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Contract N00014-91-J-1045
R&T Code 4132047---02-1

TECHNICAL REPORT NO. 4

Polybutadiene Chain Immobilization in B-Core,
Star-Branched SB Block Copolymers

by

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May 21, 1991

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| Accession For | |
| NTIS GRA&I | <input checked="" type="checkbox"/> |
| DTIC TAB | <input type="checkbox"/> |
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REPORT DOCUMENTATION PAGE

| | | | | | |
|--|-------|--|--|---|---------------------|
| 1a. REPORT SECURITY CLASSIFICATION | | | 1b. RESTRICTIVE MARKINGS | | |
| 2a. SECURITY CLASSIFICATION AUTHORITY | | | 3. DISTRIBUTION/AVAILABILITY OF REPORT approved for public release; distribution unlimited | | |
| 2b. DECLASSIFICATION/DOWNGRADING SCHEDULE | | | | | |
| 4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 4 | | | 5. MONITORING ORGANIZATION REPORT NUMBER(S) | | |
| 6a. NAME OF PERFORMING ORGANIZATION MIT Dept. of Chemical Eng. | | 6b. OFFICE SYMBOL (If applicable) | 7a. NAME OF MONITORING ORGANIZATION Office of Naval Research | | |
| 6c. ADDRESS (City, State, and ZIP Code) MIT, Building 66, Room 554 Cambridge, MA 02139-4307 | | | 7b. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 22217 | | |
| 8a. NAME OF FUNDING/SPONSORING ORGANIZATION ONR | | 8b. OFFICE SYMBOL (If applicable) | 9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-91-J-1045 | | |
| 8c. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 22217 | | | 10. SOURCE OF FUNDING NUMBERS | | |
| | | | PROGRAM ELEMENT NO. | PROJECT NO. | TASK NO. |
| | | | 4132047 | 02 | 1 |
| 11. TITLE (Include Security Classification) Polybutadiene Chain Immobilization in B-Core, Star-Branched Block Copolymers | | | | | |
| 12. PERSONAL AUTHOR(S) D.H. Rein, R.F. Baddour, R.E. Cohen | | | | | |
| 13a. TYPE OF REPORT Technical Report | | 13b. TIME COVERED FROM _____ TO _____ | | 14. DATE OF REPORT (Year, Month, Day) May 21, 1991 | 15. PAGE COUNT 9 |
| 16. SUPPLEMENTARY NOTATION | | | | | |
| 17. COSATI CODES | | | 18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) | | |
| FIELD | GROUP | SUB-GROUP | gas transport | | |
| | | | microphase separation | | |
| | | | block copolymers | | |
| 19. ABSTRACT (Continue on reverse if necessary and identify by block number) The equilibrium solubility of gases in a star-branched 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 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 reproduce experimental diffusion coefficient values for SB 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 rate of gas diffusion through the B region relative to homopolymer B, and this β factor showed a selectivity based on molecular diameter. | | | | | |
| 20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS | | | 21. ABSTRACT SECURITY CLASSIFICATION | | |
| 22a. NAME OF RESPONSIBLE INDIVIDUAL | | | 22b. TELEPHONE (Include Area Code) | | 22c. OFFICE SYMBOL |

INTRODUCTION

In a previous paper 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 the 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 (B) 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 PB chain immobilization factor whose value varied from about 2 at room temperature toward unity at the polystyrene 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 PB 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 the 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 SECTION

The Ar and CH₄ gases (Colony, Inc.) had purities in excess of 99.0%. Polystyrene homopolymer, polybutadiene 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 S and B lamellae [1]. The gas diffusion and solubility coefficients were measured at 1 atmosphere pressure in a pressure decay sorption apparatus described in detail elsewhere [1]; measurements of D and S were made over the temperature range 20 to 90 °C.

RESULTS AND DISCUSSION

Solubility Coefficient

The solubility coefficients (measured at 1 atm) for Ar and CH₄ as a function of temperature for polystyrene, S, polybutadiene, B, and diblock copolymer, SB, are shown in figures 1a and 1b. The heats of solution, E_s in units of KJ/mole for Ar were -11.6, -2.0 and -7.1 for S, B and SB, respectively; the heats of solution for CH₄ 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 ($S_{Ar} < S_{CH_4} < S_{CO_2}$) is consistent with reported correlations of increasing gas solubility with increasing ease of gas condensibility [2].

The solubility coefficient for CO₂ in the K-Resin was described [3] 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 for the composite, and v_S and v_B are the volume fractions in the composite. S* calculated from equation (1) for Ar and CH₄ in the K-Resin agreed to within 10% of the measured solubility values. This simple two-phase 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 Arrhenius form in Figure 2a and 2b. The apparent activation energies for diffusion, E_d(Kj/mole), 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 modelled the diffusion process, as in 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.

Figures 3a and 3b are Arrhenius plots comparing D_{eff} values calculated from half times of the model response and from the experimental sorption curves. The model overpredicts the measured K-Resin diffusion coefficients for Ar and CH_4 ; 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 CO_2 [1]; 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 CH_4 through homopolybutadiene, D^* is the diffusion coefficient for Ar or CH_4 through polybutadiene in the K-Resin and β is the temperature dependent immobilization factor. A value of D^* was chosen for polybutadiene at each temperature for Ar and CH_4 to match the calculated SB diffusion coefficient with the measured diffusion coefficient. Table I lists β values at several temperatures for Ar, CO_2 and CH_4 .

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 calculated by Odani et al. for a polystyrene-polybutadiene block copolymer [4]: $\beta(25^\circ C) = 0.99, 1.3, 1.8, 2.4$ and 2.4 for He, Ar, N_2 , 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, and this β showed a selectivity based on molecular diameter.

ACKNOWLEDGEMENTS

This research was supported in part by the Office of Naval Research and by the Du Pont (RFB) and Bayer (REC) Professorships in Chemical Engineering at MIT.

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Table I

| <u>Temp (k)</u> | <u>$\beta(\text{CO}_2)$</u> | <u>$\beta(\text{Ar})$</u> | <u>$\beta(\text{CH}_4)$</u> |
|-----------------|--|--------------------------------------|--|
| 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 |

FIGURE LEGENDS

Figure 1a. Temperature dependence of the equilibrium solubility coefficients for Argon in S, B, SB

Figure 1b. Temperature dependence of the equilibrium solubility coefficients for methane in S, B, SB

Figure 2a. Arrhenius plots of the argon diffusion coefficients in S, B, SB

Figure 2b. Arrhenius plots of the methane diffusion coefficients in S, B, SB

Figure 3a. Comparison of Arrhenius plots for measured and model-generated argon diffusion coefficients

Figure 3b. Comparison of the Arrhenius plots for measured and model-generated methane diffusion coefficients













