

The Effect of Glass Transition on Gas Permeabilities

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Synopsis

Gas permeabilities of a copolymer of acrylonitrile and methyl acrylate were examined at the temperature range of 25° to 80°C. The change of activation energy of gas permeability constant at the glass transition temperature (65°C) was observed with N₂, Ar, O₂, and CO₂, but no change was observed with He. The observation of the change of slope of the Arrhenius plot of gas permeability is discussed as a function of the diffusion constant (D) of a permeant gas at the glass transition temperature (T_g). The change occurs only if the value of D at T_g is smaller than a certain value (i.e., 5×10^{-8}), according to the analysis of data appearing in the literature.

INTRODUCTION

Gas permeability measurement can be used as a very sensitive method to detect small changes in the matrix of polymer. For instance, the orientation of crystals under strain affect the transport properties of gases and the changes which occur under stress can be followed by the change in gas permeabilities as a function of elongation.¹ In principle, therefore, gas permeability should reflect the change of segmental mobility or free volume at below and above the glass transition temperature of a polymer.

The change of gas permeability at the glass transition temperature has been indeed observed by Mears^{2,3} with poly(vinyl acetate). However, the distinct changes of slopes of Arrhenius plots at the glass transition temperature were observed with some but not all gases. The results of Stannett and Williams⁴ with poly(ethyl methacrylate) showed no inflection in the Arrhenius plots of permeabilities at the glass transition temperature (65°C) for all gases studied. Kumins and Roteman⁵ also report that no effect of glass transition of a vinyl chloride-vinyl acetate copolymer was found in the study of the diffusion of gases except carbon dioxide.

Whether an inflection of gas permeabilities at the glass transition can occur or not would depend on the average size of holes or free volume elements in the polymer and the size of the penetrant.⁵⁻⁸

There are three groups of data reported insofar as the effect of glass transition on the gas permeabilities is concerned. (1) No effect is observed with all gases investigated with poly(ethyl methacrylate).⁴ (2) Glass transition is observed

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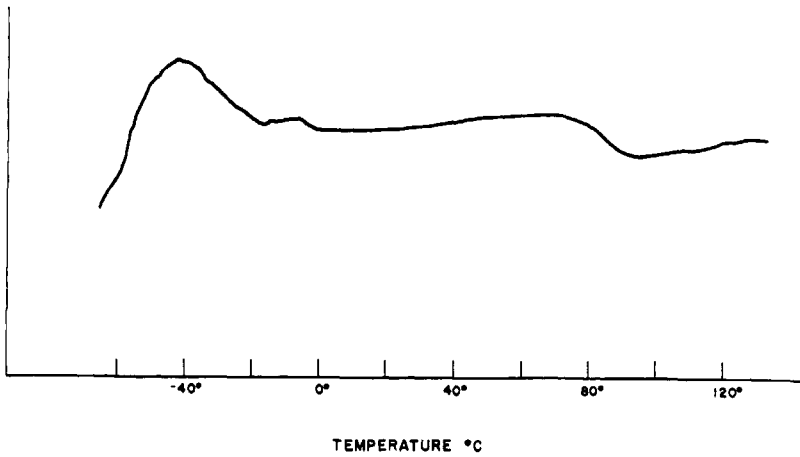


Fig. 1. Differential scanning calorimetry (DSC) data of the film sample.

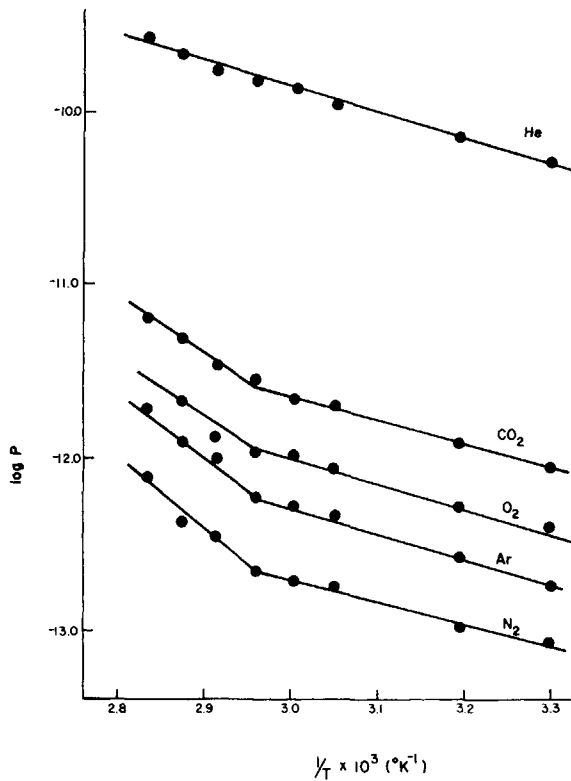


Fig. 2. Temperature dependence of gas permeabilities.

with all gases (including helium) for poly(vinyl acetate),² poly(ethylene terephthalate) in glassy crystalline state,⁹ polyacrylonitrile–vinyl acetate copolymer,¹⁰ and poly(methyl acrylate).¹¹ (3) Glass transition is observed with only limited gases for poly(vinyl chloride)–vinyl acetate copolymer with carbon dioxide⁵ and poly(vinyl chloride) with argon and krypton.⁸

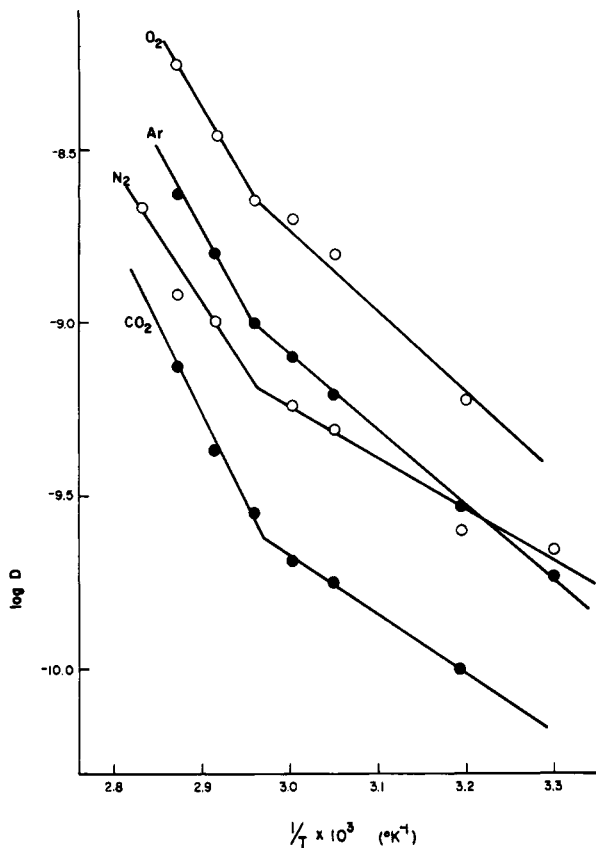


Fig. 3. Temperature dependence of diffusion constants of gases.

Stannett¹¹ noted that carbon dioxide in vinyl chloride copolymer studied by Kumins and Roteman was an indication of the possibility that "some polymers should have mean cavity values which leads to a transition effect with large penetrant molecules and no effect with smaller ones." In a later study,⁸ he and his co-workers found argon and krypton in poly(vinyl chloride) as the additional evidence for the case. Permeability data presented in this study provide further evidence for this case (i.e., case 3) and allow us to examine the effect of glass transition on the gas permeabilities with added statistical confidence.

EXPERIMENTAL

Materials

The gases used in these experiments were research grades, which were used without further purification. The Barex film, a copolymer of acrylonitrile and methyl acrylate, is a commercially available film from the Sohio Company. Thickness was 3.2×10^{-3} cm. Before measurements, the film was checked for pinholes.

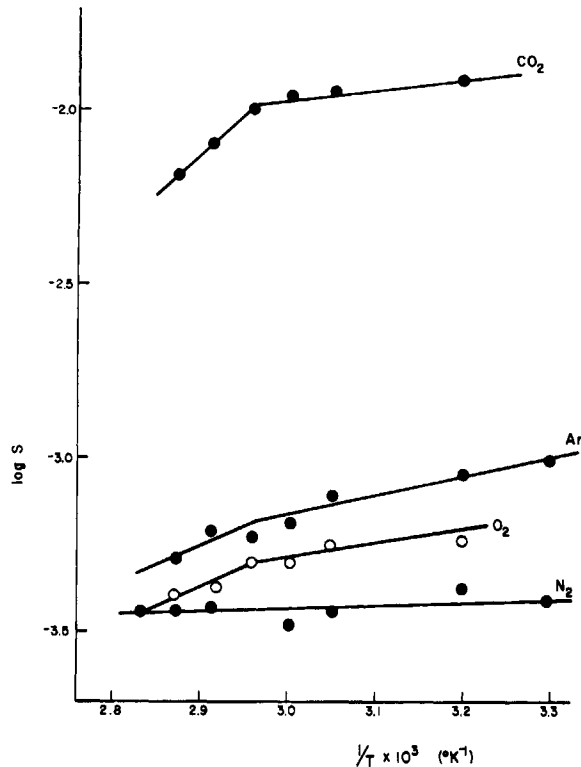


Fig. 4. Temperature dependence of apparent heats of sorption of gases.

Apparatus and Procedure

The permeability and diffusion constants, P and D , respectively, were determined by the Barrer-Daynes time lag technique using a glass high-vacuum system. The basic features of this experimental technique have been described in detail previously.¹² The solubility constant S was calculated by $S = P/D$. An MKS Baratron pressure transducer, Model 90, was used to monitor continuously the downstream pressure.

The glass transition temperature was measured by a differential scanning calorimeter (DSC), Perkin-Elmer Model DSC-1.

RESULTS AND DISCUSSION

The glass transition temperature of the sample film was estimated to be 65°C from the DSC specimen shown in Figure 1. The permeability, diffusivity, and solubility values for the various gases studied are shown in the form of Arrhenius plots in Figures 2, 3, and 4. The activation energies of permeation and diffusion and the heat of solution are summarized in Tables I, II, and III, respectively.

As seen in Figure 2, all gases except helium show clear changes of slope at around 65°C, which corresponds to the glass transition temperature. In the case of helium, there is no significant inflection in the glass transition region. The diffusion and solubility constants also show change of slopes at the glass transition region.

The data of gas permeabilities in poly(vinyl chloride) by Tikhomirov et al.⁸ showed clear changes of slopes for argon and krypton, but no inflection was found for N₂ and CO₂ which are larger than argon. These results indicate that size of gas molecules alone is not sufficient to explain the phenomena. The existence of a change in the activation energy for diffusion at the glass transition for penetrant molecules above a certain critical size was discussed in some detail by Kumins and Roteman,⁶ Frisch,⁷ Stannett and Williams,⁴ and Tikhomirov et al.⁸

There is no doubt that the relative size of a penetrant molecule to the hole size of a polymer film is an important factor; however, the size alone does not explain why some molecules which are larger in size show no inflection whereas a smaller molecule shows clear inflection in the same polymer, e.g., CO₂ and N₂ versus Ar in poly(vinyl chloride).⁸

There seems to be a simple measure for the *relative* aspect of molecular size of a penetrant to the average hole size in the film. The value of the diffusion constant itself at the glass transition temperature may be used for this purpose, since the diffusion constant at a given temperature is a function of not only the characteristic parameters of penetrant molecules but also of the polymer characteristics.

This implies that the extent of free volume utilized for the transport of a gas at or below the glass transition temperature is just as important as the increase of the free volume above the glass transition temperature.

TABLE I
The Activation Energy of Permeation E_P (kcal/mole)

	E_P , kcal/mole				
	He	CO ₂	O ₂	Ar	N ₂
$E_P(<T_g)$	6.6	6.6	6.6	6.6	6.1
$E_P(>T_g)$	6.6	15.0	13.9	16.6	16.6
$E_P(>T_g) - E_P(<T_g)$	0.0	8.4	7.3	10.0	10.5

TABLE II
The Activation Energy of Diffusion E_D

	E_D , kcal/mole			
	CO ₂	Ar	N ₂	O ₂
$E_D(<T_g)$	7.3	9.4	6.3	10.5
$E_D(>T_g)$	22.9	21.5	16.8	18.8
$E_D(>T_g) - E_D(<T_g)$	15.6	12.1	10.5	8.3

TABLE III
The Apparent Heat of Solution H_S

	H_S , kcal/mole			
	CO ₂	Ar	N ₂	O ₂
$H_S(<T_g)$	-0.7	-2.8	-0.2	-3.9
$H_S(>T_g)$	-7.9	-4.9	-0.2	-4.9
$H_S(>T_g) - H_S(<T_g)$	-7.2	-2.1	0.0	-1.0

The size of penetrant molecule is correlated reasonably well to the activation energies of the diffusion in a polymer; however, the value of the diffusion constant at a given temperature (e.g., at the glass transition temperature) cannot be predicted from the size of the gas molecule alone. For instance, the values of $D(T_g)$ in poly(ethyl methacrylate)⁴ are in the order of He > Ne > Kr > Ar > CO₂ > N₂ > O₂, which cannot be correlated to the size of the penetrant molecules. Therefore, it may be worth reexamining the phenomena as a function of the value of diffusion constant at the glass transition temperature $D(T_g)$. In Table IV, the values of $D(T_g)$ are collected from the data in which a clear change of slope of Arrhenius plots of gas permeability at a single transition temperature is reported for a gas. In Figure 5, the values of $[E_D(>T_g) - E_D(<T_g)]$, which should be zero if no change of slope is observed, are plotted against $D(T_g)$.

TABLE IV
Glass Transition Observed by Gas Permeabilities

Polymer	Gas	$D(T_g)$	Change of slope at T_g	Reference
Poly(vinyl chloride)- vinyl acetate	He	2.3×10^{-6}	no	5
	H ₂	7×10^{-7}	no	5
	Ne	3×10^{-7}	no	5
	O ₂	1.5×10^{-8}	no	5
	CO	1.2×10^{-9}	no	5
Poly(vinyl chloride)	He	8×10^{-6}	no	8
	H ₂	3×10^{-6}	no	8
	Ne	1×10^{-6}	no	8
	O ₂	2×10^{-7}	no	8
	N ₂	8×10^{-8}	no	8
	CO ₂	6×10^{-8}	no	8
Poly(ethyl methacrylate)	CH ₄	4×10^{-8}	no	8
	Ne	4.7×10^{-6} a	no	4
	He	9×10^{-5}	no	4
	Kr	6×10^{-7}	no	4
	Ar	1.6×10^{-7}	no	4
	CO ₂	1.6×10^{-7}	no	4
	N ₂	1.7×10^{-7}	no	4
	O ₂	4.8×10^{-8}	no	4
Polyacrylonitrile- methylacrylate	He	1.7×10^{-7}	no	this study
Poly(vinyl chloride)	Ar	1.5×10^{-8}	yes	8
	Kr	5×10^{-9}	yes	8
Poly(vinyl chloride)- vinyl acetate	CO ₂	3.5×10^{-10}	yes	5
Polyacrylonitrile- vinyl acetate	He	4×10^{-9}	yes	10
	Ne	1×10^{-9}	yes	10
	Ar	2×10^{-11}	yes	10
Polyacrylonitrile- methyl acrylate	O ₂	2×10^{-9}	yes	this study
	Ar	1×10^{-9}	yes	this study
	CO ₂	2.5×10^{-10}	yes	this study
	N ₂	8×10^{-10}	yes	this study
Poly(methyl acrylate)	He	5×10^{-8}	yes	11
	Ar	4×10^{-9}	yes	11
	Kr	6.5×10^{-10}	yes	11
	Ne	4×10^{-10}	yes	11

^a Calculated from the data D_0 , E_d , and T_g .⁴

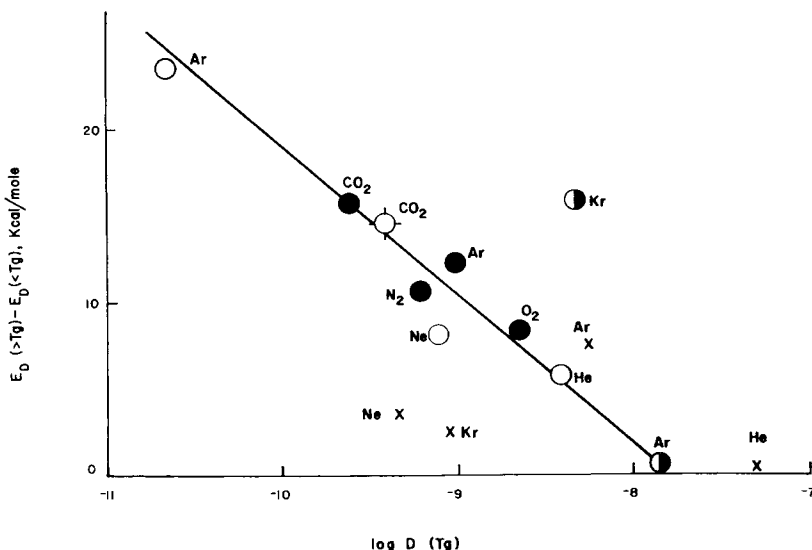


Fig. 5. Dependence of change of activation energy of diffusion at glass transition temperature on the value of diffusion constants at the glass transition temperature: (O) data of ref. 10; (●) data of ref. 8; (X) data of ref. 11; (◐) data of ref. 5; (●) this study.

Data shown in Table IV and Figure 5 clearly indicate that the observation of a change of slope in an Arrhenius plot of gas permeability at the glass transition temperature is highly dependent on the value of $D(T_g)$. The fact that many points in Figure 5 fall nearly on a straight line is of a fortuitous nature, perhaps because two copolymers of acrylonitrile provided the majority of the data. It is interesting to note that the value of argon in poly(vinyl chloride) by Tikhomirov et al. and helium in poly(methyl acrylate) by Burgess et al. which showed no break in the diffusion constants but showed a break in the permeability constants may represent the critical cases and the values of $D(T_g)$ (i.e., 2×10^{-8} to 5×10^{-8} cm²/sec) seem to indicate the order of magnitude of the threshold value.

Whether the threshold value of approximately 5×10^{-8} cm²/sec for $D(T_g)$ has any significance in general case may depend on further investigations; however, it seems quite clear that if the value of $D(T_g)$ is above a certain value (e.g., 5×10^{-8} cm²/sec), no effect of glass transition on gas permeabilities would be observed regardless of the size of gas molecules. This analysis based on the value of $D(T_g)$ seems to support the theoretical considerations presented on this subject by various authors and provides a simple analytical tool to demonstrate the "relative" aspect of molecular size of permeant gases in the transport phenomena.

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