Gas Transport in Poly(vinyl Benzoate)

TAKUJI HIROSE, KEISHIN MIZOGUCHI, and YOSHINORI KAMIYA,
Packaging Materials Division, Industrial Products Research Institute, 1-1-4, Yatabe-Machi Higashi, Tsukuba-Gun, Ibaraki, Japan

Synopsis

The transport parameters of nine gases (O_2, N_2, CO_2, He, Ne, Ar, Kr, Xe) through poly(vinyl benzoate) (PVB) have been measured by the time lag method above and below the glass transition temperature, T_g. The results are compared with the related data of poly(vinyl acetate) (PVAc) by Meares and discussed as the effect of replacement of the methyl group by a phenyl group in the side chain of PVAc. Small molecules, such as H_2, He, and Ne, diffuse more easily through PVAc than PVB, but the tendency is reversed for the larger gases. The activation energy for diffusion is proportional to the squares of the Lennard–Jones diameters of the gases below the T_g. On the other hand, above the T_g, linear relation is obtained to the cubes of the diameters. Solubility behavior is discussed by comparing the heats of solution for PVB and PVAc.

INTRODUCTION

A number of gas transport studies have been reported, and the correlation between the transport parameters and physical and chemical properties discussed in them. As reviewed by Stannett,[1] some reasonable and functional relationships have been developed, but they do not seem enough to explain transport process.

On the other hand, the usage of membranes for gas separation has recently been discussed,[2] and rigorous studies have been accomplished to explore the gas separation membranes with good separation factors and permeation rates. Although some of them have succeeded in the practical systems, it is strongly desired to establish how to design polymers for separation membranes. In order to explore advanced polymers, it seems important to study the fundamental correlations between the permeabilities and the chemical structures of polymers, and we intended to research from this standpoint.

We present this paper as the first report on gas transport studies of polymers derived from poly(vinyl alcohol) (PVA). Poly(vinyl benzoate) (PVB), which is prepared from PVA and benzoyl chloride, is a homolog vinyl polymer of poly(vinyl acetate) (PVAc). The transport of gases through PVB has not been examined yet. The present paper is concerned with the comprehensive study of the transport parameters in PVB, and we compare them with the data of PVAc studied by Meares.[3]

EXPERIMENTAL

Materials

Two methods are known for the synthesis of poly(vinyl benzoate). Pizzirani et al. prepared this polymer by bulk polymerization.[4] But this method is troublesome in the synthesis of monomer, and the conversion should be

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kept low in order to prevent crosslinking. Another method for the preparation of this polymer was reported by Staudinger et al.[5] and Noma et al.[6] We adopted this procedure as follows. In a glass apparatus protected from moisture by a calcium chloride tube, 5 g of poly(vinyl alcohol) was suspended in 100 mL of anhydrous pyridine and heated overnight with stirring at 90°C. To the suspension 23 g of benzoyl chloride was slowly added, and the reaction mixture was cooled to 50°C and maintained 4 h. Gradually PVA was dissolved to a clear solution, and then a crystalline precipitate formed. The viscous solution was diluted with 400 mL of acetone, filtered through glass cloth to remove the precipitated, and poured into distilled water with vigorous agitation to precipitate the polymer. Low molecular weight materials were removed by repeated precipitation from tetrahydrofuran with a mixture of water and methanol until the polymer was free from chloride ion.

The degree of esterification was estimated by an elemental analysis for carbon, hydrogen and nitrogen. It was practically complete (>97% esterified), and no nitrogen was detected.PVA, obtained from Aldrich Chemical Co., was of high molecular weight (MW 126,000; 98% hydrolyzed) and used as received.

The gases were at least greater than 99.9% pure and used without further purification.

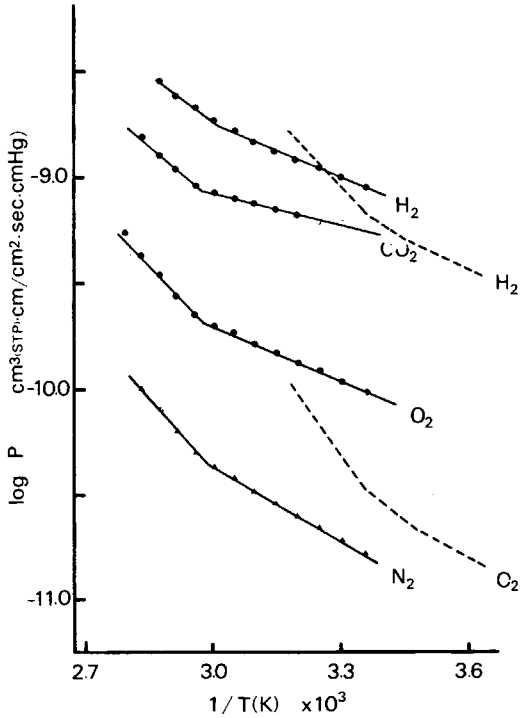

Fig. 1. Temperature dependence of the permeability coefficients for oxygen, nitrogen, hydrogen, and carbon dioxide in poly(vinyl benzoate): (- - -) data in poly(vinyl acetate) of Meares.[3]

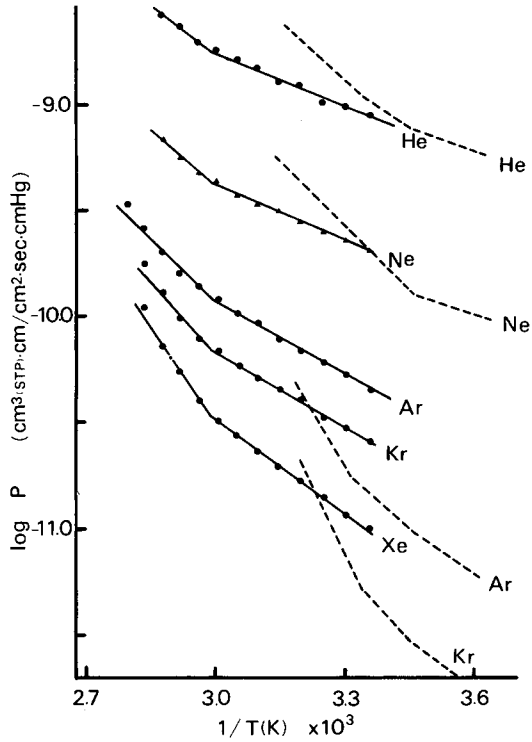

Fig. 2. Temperature dependence of the permeability coefficients for the noble gases in poly(vinyl benzoate): (- - -) data in poly(vinyl acetate) of Meares.[3]

Film Preparation

Films of PVB were prepared by casting from a 10% solution in benzene on a glass plate floating on mercury and allowed to air dry at room temperature for a few days. Then they were immersed in distilled water to remove the glass plate easily. The transparent films were dried under vacuum at 60°C for several days.

The thicknesses of the membranes tested were 50–200 μm. The density of the membranes was determined by the floating method with an Anton Paar K.G. Density Meter (DMA 02 D) and a KI aqueous solution at 25°C.

Procedures

The high vacuum time lag method developed by Barrer[7] was used for measuring the permeability and diffusion coefficients. The experimental apparatus was almost same as reported before.[8] The downstream pressures were monitored with an MKS Baratron 310 CHS-10 type pressure transducer, which was calibrated against the McLeod gage. The permeation cell, with a mercury seal to protect the membranes from water, was placed in a thermostat controllable water bath. PVB membranes were placed in the cell and were outgassed under high vacuum (less than 10^{-3} torr) for a few

days at temperatures increasing slowly to 85°C before permeation measurements. Ingoing pressures were from 20 to 50 cm Hg.

The specific volume–temperature relationship on PVB membranes was measured in a conventional mercury-filled dilatometer and the heating rate was about 0.5°C/min.

RESULTS AND DISCUSSION

The temperature dependence of the permeability coefficients P, which were obtained from steady state permeation rates, are presented in Figures 1 and 2 in the form of Arrhenius plots. P of each gas has been measured at many temperatures in the range 25–85°C, and each recorded value is the mean at least two experiments at the same temperature. P and the diffusion coefficient D for CO_2 decreased maximally about 7% and 10%, respectively, as the increase of ingoing pressure. But all of other gases were independent of ingoing pressure. So assuming that Fick's and Henry's laws are valid for all gases, D was calculated from

$$D = l^2/6\theta \tag{1}$$

where l is the membrane thickness and θ is the time lag, and the solubility coefficient S was given by

$$S = P/D \tag{2}$$

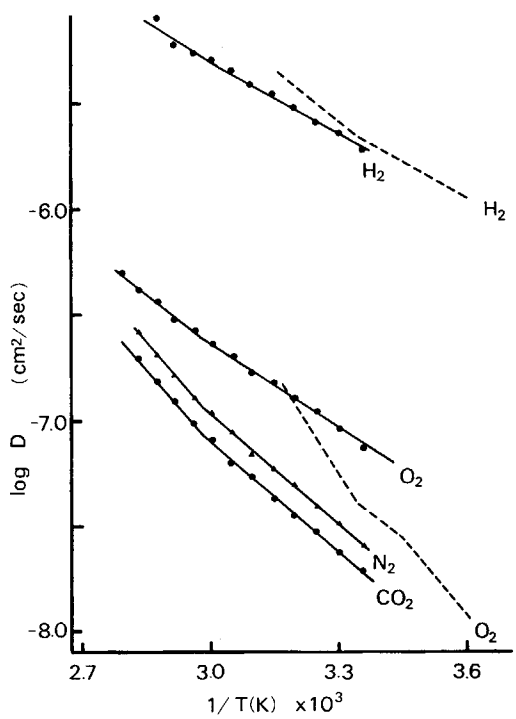

Fig. 3. Temperature dependence of the diffusion coefficients for oxygen, nitrogen, hydrogen, and carbon dioxide in poly(vinyl benzoate): (- - -) data in poly(vinyl acetate) of Meares.[3]

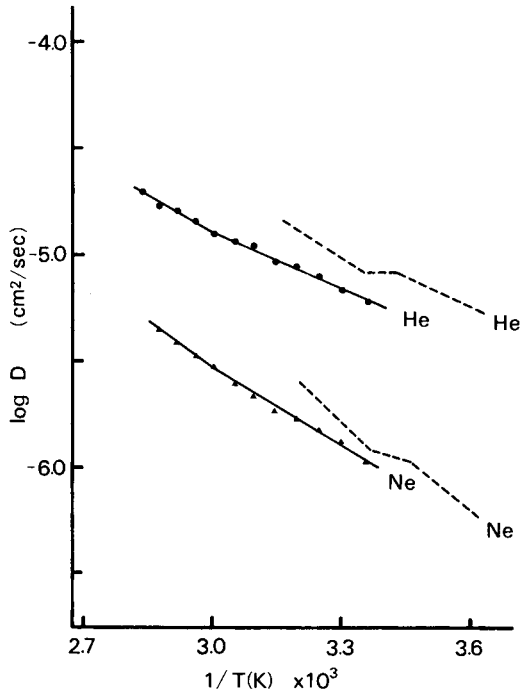

Fig. 4. Temperature dependence of the diffusion coefficients for helium and neon in poly(vinyl benzoate): (- - -) data in poly(vinyl acetate) of Meares.[3]

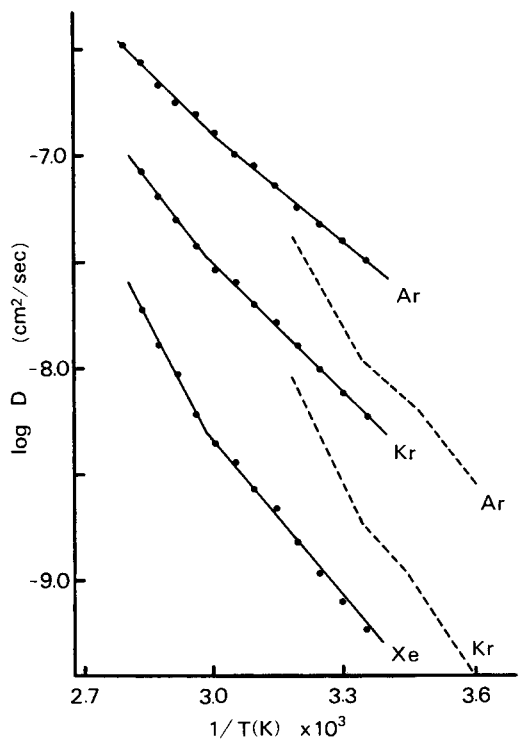

Fig. 5. Temperature dependence of the diffusion coefficients for argon, krypton, and xenon in poly(vinyl benzoate): (- - -) data in poly(vinyl acetate) of Meares.[3]

The pressure dependence of S recognized only for CO_2 was ignored by this analysis. D is presented in the form of Arrhenius plots in Figures 3–5, and S is ploted in Figures 6 and 7. Each plot has a change of slope at about 62°C. The dilatometry results, however, reveal a T_g at 65.5°C in Figure 8. The gas transport parameters calculated from each plot including the data below the T_g are given in Tables I and II.

PVB is an amorphous and glassy polymer, and the membranes used are transparent and free from orientation. So we may compare these results with the data of PVAc by Meares,[3] which are also presented as dashed lines in Figures 1–7. PVB has a higher T_g and a little higher density than PVAc, as compared in Table III, which is due to the difference between the methyl group and the phenyl group of each ester part.

The transport phenomena of these polymers are interesting as seen in Figures 1–7. The P and D of PVB are higher than those of PVAc to each gas except H_2, He, and Ne. This means that small molecules diffuse more easily through PVAc than PVB, but, increasing the size of a penetrant gas, the diffusivity in PVB gets larger than PVAc. On the other hand, the activation energy for diffusion, E_d, in PVB are lower than in PVAc for all gases (Figs. 3–5). Though the diffusivities may be related to such properties as densities, chain stiffnesses, thermal expansivities, etc., at present, it is difficult to discuss the correlation in detail because of the complexity. But it is clear the difference of acyl group of each polymer is the source.

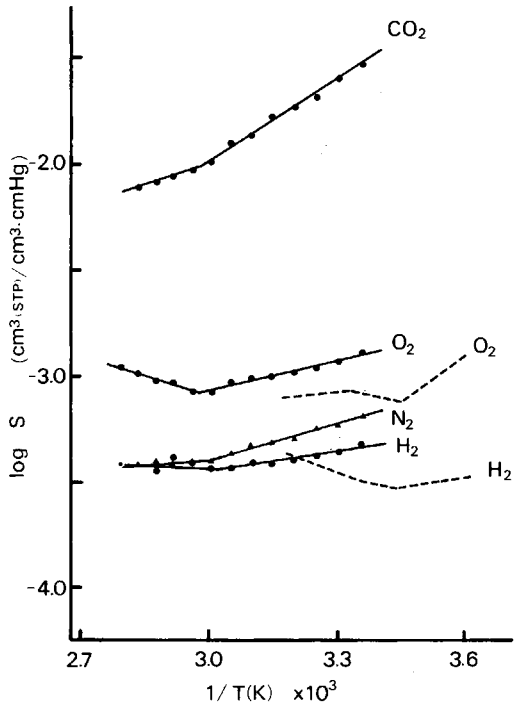

Fig. 6. van't Hoff plots of the solubility coefficients for oxygen, nitrogen, hydrogen, and carbon dioxide in poly(vinyl benzoate): (- - -) data in poly(vinyl acetate) of Meares.[3]

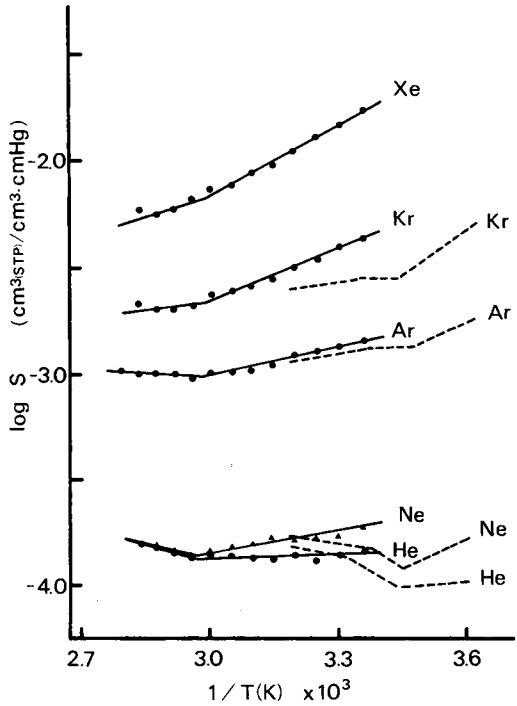

Fig. 7. van't Hoff plots of the solubility coefficients for the noble gases in poly(vinyl benzoate): (- - -) data in poly(vinyl acetate) of Meares.[3]

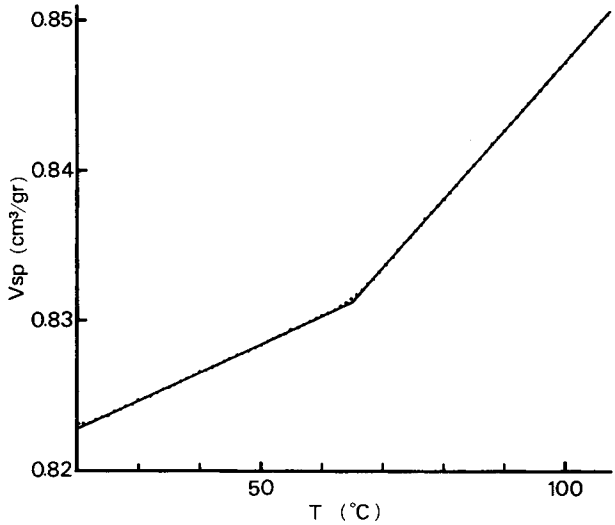

Fig. 8. Specific volume vs. temperature plot for poly(vinyl benzoate).

TABLE I
Gas Transport Parameters for Oxygen, Nitrogen, Hydrogen, Carbon Dioxide, and the Noble Gases in Poly(vinyl Benzoate) below T_g[a]

Gas	P_0	E_p	D_0	E_d	S_0	ΔH_s
O_2	8.05×10^{-8}	3.98	1.95×10^{-3}	6.00	4.12×10^{-5}	−2.02
N_2	1.38×10^{-7}	5.36	1.55×10^{-2}	7.87	8.94×10^{-6}	−2.52
H_2	7.37×10^{-7}	3.98	1.32×10^{-2}	5.22	5.60×10^{-5}	−1.24
CO_2	2.66×10^{-8}	2.29	1.14×10^{-2}	7.87	2.34×10^{-6}	−5.59
He	4.61×10^{-7}	3.71	5.61×10^{-3}	4.03	8.22×10^{-5}	−0.32
Ne	1.82×10^{-7}	4.03	1.25×10^{-2}	5.54	1.45×10^{-5}	−1.51
Ar	2.66×10^{-7}	5.13	1.11×10^{-2}	7.55	2.39×10^{-5}	−2.42
Kr	2.51×10^{-7}	5.45	3.14×10^{-2}	9.16	8.00×10^{-6}	−3.71
Xe	9.64×10^{-7}	6.82	7.22×10^{-2}	11.0	1.34×10^{-5}	−4.17

[a] Units: P_0 = cm³(STP) · cm/cm² · s · cm Hg; E_p = kcal/mol; D_0 = cm²/s; E_d = kcal/mol; S_0 = cm³(STP)/cm³ · cm Hg; ΔH_s = kcal/mol.

E_d increases from He to Xe and is plotted against the Lennard–Jones diameters[9] of the gas molecules d, d^2, and d^3 (Å) (Fig. 9). E_d is proportional to d^2 below the T_g [Fig. 9(b)], as Meares observed[3]; however, above the T_g, fairly linear with d^3, especially for the noble gases, the relation seems most linear [Fig. 9(c)], as Ash et al. concluded.[10] These results necessitate further study, and we will report in the near future.

It is usually accepted that the heat of solution is the sum of the work required to create a hole to accommodate the penetrant gas and the interaction energy between the gas and the polymer. Meares discussed that the interaction energy is given by the heat of solution below the T_g and the work of hole formation is given as $\{\Delta H_s(T > T_g) - \Delta H_s(T < T_g)\}$.[3] When we compare PVB and PVAc from this point of view, the interaction energy of PVB is smaller than that of PVAc in spite of the large solubility for each gas. In contrast, the value of $\{\Delta H_s(T > T_g) - \Delta H_s(T < T_g)\}$ are smaller than PVAc except Ar as presented in Table III, that is, the work of hole formation for other gases are smaller in PVB. We assume the following from these results: π–π interactions between phenyl groups make other parts of polymer segments separate each other and the interaction between

TABLE II
Gas Transport Parameters for Oxygen, Nitrogen, Hydrogen, Carbon Dioxide, and the Noble Gases in Poly(vinyl Benzoate) above T_g[a]

Gas	P_0	E_p	D_0	E_d	S_0	ΔH_s
O_2	3.68×10^{-4}	9.61	1.35×10^{-2}	7.28	2.72×10^{-2}	2.34
N_2	1.68×10^{-4}	10.1	1.19	10.8	1.42×10^{-4}	−0.69
H_2	3.34×10^{-5}	6.50	3.41×10^{-2}	5.86	9.80×10^{-4}	0.64
CO_2	9.79×10^{-5}	7.78	8.81×10^{-1}	10.8	1.11×10^{-4}	−2.98
He	6.10×10^{-5}	6.96	4.12×10^{-2}	5.36	1.48×10^{-3}	1.60
Ne	1.01×10^{-4}	8.24	8.60×10^{-2}	6.82	1.17×10^{-3}	1.42
Ar	1.15×10^{-4}	9.16	1.13×10^{-1}	9.09	1.02×10^{-3}	0.069
Kr	3.42×10^{-4}	10.3	2.53	12.1	1.35×10^{-4}	−1.84
Xe	4.02×10^{-4}	13.9	1.51×10^{-3}	17.6	2.66×10^{-5}	−3.70

[a] Units: P_0 = cm³(STP) · cm/cm² · s · cm Hg; E_p = kcal/mol; D_0 = cm²/s; E_d = kcal/mol; S_0 = cm³(STP)/cm³ · cm Hg; ΔH_s = kcal/mol.

TABLE III
Differences of the Heats of Solution above and below T_g for Oxygen, Hydrogen, Neon, Argon, and Krypton in Poly(vinyl Benzoate) and Poly(vinyl Acetate)[3] with T_g and Densities

Polymer	$\{\Delta H_s(T > T_g) - \Delta H_s(T < T_g)\}$ (kcal/mol)						T_g (°C)	Density (g/cm³)
	O_2	H_2	He	Ne	Ar	Kr		
PVB	4.35	1.88	1.92	2.93	2.49	1.87	62	1.214
PVAc	5.16	3.89	3.12	5.67	1.82	5.94	26	(1.17–1.176)[a]

[a] Refs. 11 and 12.

them weak, that is, the interaction energies between polymer segments, other than π–π interaction energy, get small. Whereas the interaction energies between polymer segments in PVAc are comparatively homogeneous everywhere. Penetrant gases will make holes to solute where the interaction between polymer segments is small. Therefore it can be understood that the hole formation energy in PVB gets smaller than PVAc. To discuss in more detail, it seems necessary to measure the solubility for PVB individually by sorption experiments, and this is now in progress.

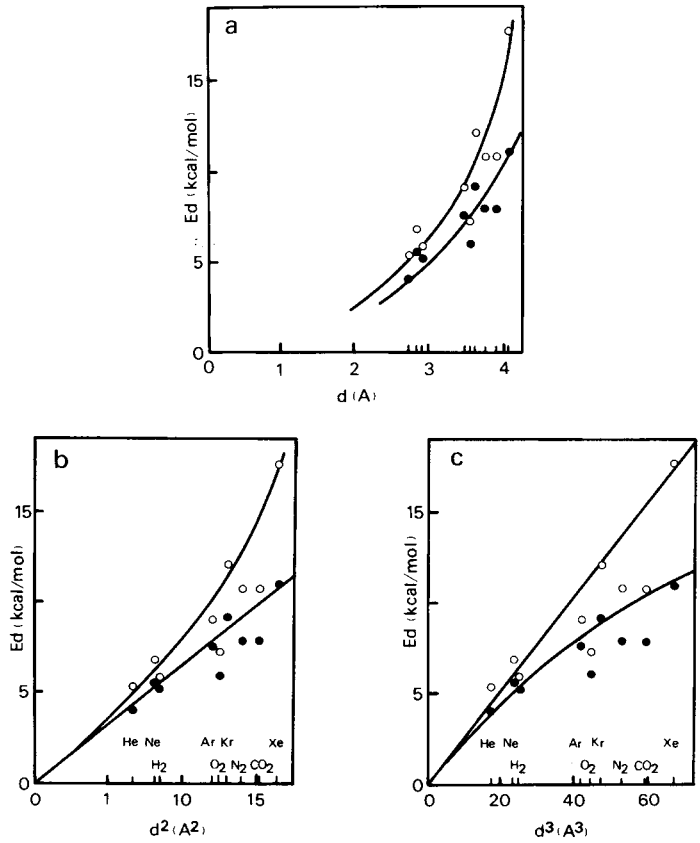

Fig. 9. Activation energies for diffusion for nine gases in poly(vinly benzoate) vs. d (their Lennard–Jones molecular diameters) (a), d^2 (b), d^3 (c) above (○) and below (●) the glass transition temperature.

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