is evident.

Here we report a study of the permeation of hydrogen in poly(vinylidene chloride–ethyl acrylate) containing a mole fraction of 0.864 vinylidene chloride units. Poly(vinylidene chloride) homopolymer is semi-crystalline, and its relative lack of solubility, and instability at melting point make the preparation of polyvinylidene films impractical. The homopolymer is of no technical importance, but copolymers containing about 90% of vinylidene chloride are used in barrier coatings[3]. Such copolymers are at most only slightly crystalline, and are readily soluble in some common solvents.

Here ethyl acrylate was chosen as the comonomer because the copolymerization reactivity ratios of this monomer with vinylidene chloride are both close to unity [*r*(vinylidene chloride) = 1.11 ± 0.12, *r*(ethyl acrylate) = 0.95 ± 0.02][5], which means that the copolymer and monomer feed compositions are very close, and consequently a copolymer of homogeneous composition is obtained even at high conversions. A copolymer with slightly less than 90% of vinylidene chloride was chosen, as copolymer films change from being clear to opaque at about this vinylidene chloride content as the increasing content of this monomer leads to the development of crystallinity[5].

EXPERIMENTAL

The copolymer was prepared from bulk monomers as previously described[5]. Chlorine analysis showed it to contain 0.864 mole fraction of vinylidene chloride units. Films were cast by pouring a solution of the copolymer in tetrahydrofuran into a glass casting ring which rested on a sheet of glass. After evaporation of the solvent, films were further dried under vacuum for several days. They were clear and free from haze. Film thicknesses were measured at several points with a micrometer. Throughout this work film thickness was 37 μm. Hydrogen was obtained from the British Oxygen Co.

The time-lag technique[6] was employed using a permeation cell constructed of glass in which a coarse sintered glass disc supported the film from distortion by gas pressure. The film was stuck to the annulus surrounding the sintered disc with an epoxide adhesive. The permeation cell was surrounded by water thermostatted to ±0.02°C. The cell was fused to a high vacuum line which was pumped by a mercury diffusion pump backed by a rotary pump. The vacuum line incorporated a mercury manometer, which was used to measure pressure on the high pressure side of the film, and a 3 dm^3 ballast vessel filled with hydrogen. Driving pressures of hydrogen were between 0.02 and 0.05 $\mathrm{MN/m}^2$; at least three separate experiments at different pressures were undertaken at each temperature.

Permeation was detected by measuring the pressure of hydrogen on the low pressure side of the film at various time intervals, up to 200 sec. Pressures (which were in the range up to 3 $\mathrm{N/m}^2$) were measured with a Pirani gauge powered from a constant voltage transformer. The gauge was calibrated against a high sensitivity McLeod gauge at various pressures of hydrogen. A liquid-nitrogen trap separated the permeation cell from the Pirani gauge in order to condense any residual monomer or solvent which might be desorbed from the film.

RESULTS AND DISCUSSION

Plots of pressure on the low pressure side of the film against time initially showed a build-up region that led to a straight line. The intercept of the extrapolated straight line on the time axis is termed the time lag τ, and the diffusion coefficient D can be calculated from this by the following equation[6], in which l is the film thickness:

$$D = l^2/6\tau$$

The permeability coefficient P is obtained from the slope of

Table 1 Transport coefficients of hydrogen in poly(vinylidene chloride–ethyl acrylate) containing 0.864 mole fraction of vinylidene chloride

Temperature	Number of experiments	$10^{12}D$ (m^2/sec)	$10^{18}P$ (m^3 at STP) m^{-1} sec^{-1} Pa^{-1}	10^7S (m^3 at STP) m^{-3} Pa^{-1}
25	4	1.4	0.98	7.0
30	3	2.7	0.94	3.5
35	4	3.1	1 48	4.8
45	4	4.9	2.15	4.4

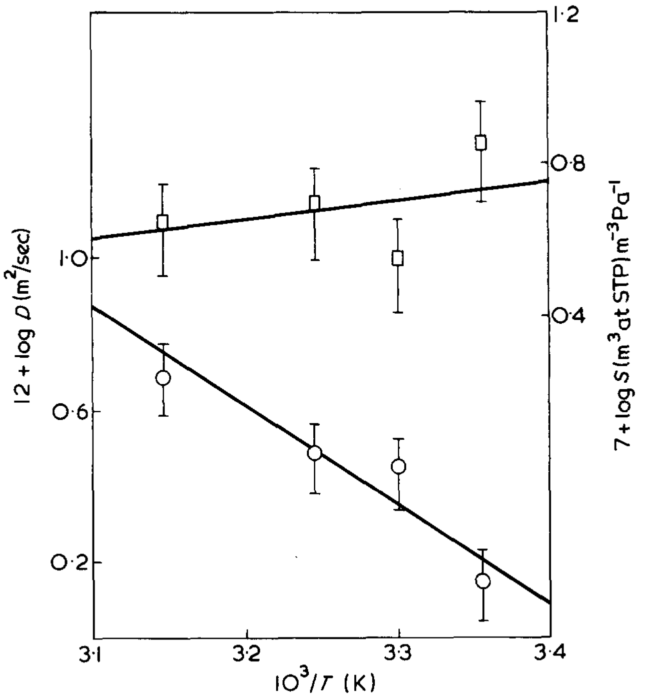

Figure 1 Dependence of diffusion coefficient (○) and solubility coefficient (□) upon temperature for hydrogen in poly(vinylidene chloride–ethyl acrylate) containing mole fraction 0.864 of vinylidene chloride unit

the straight-line region. The solubility coefficient S is related to P and D by:

$$P = SD$$

Values P, S and D are collected in *Table 1*. The estimated error in D and S is 20% and that in P is 7%.

Figure 1 shows dependence of S and D upon temperature, and from this the activation energy for diffusion E_D and the heat of solution ΔH_S can be estimated as:

$$E_D = 49 \pm 5 \text{ kJ/mol}$$

$$\Delta H_S = -10 \pm 5 \text{ kJ/mol.}$$

These results can be compared with the transport data for hydrogen in polymers which have been collected by other authors[7,8]. In other polymers D at 25°C is in the range 0.5 x 10^{-10} m^2/sec (PVC) to 67.1 x 10^{-10} m^2/sec (silicone rubber), while the value for the copolymer at 25°C is much less (1.40 x 10^{-12} m^2/sec). Similarly, activation energies of diffusion range from 9.3 kJ/mol (silicone rubber) to 36.8 kJ/mol (atactic polypropylene) while the activation energy of diffusion for hydrogen in the copolymer is 49 kJ/mol.

Solubility coefficients of hydrogen in other polymers are in the range 0.13 x 10^{-7} to 3.5 x 10^{-7} (m^3 at STP) cm^{-3} Pa^{-1} and the value for the copolymer is 7.00 x 10^{-7} (m^3 Pa^{-1}.

Clearly the unusual barrier properties of the copolymer are due to unusually low diffusion coefficients caused by a high activation energy for diffusion, rather than exceptional solubilities.

The glass transition temperature of the copolymer[5] is 5°C, which means that it may be used as a flexible packaging film. Copolymers of vinylidene chloride and ethyl acrylate are unusual in that the glass transition temperature is greatest when the copolymer contains equal numbers of each type of monomer unit; so decreasing the mole fraction of vinylidene chloride from 0.864 would initially increase the glass transition temperature and also increase the diffusion and coefficients. The latter claim assumes that it is units of vinylidene chloride rather than those of ethyl acrylate that are responsible for the high value of E_D in these copolymers. Support for this comes from the observed low permeabilities of copolymers of vinylidene chloride with vinyl chloride[9] and acrylonitrile[1,2].

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