

Gas Solubility and Diffusion in a Polystyrene–Polybutadiene Block Copolymer

D. H. REIN, R. F. BADDOUR, and R. E. COHEN*

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139-4307

SYNOPSIS

Over the temperature range of 20 to 90°C, the equilibrium solubility of methane or argon in a star-branched polystyrene–polybutadiene (SB) block copolymer can be reliably estimated from a volume-fraction-weighted average of the homopolymer solubilities; the value of heat of solution for SB block copolymer lies between the two values associated with the constituent homopolymers. Diffusion coefficients for gases in the block copolymer are bracketed by the homopolymer values over the range of temperature employed, but the activation energies for diffusion in SB are higher than either of the homopolymer values. The anomalous temperature dependence and the inability of a computer simulation to reproduce experimental diffusion coefficients supported the concept of a temperature-dependent restriction on chain mobility in the polybutadiene regions of the block copolymer. This β factor embodies the relative reduction in the rate of gas diffusion through the B regions of the copolymer compared to B homopolymer; β has a value of about 2–3 at room temperature but decreases to unity when the polystyrene chains become mobile at the polystyrene T_g .

INTRODUCTION

In a previous work we presented results of measurements of CO₂ diffusion and solubility in a polystyrene–polybutadiene block copolymer with well-oriented lamellar morphology.¹ The diffusion process in the block copolymer was also simulated using a two-dimensional finite-difference model with homopolymer data as input. The measured and predicted CO₂ effective diffusion coefficients for the block copolymer led to the conclusion that there are significant differences in the CO₂ transport through the polybutadiene lamellae of the block copolymer compared to the corresponding polybutadiene homopolymer. We proposed that the covalent connections of the polybutadiene chain ends to the glassy polystyrene in the block copolymer led to significantly decreased polybutadiene chain motion and a resulting reduction in the rate of CO₂ diffusion. This led to the introduction of a polybutadiene chain immobilization factor whose value varied from about 2 at room temperature toward unity at the polysty-

rene T_g . By comparison, the CO₂ equilibrium solubility in the block copolymer was adequately represented by a weighted average of the homopolymer solubilities and was not affected by the restricted mobility of the polybutadiene chain ends.

A valid criticism of the previous work is that the conclusions regarding polybutadiene chain immobilization were based on measurements using a single gas, CO₂, which is a relatively condensible species sometimes exhibiting anomalous behavior in transport measurements. The present paper extends the study to Ar and CH₄. The diffusion and solubility measurements presented below demonstrate clearly that the character of the observations seen in the previous study are not unique to CO₂; the mobility restriction of polybutadiene in the block copolymer is apparent for all three gases, and its importance in the gas transport process depends on the molecular diameter of the gas.

EXPERIMENTAL

The Ar and CH₄ gases (Colony, Inc.) had purities in excess of 99.0%. Polystyrene homopolymer, poly-

* To whom correspondence should be addressed.

butadiene homopolymer, and K-resin block copolymer used in this study were the same materials used in our previous work.¹ The K-resin is a star-branched block copolymer of polystyrene and polybutadiene in which the polybutadiene chains form the central core capped by radiating polystyrene arms. Although styrene is the majority repeat unit, the K-resin forms a morphology of alternating polystyrene and polybutadiene lamellae.¹ The gas diffusion and solubility coefficients were measured at 1 atm pressure in a pressure decay sorption appa-

atus described in detail elsewhere¹; measurements of D and S were made over the temperature range 20–90°C.

RESULTS AND DISCUSSION

Solubility Coefficient

The solubility coefficients (measured at 1 atm) for Ar and CH₄ as a function of temperature for poly-

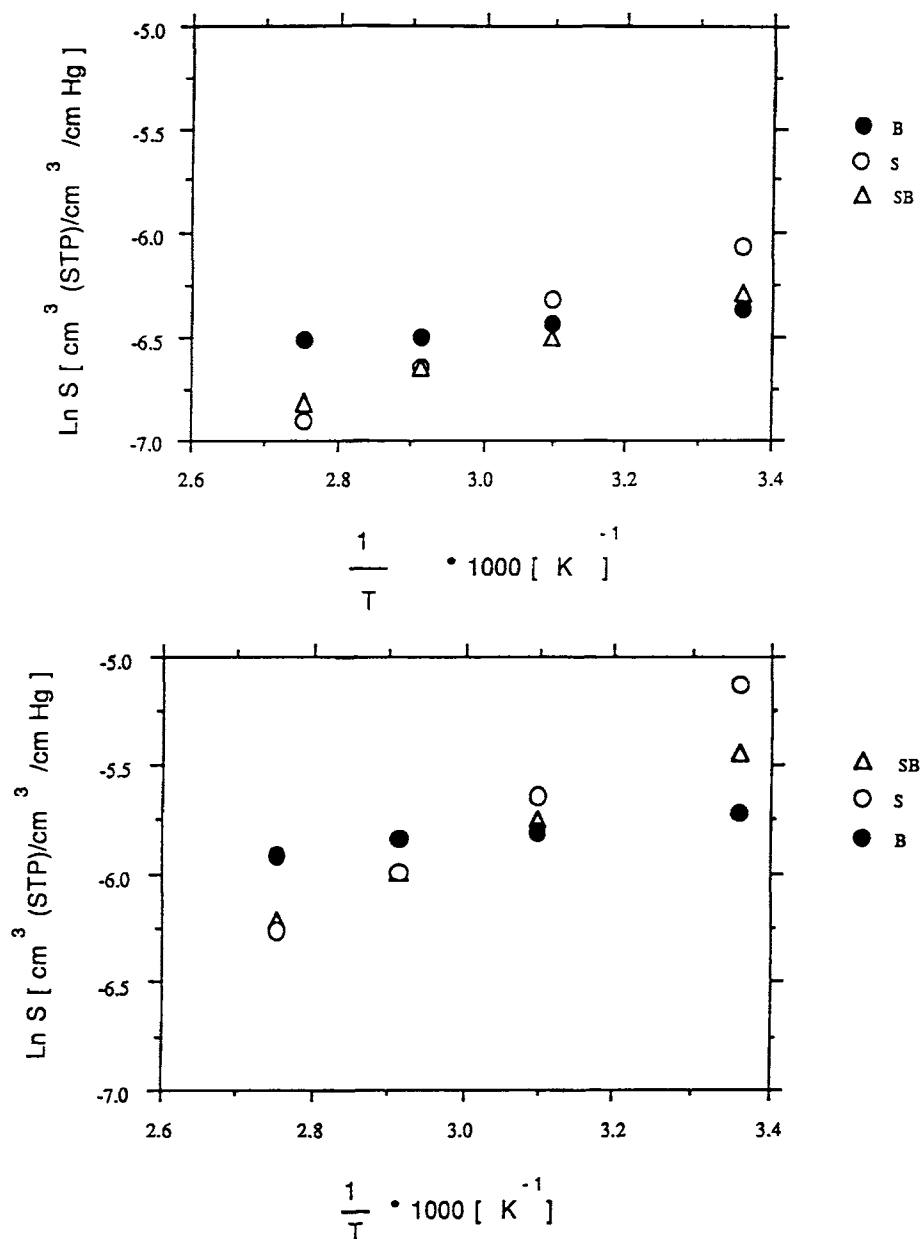


Figure 1 (a) Temperature dependence of the equilibrium solubility coefficients for argon in S, B, and SB; (b) temperature dependence of the equilibrium solubility coefficients for methane in S, B, and SB.

styrene, S, polybutadiene, B, and diblock copolymer, SB, are shown in Figure 1(a) and 1(b). The heats of solution, E_s , in units of kJ/mol for Ar were -11.6 , -2.0 , and -7.1 for S, B and SB, respectively; the heats of solution for CH_4 were -15.6 , -2.7 , and -10.5 for S, B and SB, respectively. For both gases the value of the heat of solution for the copolymer lies between the two homopolymer values. Also at all temperatures, the observed trend of gas solubilities ($S_{\text{Ar}} < S_{\text{CH}_4} < S_{\text{CO}_2}$) is consistent with reported

correlations of increasing gas solubility with increasing ease of gas condensability.²

The solubility coefficient for CO_2 in the K-resin was described³ over the temperature range 20 – 90°C as

$$S^* = v_S S_S + v_B S_B \quad (1)$$

Where S_S and S_B are the solubility coefficients for the pure materials, S^* is the solubility coefficient

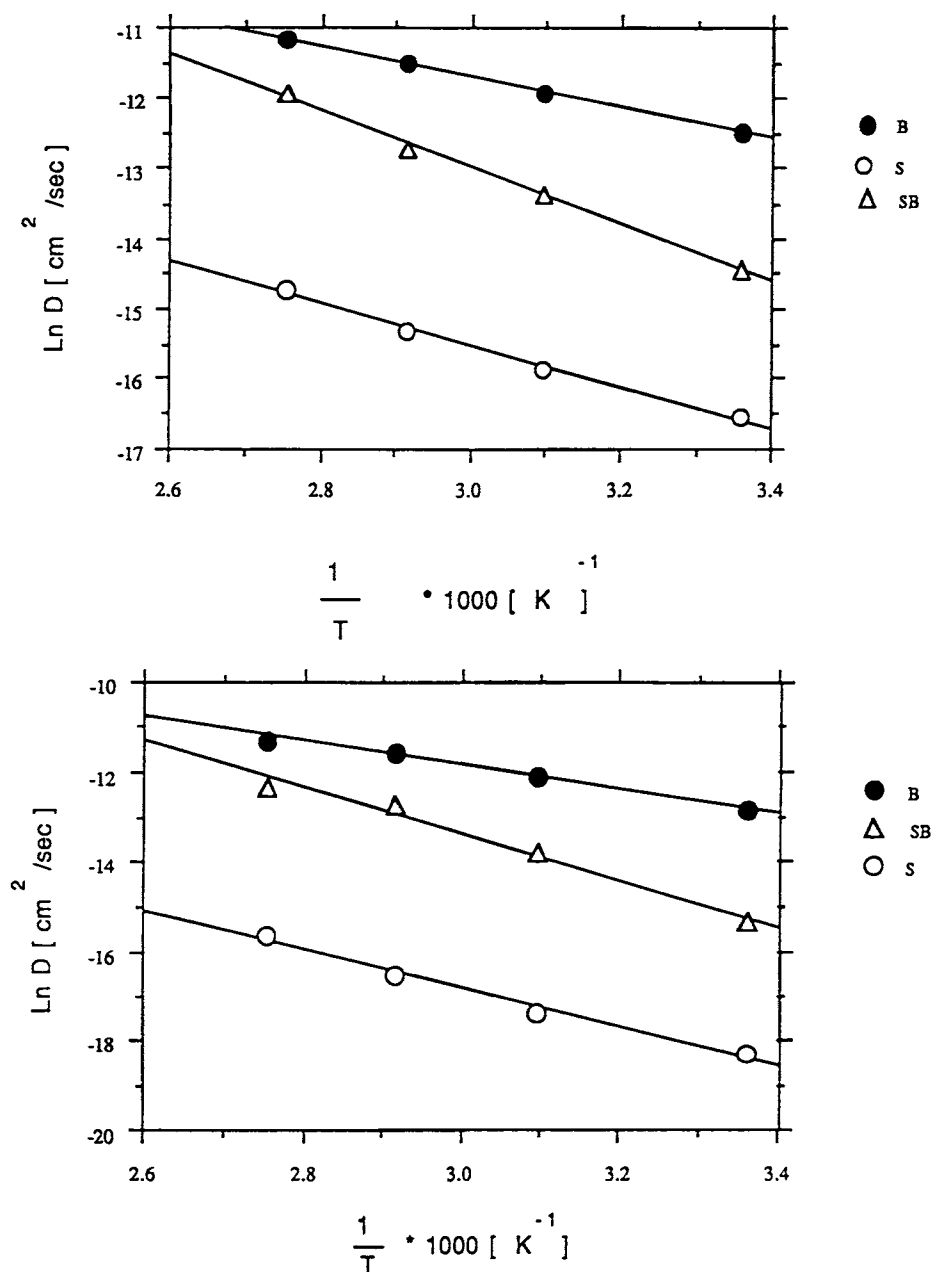


Figure 2 (a) Arrhenius plots of the argon diffusion coefficients in S, B, and SB; (b) Arrhenius plots of the methane diffusion coefficients in S, B, and SB.

for the composite, and v_S and v_B are the volume fractions in the composite. S^* calculated from Eq. (1) for Ar and CH₄ in the K-resin agreed to within 10% of the measured solubility values. This simple model thus adequately describes the gas solubility behavior in a heterogeneous block copolymer system for a variety of gases for which values of solubility differ by more than an order of magnitude.

Diffusion Coefficient

Ar and CH₄ diffusion coefficients for S, B, and SB are plotted as a function of temperature in an Ar-

rhenius form in Figure 2(a) and 2(b). The apparent activation energies for diffusion, E_d (kJ/mol), for Ar were 25, 18, and 34 for S, B and SB, respectively, while for CH₄ they were 36, 22, and 43. For both Ar and CH₄, the apparent activation energy for diffusion in SB is larger than for either homopolymer; over the temperature range of measurement, however, the diffusion coefficients for SB were always bracketed by the homopolymer values.

In order to investigate this larger-than-expected temperature dependence of the block copolymer gas diffusion, we modeled the diffusion process, as in

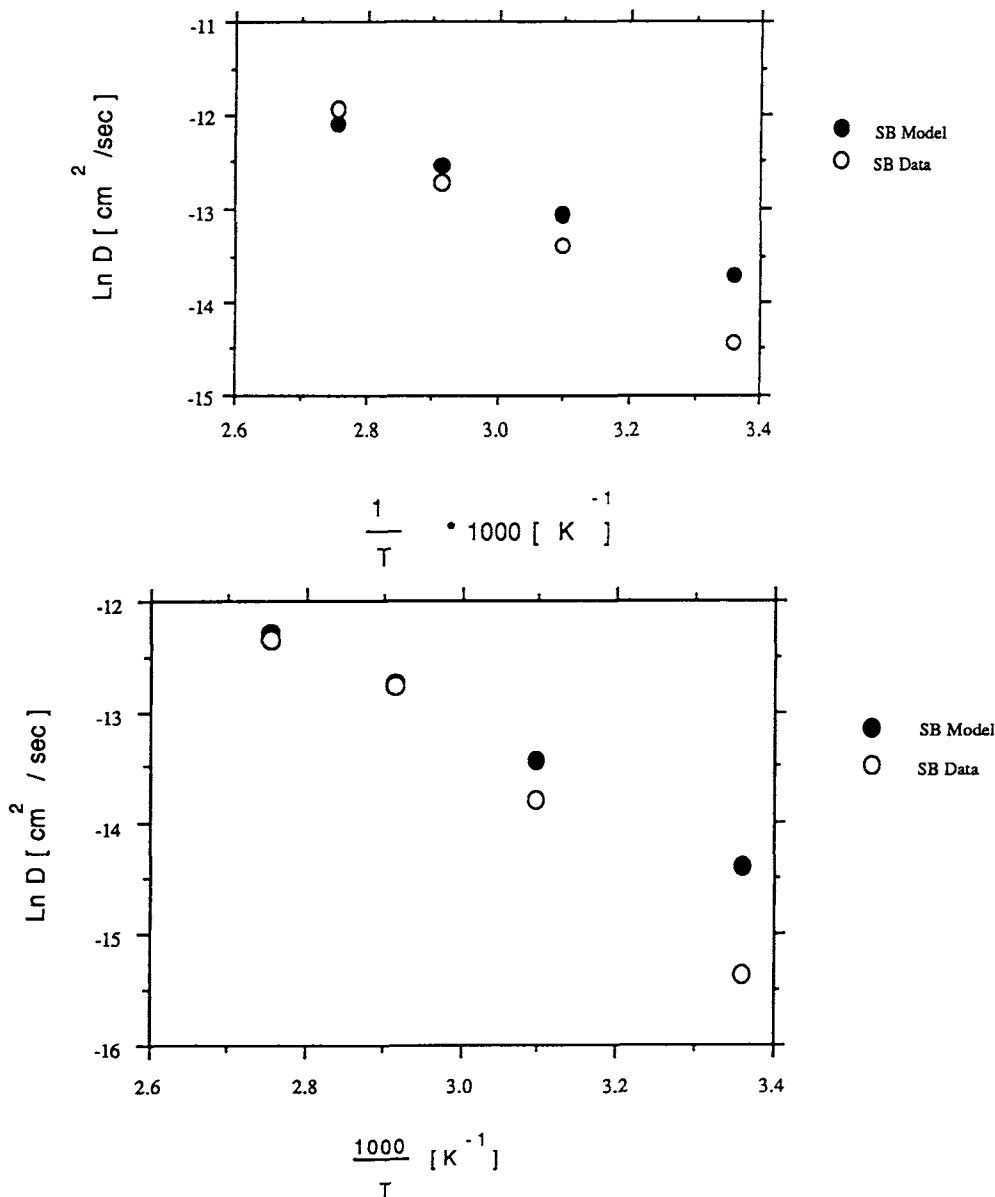


Figure 3 (a) Comparison of Arrhenius plots for measured and model-generated argon diffusion coefficients; (b) comparison of the Arrhenius plots for measured and model-generated methane diffusion coefficients.

Table I Polybutadiene Immobilization Factors

Temp. (K)	β (CO ₂)	β (Ar)	β (CH ₄)
293	1.9	—	—
298	—	2.3	2.9
323	1.5	1.5	1.6
343	1.3	1.3	1.0
363	1.2	1.0	1.0

our previous work with CO₂, using a computer simulation of unsteady diffusion into a composite material of well-defined parallel lamellar structure.¹ Measured S and B diffusion and solubility coefficients and the known block copolymer morphology were used as input into the model.

Figure 3(a) and 3(b) are Arrhenius plots comparing D_{eff} values calculated from half times of the model response and D_{eff} values obtained from the experimental sorption curves. The model overpredicts the measured K-resin diffusion coefficients for Ar and CH₄; the amount of overprediction decreases as the temperature approaches the T_g of polystyrene. This is essentially identical in form to the results obtained previously for CO₂¹; therefore we have again accounted for the unusual behavior of the copolymer through a temperature-dependent factor, β , which is based on the concept of restrictions on B chain motions in the block copolymer. Thus to obtain agreement between the model and experiments, the value of diffusion coefficient for polybutadiene used for input into the model was adjusted at each temperature according to

$$\beta = D/D^* \quad (2)$$

where D is the diffusion coefficient for Ar or CH₄ through polybutadiene homopolymer, D^* is the diffusion coefficient for Ar or CH₄ through the polybutadiene in the K-resin, and β is the temperature-dependent immobilization factor. A value of D^* was chosen at each temperature for Ar and CH₄ to match the calculated SB diffusion coefficient with the measured diffusion coefficient. Table I lists β values at several temperatures for Ar, CO₂, and CH₄.

The three gases show similar values of β over the temperature range 20–90°C and β always decreases toward unity as the T_g of the polystyrene is approached. These values for β are in good agreement with those determined by Odani et al. for a polystyrene-polybutadiene block copolymer⁴: β (25°C) = 0.99, 1.3, 1.8, 2.4, and 2.4 for He, Ar, N₂, Kr, and Xe, respectively. At the lower end of the temperature range explored in our work, 20–50°C, it also appears

that β is larger for gases with larger molecular diameters.

CONCLUSIONS

Transient sorption measurements using Ar and CH₄ gases and a SB block copolymer confirm earlier observations obtained using CO₂ gas, namely: The equilibrium solubility of gas in the SB block copolymer can be reliably estimated from a volume-fraction-weighted average of the homopolymer solubilities; the value of heat of solution of gas in the SB block copolymer lies between the two values associated with the constituent homopolymers; diffusion coefficients for gases in SB block copolymers are bracketed by the homopolymer values over the range of temperature employed, but the activation energies for diffusion in SB are higher than either of the homopolymer values. The anomalous temperature dependence and the inability of a computer simulation to produce expected diffusion coefficient values for SB from homopolymer data supported the concept of a temperature-dependent restriction on chain mobility in the polybutadiene regions of the SB block copolymer. This β factor has values of about 2–3 at room temperature but decreases to unity when the polystyrene chains become mobile at the polystyrene T_g . The immobilization of the B chains caused a decrease in the gas diffusion through the B region relative to homopolymer B; β showed a selectivity based on molecular diameter.

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