Permeation of Gases in Poly(2-vinylpyridine)-Block-Polyisoprene

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Transport and solution behavior of a series of inert gases (helium, argon, nitrogen, krypton, and xenon) in poly(2-vinylpyridine)-block-polyisoprene was studied by transient permeability measurements at temperatures from 25 to 60°C. Temperature dependence of permeability, diffusivity, and solubility for each system was represented by the Arrhenius-type equation in the temperature region studied. It was indicated that the transport of inert gases, except for helium, at lower temperatures are governed primarily by the process taking place in the rubbery polyisoprene phase.

INTRODUCTION

In our previous papers,[1~6] it has been shown that the diffusion and permeation of inert gases, except for helium, in polystyrene-block-pulybutadiene-block-polystyrene (SBS block copolymer) at room temperature are primarily governed by the process taking place in the rubbery polybutadiene (PB) phase of the copolymer films. The impermeable glassy polystyrene (PS) phase has been found to give rise to a tortuosity effect on the diffusive path of penetrant and also an immobilization effect on a part of PB chains. A study of diffusion and solution of n-hexane vapor in the SBS block copolymers has revealed that the chain immobilization effect interfering with the transport of penetrant molecules is attributable to partial mixing of component chains at the interface between the PB and PS phases.[7] The diffuse interphase between the PB and PS phases in SBS block copolymer films has been suggested also by Chiang and Sefton[8] and Caneba et al.[9] from studies of organic vapor transport.

This paper describes the permeation behavior of inert gases in poly(2-vinylpyridine)-block-polyisoprene [P(2VP-b-I)] at temperatures from 25 to 60°C. In the temperature region, the P2VP and the PI phases are in the glassy and the rubbery states, respectively. The results will be compared with those obtained for inert gases in the SBS block copolymers.

EXPERIMENTAL

Materials

The block copolymer P(2VP-b-I) and a homopolymer P2VP were identical with

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those used previously.[10,11]   These samples were generously provided by Dr. M. Fukuda of Toyo Soda Manufacturing Company.   After purification, films used for measurements were prepared by solvent casting.   Dichloromethane and methanol, both of G.R. grade, were employed for casting P(2VP-b-I) and P2VP samples, respectively.   Final traces of solvent were removed from the cast film by heating in vacuum to 40°C for more than 10 days.

The film thickness was determined by taking the arithmetic average of numerous readings of a micrometer screw gauge over the area of the film.   Films used for measurements were approximately 3.80×10^{-2} cm and 6.9×10^{-3} cm thick for P(2VP-b-I) and P2VP, respectively.

The morphology of the block copolymer film specimens was observed by an electron microscope using the OsO_4 fixation technique and has been described in detail elsewhere.[10]   In brief, the domain structure of the film specimens was characterized by lamellas, and the orientation of the alterneting lamellas of P2VP and PI was at random in the specimens.

Slightly vulcanized PI membranes of approximately 5.50×10^{-2} cm thick were furnished from the Japan Synthetic Rubber Co., Ltd., through the courtesy of Dr. M. Abe.   The *cis* content of the PI sample was 98%, and fillers were not added.

Helium, argon, krypton, xenon, and nitrogen were used as penetrant in permeation experiments.   These gases were obtained from Takachiho Kagakukogyo, Co., Ltd., and the purity of each gas quoted by the supplier exceeded 99.99% by volume.

Method

Permeation experiments were performed by the cell partition method in the temperature region from 25 to 60°C.   Details of the apparatus and procedure have been described elsewhere.[1]

RESULTS AND DISCUSSION

The maximum pressure employed in permeation measurements was about 30 cmHg for all gases.   Fick's and Henry's laws were accurately obeyed for all inert gases over the temperature and pressure range studied.   Figure 1 summarizes temperature dependence of permeability coefficient P, which was determined from the steady-state permeation rate.   It is seen for all the systems that the temperature dependence of P can be well expressed by the Aarrhenius-type equation with a constant apparent energy for peameation.

Except for helium, the diffusion coefficient D_θ was obtainable from the time lag for permeation, and the solubility coefficient S_θ was estimated by

$$S_\theta = P/D_\theta \qquad (1).$$

Here the subscript θ denotes that the quantities were determined from the time-lag method.   In the case of helium, the diffusion coefficient was so large that the time lag method could not be applied accurately.

Table I gives values of P, D_θ, and S_θ determinned from permeation experiments for argon in P(2VP-b-I), PI, and P2VP at 25°C.   It can be seen that the values of P and D_θ in the block copolymer are intermediate between those in PI and P2VP
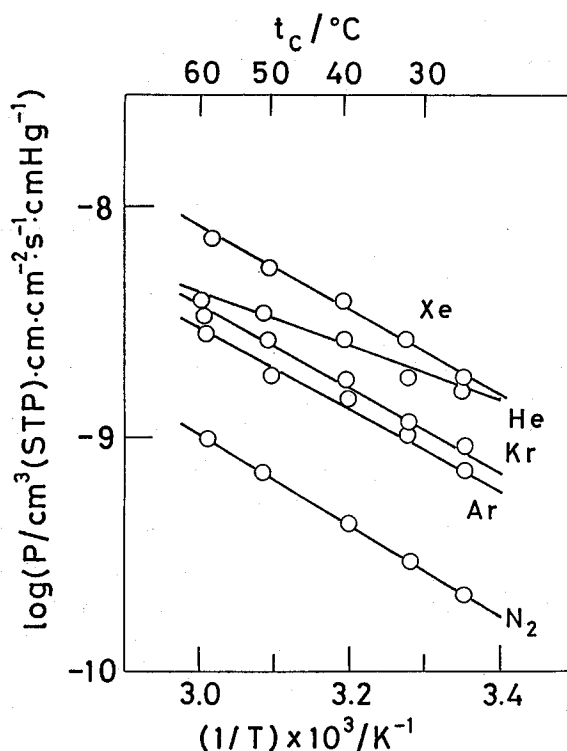
Fig. 1. Temperature dependence of permeability coefficients of five
gases in P(2VP-b-I).

homopolymers. It is also notable that D_θ in the P2VP homopolymer is quite small
as compared with those in P(2VP-b-I) and PI, but S_θ is not. This indicates that the
transport process, *i.e.* the permation and deffusion, of argon in the P(2VP-b-I) film
are governed primarily by that in rubbery PI phase. This view is consistent with that
for the behavior obtained for inert gases in SBS block copolymers at 25°C.[1,3~6)]

In the temperature region studied, the temperature dependence of D_θ can be
expressed by the Arrhenius-typ equation with constant E_D

$$D_\theta = D_0 \exp(-E_D/RT) \tag{2},$$

where the frequency factor D_0 and the activation energy for diffusion E_D are inde-

Table I. Permeability, diffusion, and solubility coefficients at 25°C for argon in
block copolymer P(2VP-b-I) and homopolymers PI and P2VP

Polymer	P^a	D_θ^b	S_θ^c
P(2VP-b-I)	7.15×10^{-10}	2.50×10^{-7}	2.67×10^{-3}
PI	2.90×10^{-9}	1.33×10^{-6}	2.18×10^{-3}
P2VP	1.92×10^{-11}	8.02×10^{-9}	2.39×10^{-3}

[a] P in cm^3 (STP)·cm·cm^{-2}·s^{-1}·cmHg^{-1}.
[b] D_θ in cm^2·s^{-1}.
[c] S_θ in cm^3 (STP)·cm^{-3}·cmHg^{-1}.

Table II. Energies of activation for diffusion

| Gas | E_D/kJ mol^{-1} | | d_{298}/A[b] |
	P(2VP-b-I)	SBS block copolymer[a] (L-1 sample)	
Ar	29. 5	24. 7	3. 61
N$_2$	32. 2	30. 6	3. 75
Kr	33. 1	31. 6	4. 11
Xe	42. 3	35. 2	4. 80

[a] Ref. 5.   [b] Ref. 12.

pendent of temperature. Table II lists the values of E_D together with those obtained for an SBS block copolymer, L-1,[5] which has the same domain structure of alternating lamellar type as that of the P(2VP-b-I). Diameters of the inert gases at 25°C, d_{298}, which have been estimated from gas viscosities,[12] are also given in the table.

It is seen that the values of E_D for P(2VP-b-I) are not very different from those for the SBS block copolymer sample. Essentially the same dependence of E_D on d was observed for both copolymers. These values of E_D are, however, considerably smaller than the values obtained in glassy polymers such as polystyrene.[5] These results of E_D again suggest that, in P(2VP-b-I) films, the diffusion of inert gases in the rubbery PI matrix dominates over that in the glassy P2VP phase.

Brandt has presented a model for the diffusion of small molecules in polymers and derived an expression for the activation energy for diffusion.[13] In this treatment, the activation energy is assumed to consist of two factors: (a) an intermolecular energy term and (b) an intramolecular energy term. The intermolecular term is due to the repulsion which the polymer chains experience from their neighbors on making room for the penetrant molecule, and is a function of the cohesive energy density of the polymer. The diffusion process of small molecules in rubbery polymers is considered to be governed mostly by this effect. According to Brandt's expression the intermolecular term depends linearly on the diameter of the penetrant molecule. The intramolecular term is considered to arise from the bending of the two neighboring chains and is expressed as a function of the flexibility of the chain segments. For diffusion in glassy polymers this term dominates, and the activation energy is proportional to the square of the diameter of the penetrant molecule.

In Fig. 2 the measured activation energies for diffusion, E_D, are plotted against the diameter of the gas molecule, d. The observed linear dependence of E_D on d indicates that the diffusion processes of the inert gases in the P(2VP-b-I) film are governed primarily by the mobility of polymer chains in the rubbery PI matrix. This is consistent with the suggestion mentioned above.

The temperature dependence of the solubility coefficient S_θ for inert gas solution in P(2VP-b-I) can be expressed by the Arrhenius-type equation

$$S_\theta = S_0 \exp(-\Delta H_s/RT) \tag{3},$$

where ΔH_s is the apparent heat of solution. As shown in Table III, measured values of ΔH_s for solution of the inert gases in P(2VP-b-I) sample agree fairly well with the corresponding values for the SBS block copolymer L-1 sample.
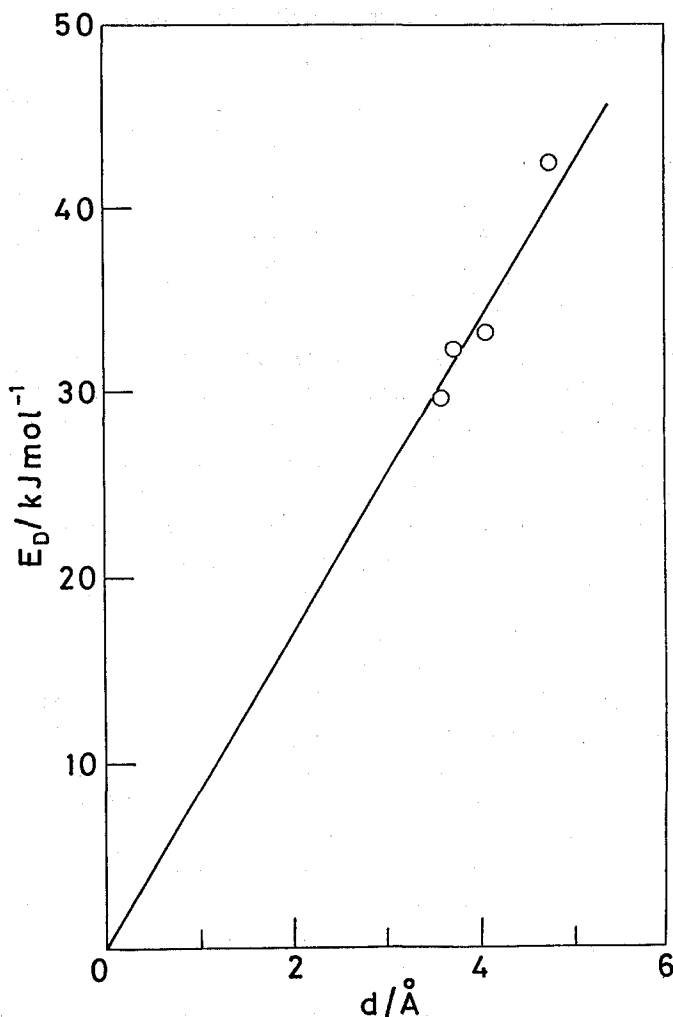
Fig. 2. Correlation of activation energies for diffusion with gas diameters.

For inert gas solution in the SBS block copolymer a linear relation between the logarithm of the equilibrium solubility coefficient at 25°C, S_{25}, and the Lennard-Jones force constant, ε/k, has been found, where k is the Boltzmann constant.[2] Such

Table III. Heats of solution

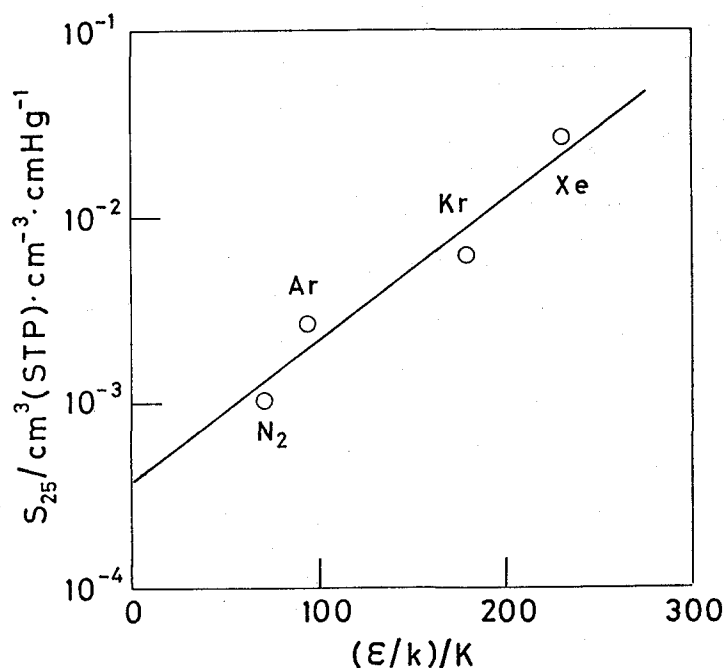| Gas	$\Delta H_s/kJ$ mol^{-1}	
	P(2VP-b-I)	SBS block copolymer[a] (L-1 sample)
Ar	−5.0	1.2
N₂	0.0	4.0
Kr	−6.5	−2.9
Xe	−14.2	−10.2

[a]Ref. 5.

Fig. 3. Correlation of solubility coefficients at 25°C with the Lennard-Jones force constants.

a linear relationship was first noticed by Michaels and Bixler for solution of gases in polyethylene and in low-molecular-weight, nonpolar liquids.[14] Also, a theoretical basis of the linear relationship has been given by them through a thermodynamic argument.[14] In Fig. 3, S_{25} is plotted semilogarithmically against ε/k for the present systems. The fit of data points to a straight line is good, and the straight line is expressed by the equation

$$\ln S_{25} = 0.018(\varepsilon/k)/\mathrm{K} - 7.88 \tag{4}.$$

The slope of the line is favorably compared with the predicted slope of 0.026 by Michaels and Bixler,[14] and also with the observed one of 0.025 for the system of inert gases and the SBS block copolymer.[2]

Michaels and Bixler have also demonstrated, using the same thermodynamic model, that the heat of solution should be given by the equation

$$\Delta H_s/\mathrm{kJ\ mol^{-1}} = \chi RT - 0.0653\ [(\varepsilon/k)/\mathrm{K}] \tag{5},$$

where χ is the mixing parameter.[14] Measured values of ΔH_s for the present system given in Table III were found to be represented well by a straight line having a slope of -0.080, if they are plotted against ε/k. This slope is in excellent agreement with that, -0.087, observed for inert gas solution in the SBS block copolymer,[2] and also is close to the above predicted value. Thus, it may be concluded that the solution behavior of inert gases in the P(2VP-b-I) sample also resembled quite closely that in the SBS block copolymer sample.

The transport behavior for inert gases in the SBS block copolymer at 25°C has

been analyzed in terms of a simple model consisting of a parallel array of elements representing the component homopolymers.[1,3,4,6] Though the model adequately explained the permeation behavior of smaller molecules like helium, for larger molecules the values of P calculated by the model were higher than the measured values. To describe the observed results satisfactorily, the model was modified by introducing two impedance factors: the tortuosity factor τ and the chain immobilization factor β. For transport of argon, we have estimated values of these impedance factors by comparing the transport behavior for P(2VP-b-I) with those for PI and P2VP homopolymers. Since P was determined more accurately than D_θ in our experiments, the impedance factors were evaluated from the measured values of P.

As has been shown in Table I, the diffusion coefficient D_θ for the P2VP homopolymer is considerably smaller than that for PI homopolymer and the difference in the solubility coefficient S_θ for these homopolymers is small. In such a case, the observed value of P for block copolymer may be approximated by the relation[4,6]

$$P = v_I P_I / \Phi \qquad (6)$$

where v_I is the volume fraction of isoprene component, P_I the permeability coefficient in PI homopolymer, and Φ the impedance factor given by the product of τ and β. By using values of density of 0.91 and 1.11 g·cm^{-3} for PI and P2VP, respectively, we have calculated v_I for the copolymer sample from its weight fraction of isoprene component, and obtained the value of 0.55. The value of Φ was then estimated to be 2.33 by employing values of P for P(2VP-b-I) and PI together with that of v_I. For the block copolymer film having the domain structure of alternating lamellar type, the value of τ for inert gas permeation through the rubbery matrix may be estimated to be 1.225 based upon the appropriate geometric considerations.[1,6] With the value of τ thus estimated, β is calculated as 1.82. These values of Φ and β are compared well with those for transport of argon in the SBS block copolymer L-1 sample. For the latter system, values of Φ and β were estimated as 1.71 and 1.39, respectively.[4,6]

Transport and solution behavior of inert gases in the P(2VP-b-I) sample resembles quite closely in all respects with that in the SBS block copolymer sample having the domain structure of the same type. Also in the P(2VP-b-I) films, the transport processes of inert gases at room temperature were found to be governed primarily by the mobility of the rubbery PI phase, and the glassy P2VP domains play the same role in these processes as filler particles do in rubber membranes.

CONCLUSIONS

Transport and solution behavior of inert gases in the P(2VP-b-I) films at temperatures from 25 to 60°C resembles closely in all respects with that in SBS block copolymer film having domain structure of the same type. It is concluded that the transport processes of inert gases, except for helium, at room temperature are governed primarily by the mobility of rubbery PI phase and that the glassy P2VP domains behave like inert filler particles in the rubbery polymer membrane.

ACKNOWLEDGMENTS

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