

The Influence of Chain Configuration and, in Turn, Chain Packing on the Sorption and Transport Properties of Poly(*tert*-butyl acetylene)

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SYNOPSIS

A series of poly(*tert*-butyl acetylene) (PTBA) polymers was prepared with *cis* contents, as characterized by ^{13}C NMR spectroscopy, ranging from 44% to 100%. The sorption and transport properties of propane in this systematically varied series were determined by a sensitive gravimetric sorption technique. As the *cis* content of the polymer increased, propane solubility and diffusivity decreased markedly and the *d*-spacing, determined by wide angle x-ray diffraction spectroscopy, decreased monotonically with increasing *cis* content, suggesting that higher order molecular structure, related explicitly to configurational variations, may strongly influence chain packing in these rigid, glassy materials and, in turn, sorption and transport properties of small molecules in this polymer series. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

It is generally recognized that rubbery polymers with relatively flexible chains, such as poly(*cis*-isoprene) and poly(dimethylsiloxane), are more permeable than common glassy polymers. This notion is largely supported by the oxygen permeability data, presented in Table I, for a wide variety of polymers, wherein all of the polymers with permeabilities less than 1 Barrer are relatively stiff chain glassy polymers.¹⁻⁸

This seeming generality is challenged by the observation that poly(1-trimethylsilyl-1-propyne) (PTMSP), a stiff-chain disubstituted polyacetylene with a T_g in excess of 200°C,² exhibits gas permeability that is almost an order of magnitude higher

than the flexible chain rubbery poly(dimethylsiloxane), which has typically been regarded as the most permeable polymer available.¹ The high permeability of PTMSP cannot be rationalized easily, based solely on primary chain structure.⁹ For example, if the extraordinarily high permeabilities of the PTMSP were derived from the presence of a pendant silyl group, then poly(trimethylsilylacetylene) should be more permeable than poly(*tert*-butylacetylene) (PTBA). This is not observed, however, in the data presented in Table II, describing the oxygen permeability of several members of a related series of substituted polyacetylenes. Moreover, since PTBA also exhibits high permeability to penetrants, it is not apparent that double substitution along the chain backbone is essential for high permeability.

Clearly, the high permeability of PTMSP and the relative permeabilities of substituted poly(acetylenes) cannot be rationalized solely on the basis of primary structural considerations. Higher order structural features, such as differences in *cis/trans*

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Table I Oxygen Permeability of Selected Polymers at 25°C

Polymer	Permeability (Barrer) ^a	Permeability Reference	Glass Transition Temperature (°C)
Poly(1-(trimethylsilyl)-1-propyne)	4000	1	> 200 ²
Poly(dimethylsiloxane)	600	1	-127 ³
Poly(<i>cis</i> isoprene)	23	4	-73 ³
Poly(<i>trans</i> isoprene)	5	5	-58 ³
Poly(vinyl chloride)	0.01	4	81 ³
Poly(vinylidene chloride)	0.001	4	-18 ³
VECTRA liquid crystalline polymer	0.0001	6	100 ⁷
Poly(vinyl alcohol) (bone dry)	0.000001	8	85 ³

$$^a 1 \text{ Barrer} = 10^{-10} \frac{\text{cm}^3 (\text{STP}) \text{ cm}}{\text{cm}^2 \text{ sec cm Hg}}$$

tactic ratio and, in turn, chain configuration and packing, may, therefore, have a strong influence on the sorption and transport properties of substituted poly(acetylenes) which, in turn, determine the permeation behavior of the respective polymers.

In 1980, Masuda et al.¹⁰ showed that the *cis/trans* ratio of PTBA can be changed by varying the solvent or solvent mixture of the reaction. In 1985, the same group¹ demonstrated that there is a systematic effect of *cis* content on the oxygen permeability and oxygen/nitrogen permselectivity of a series of PTBA polymers. Izumikawa et al.¹¹ and Costa et al.¹² have suggested that the *cis/trans* ratio of poly(trimethylsilylpropyne), the most permeable member of the substituted poly(acetylene) family, can be changed by varying the catalyst used in the reaction. Moreover, Izumikawa et al.¹¹ suggest that the most permeable polymers of the PTMSP series, polymerized with TaCl₅, are rich in *trans*-configuration.

In summary, although there are somewhat disparate reports in the literature, which might imply that, for example, the high permeability of PTMSP is related specifically to a high *trans* content,^{1,11} there are no reported results that demonstrate this effect

systematically. This study was motivated, therefore, by the earlier work of Takada et al.,¹ studying the PTBA system and the requirement to demonstrate the effect of *cis/trans* content on the individual sorption and transport properties, which provide fundamental insight into the effect of configuration on the permeability behavior of a substituted polyacetylene series with systematically varied *cis/trans* configuration. The results are subjected, moreover, to data analysis, regarding both sorption and transport, which bear upon current theories of the glassy state.

EXPERIMENTAL

Characterization of Sorption and Transport Properties

The sorption and transport of propane in PTBA were determined using interval gravimetric sorption experiments performed on a Cahn electrobalance system at 35°C.^{13,14} The Cahn electrobalance system comprises a Cahn RG-2000 electrobalance, enclosed in a glass sorption chamber. A uniform thickness polymer film is suspended from the electrobalance and the time-dependent weight change is directly recorded on a Fisher Recordall series 5000 strip chart recorder. The sorption system is serviced by a high vacuum line for sample degassing and penetrant removal. The kinetic sorption technique avoids problems related to seals, pinholes, imperfections, and leaks, which can confound direct characterization of permeation in polymeric materials.¹⁵

Propane was chosen as a penetrant to permit a direct comparison between propane isotherms in PTBA and published propane isotherms in PTMSP.¹⁶ Moreover, at the subambient penetrant

Table II Oxygen Permeability at 25°C of Selected Substituted Poly(acetylenes)¹

Polymer	Permeability (Barrer) ^a
Poly(1-(trimethylsilyl)-1-propyne)	4000
Poly(<i>tert</i> -butyl acetylene)	300
Poly(trimethylsilylacetylene)	36

$$^a 1 \text{ Barrer} = 10^{-10} \frac{\text{cm}^3 (\text{STP}) \text{ cm}}{\text{cm}^2 \text{ sec cm Hg}}$$

Table III Synthesis Conditions and Properties of Poly(*t*-butyl acetylene) Samples^a

<i>cis</i> Content (%)	Intrinsic Viscosity in Toluene (30°C)	Catalyst	Solvent	Monomer : Catalyst Ratio
44	0.33	MoCl ₅	Toluene	50
50.2	0.41	MoCl ₅	Toluene	50
50.4	1.05	MoCl ₅	Toluene	50
60	0.43	MoCl ₅	Anisole	33
68	0.25	MoCl ₅	Anisole	33
84	1.69	MoCl ₅	Anisole	33
100	1.10	MoCl ₅	Benzonitrile	33

^a The initial monomer concentration was 1 M; polymerization temperature and time were 30°C and 24 h, respectively.

pressures accessible with our apparatus, propane is more soluble than gases, such as oxygen and nitrogen, in the polymers, which allows for more accurate determination of penetrant solubility and diffusivity. The polymer film to be studied was placed in the sample chamber of the sorption system and was exposed to vacuum for at least 24 h to remove air gases. Propane was then introduced to the sample chamber at a fixed pressure, and the subsequent increase in sample weight was recorded as a function of time. When the sample weight had been constant for several hours, the propane pressure in the sorption chamber was increased to begin the next experiment. These weight uptake data were corrected for the effect of buoyancy by performing a blank run with no polymer in the sample pan of the balance. From these data, propane solubility and diffusivity in the sample may be determined as a function of propane pressures.¹⁵ Propane pressures up to approximately 700 torr were studied.

Polymer Synthesis

Synthetic methods for preparing PTBA samples with systematically varied *cis/trans* ratios have been well documented.^{1,9,10,17,18} These methods lead to high molecular weight polymers with yields of 60–100%. The *cis* content of the PTBA samples included in this study was varied from 44 to 100% by the proper choice of catalyst and solvent mixture. For example, MoCl₅ and oxygen- or nitrogen-containing solvents, such as anisole, 1,2-dimethoxyethane, methyl benzoate, acetophenone, nitrobenzene, benzonitrile, and acetonitrile, produce PTBA samples with only *cis* isomer. Conversely, MoCl₅ in toluene can catalyze the production of PTBA with as little as 44% *cis*. A proper choice of nonpolar or oxygen-containing solvents, along with MoCl₅, were used to obtain PTBA samples with between 44% to 100% *cis* content. The synthesis conditions and properties of these poly-

mers are presented in Table III. In all cases, the initial monomer concentration was 1 M and the polymerization reactions were carried out at 30°C for 24 h. Different catalyst batches of MoCl₅ were used in the respective polymerizations. The differences in polymer properties, resulting from the variation in catalyst batch, are commonly observed in transition metal catalyzed polymerizations.

Characterization of *cis* Content of PTBA by ¹³C NMR

The *cis/trans* ratio of the PTBA samples was determined using ¹³C NMR. A sample ¹³C NMR spectrum is presented in Figure 1. The three methyl carbons on the tertiary butyl group of PTBA give rise to two peaks at approximately 31 and 32 ppm in the ¹³C NMR spectrum. Complementary theoretical¹⁹ and experimental studies^{1,9,10,17,18} have led to the assignment of the peak at 31 ppm to the *cis* configuration, while the peak at 32 ppm is ascribed to the *trans* configuration. Okano et al.¹⁷ characterized the

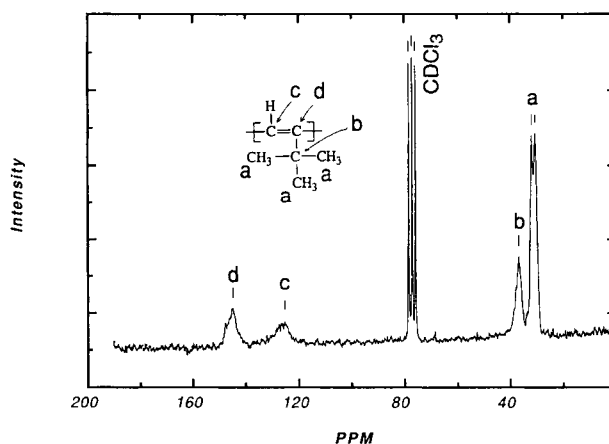


Figure 1 Carbon-13 NMR spectrum of 50.4% *cis* PTBA.

ratio of the area under the 31 ppm peak, divided by the sum of the areas under both peaks, as being equal to the *cis* content of PTBA. The *cis* and *trans* peaks overlap, however, and precise determinations of the area of each peak is difficult. Peak heights are more easily separable and measurable; therefore, the ratio of the intensity of the 31 ppm peak to the sum of the intensities (peak heights) of the 31 and 32 ppm peaks was taken to be directly proportional to the *cis* content. In cases where the peaks were separated sufficiently to permit a determination of the peak area, the *cis* content, calculated from peak areas, was always within 10% of that calculated from peak heights.

Wide Angle X-ray Diffraction Spectroscopy

A Phillips–Norelco wide angle X-ray diffraction (WAXD) spectrometer was used to determine the *d*-spacing of the PTBA samples. A sample WAXD spectrum is shown in Figure 2. The *d*-spacing was calculated from Bragg's relation:

$$n\lambda = 2d \sin\theta \quad (1)$$

Where θ corresponds to the location of the center of the broad intense peak in the X-ray pattern, λ is the wavelength of X-ray radiation (CuK α wavelength = 1.54 Å), and $n = 1$ for the more intense peak and $n = 2$ for the less intense peak.

Sample Preparation

Uniform films of constant thickness were cast from 10 wt % toluene solutions onto a glass plate floating on mercury. The films were subsequently dried for

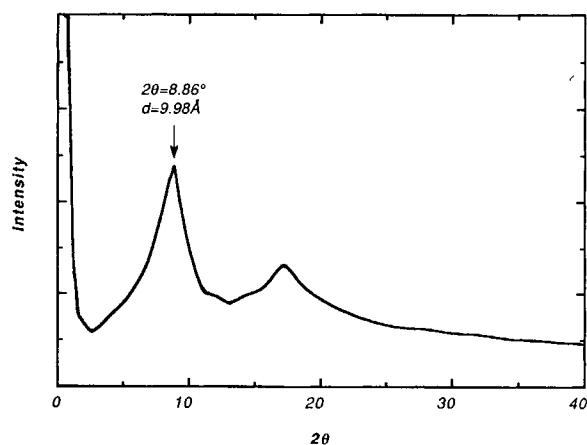


Figure 2 Wide angle x-ray diffraction spectrum of 68% *cis* PTBA.

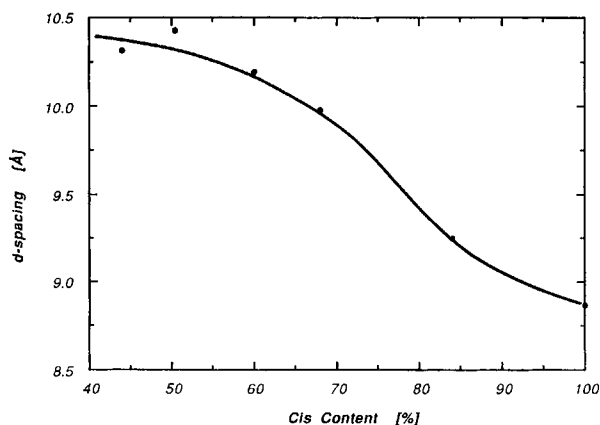


Figure 3 Influence of *cis* content on *d*-spacing from WAXD.

24 h in a vacuum oven at 90°C. No traces of residual solvent were observed by DSC.

RESULTS AND DISCUSSION

Influence of *cis* Content on WAXD Spectra

PTBA has been reported to be a completely amorphous polymer over the entire range of tactic ratios.¹⁷ In amorphous polymers, the *d*-spacing is often presumed to be sensitive to the degree of chain packing, with higher *d*-spacings corresponding to less closely packed polymer chains and lower *d*-spacings corresponding to more densely packed chains. In fact, Tasaka et al.²⁰ have observed that the *d*-spacing increases linearly with specific volume in PTMSP. Moreover, the computer simulation results of Jacobson²¹ confirm that the *d*-spacing of PTBA is sensitive to chain packing. The data presented in Figure 3, therefore, indicate that the *d*-spacing and, presumably, the interchain spacing, decrease with increasing *cis* content.

Influence of *cis* Content on Propane Solubility in PTBA

Propane sorption isotherms, obtained at 35°C for PTBA samples of varying *cis/trans* ratios, are presented in Figure 4. The propane activity is calculated as the ratio of the partial pressure of propane in contact with the polymer sample to the vapor pressure of propane at 35°C. The propane solubility, in general, decreases with increasing *cis* content. The isotherms are all concave towards the abscissa, which is a commonly observed form of isotherms characterizing the sorption of gases and low activity

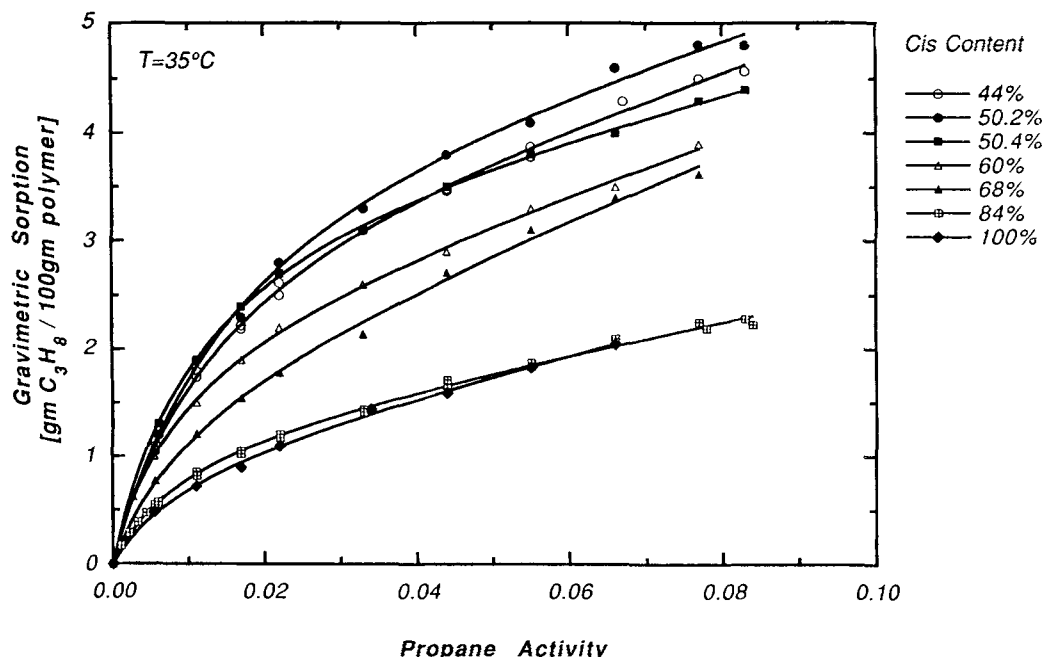


Figure 4 Propane sorption into PTBA of varying *cis/trans* ratio.

organic vapors into glassy polymers. Such isotherms are typically described by the Dual Mode sorption model, which has the following mathematical form:²²

$$C = k_d \frac{p}{p_o} + C'_H \frac{b \frac{p}{p_o}}{1 + b \frac{p}{p_o}} \quad (2)$$

where *C* is the concentration of gas in the polymer and has units, in this case, of grams of propane sorbed per 100 grams of dry polymer. The Henry's Law parameter, *k_d*, describes gas or vapor sorption into the densified matrix of the polymer. The Langmuir capacity, *C'_H*, describes the gas or vapor sorption capacity of the less dense nonequilibrium volume associated with the glassy state of the polymer. The Langmuir affinity, *b*, is an equilibrium constant, characterizing the binding of the gas or vapor molecule to a Langmuir site in the polymer. The propane isotherms presented in Figure 4 are well-described by this model, and the curves through the data points in Figure 4 are fits of this model to the data, using parameters derived from a nonlinear least squares regression analysis of all data for a given isotherm.

The parameters of the Dual Mode sorption model, as a function of *cis* content, are presented in Figures 5 (a,b) and 6. The only parameter showing a strong dependence upon the *cis* content of the polymer is the Langmuir sorption capacity, which decreases

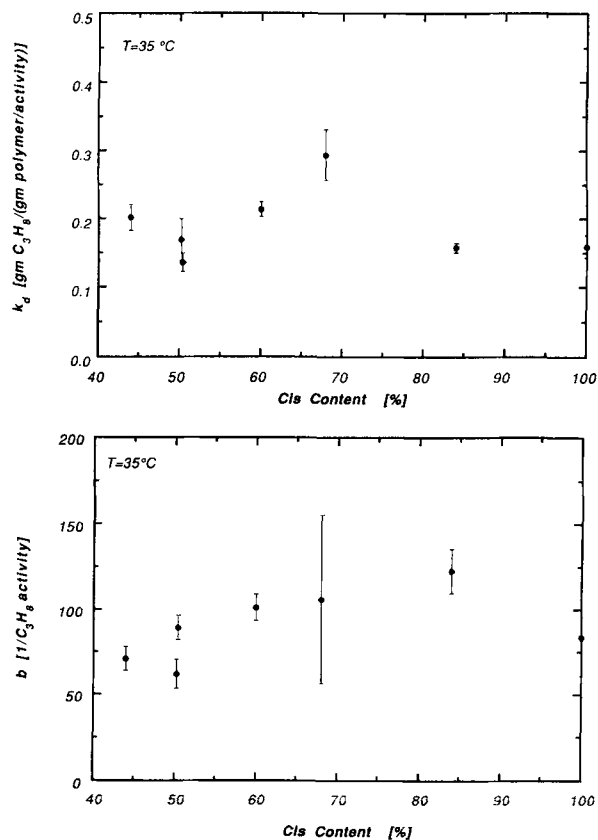


Figure 5 (a) Influence of *cis* content on Henry's law parameter. (b) Influence of *cis* content on Langmuir affinity.

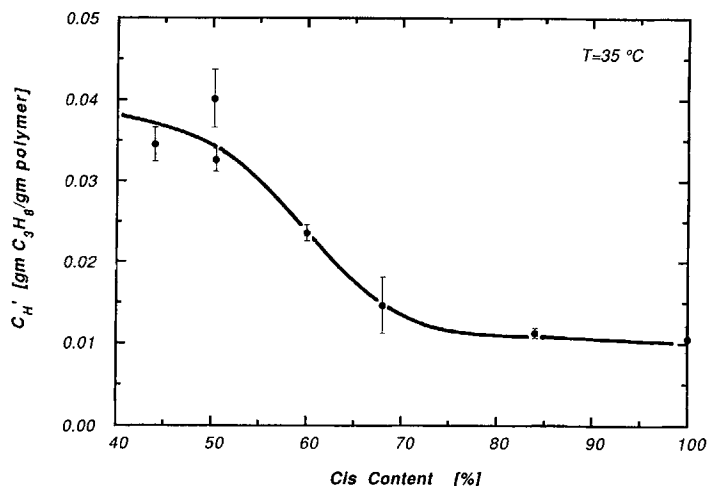


Figure 6 Influence of *cis* content on Langmuir capacity.

approximately fourfold as the *cis* content is varied from 44% to 100%. Based upon the hypotheses of the Dual Mode model, changes in the Langmuir sorption capacity, without concomitant changes in the Henry's Law or the Langmuir affinity parameters, suggest that the amount of nonequilibrium volume associated with the glassy state decreases with increasing *cis* content and that the equilibrium polymer-penetrant interactions are independent of *cis* content.

The decrease in the *d*-spacing with increasing *cis* content, at *cis* contents greater than 50%, is consistent with the data presented in Figures 5 and 6, if the *d*-spacing is assumed to be a measure of chain packing. To demonstrate the consistency of the data graphically, a cross-plot of the Langmuir sorption capacity and *d*-spacing is presented in Figure 7. As the Langmuir capacity increases, which would be

characteristic of an increasing amount of nonequilibrium excess volume, the *d*-spacing increases, which indicates less dense or poorer packing of the chains.

Influence of *cis* Content on Propane Diffusivity in PTBA

Typical gravimetric sorption kinetics are shown in Figure 8. Diffusion coefficients were determined from the kinetics of propane sorption in constant-thickness films. Sorption kinetics curves that are sigmoidal, such as the curve in Figure 8, are often observed when organic vapors diffuse into glassy polymers.²³ This well-known phenomenon can be related to the finite time required, after the start of a sorption experiment, to establish a fixed penetrant concentration at the polymer-vapor interface, and

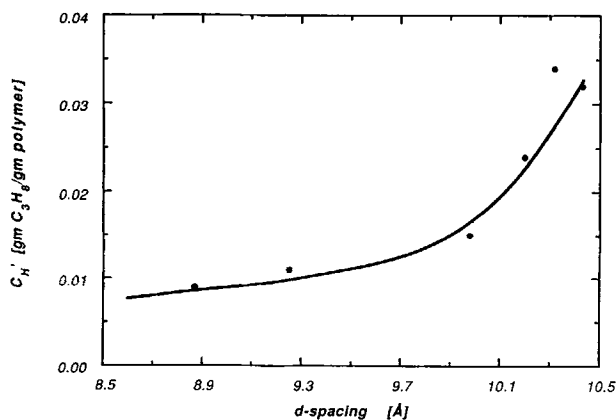


Figure 7 The relationship between Langmuir sorption capacity and WAXD *d*-spacing.

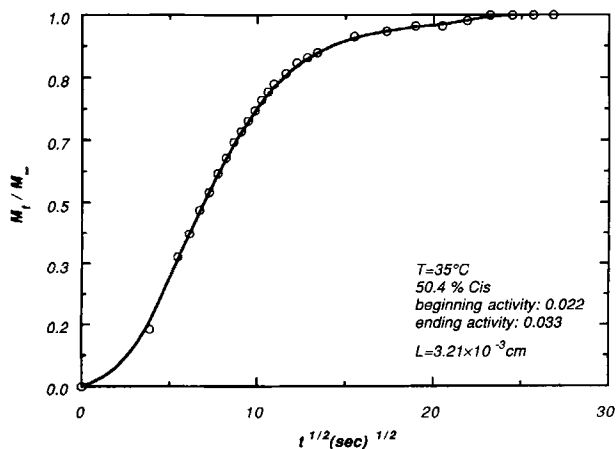


Figure 8 The diffusion kinetics in PTBA.

is observed when the time scales for penetrant diffusion into the polymer and surface concentration equilibration are similar.^{24,25}

Since the results of some experimental gravimetric sorption curves were confounded by the effect of this time-dependent boundary condition, diffusion coefficients were estimated by fitting the long-time sorption data to the following equation:

$$\ln \left[1 - \frac{M_t}{M_\infty} \right] = K - \frac{D\pi^2}{L^2} t \quad (3)$$

where M_t is the mass of penetrant sorbed at time t , M_∞ is the equilibrium mass sorption, D is the mean effective diffusion coefficient characterizing the kinetics of sorption, L is the film thickness, and K is a constant related to the rate of diffusive penetrant absorption in the polymer and the rate of change of surface concentration. In the data analysis, K was treated as an adjustable constant. Equation [3] is a valid approximation for $M_t/M_\infty > 0.4$ if the surface concentration has reached equilibrium.²⁴ A graphical representation of a fit to Equation [3] is presented in Figure 9 for a sample containing 50.4% *cis* isomer. For each PTBA sample, characterized by a specific *cis/trans* content, diffusion coefficients were determined by fitting data to Equation 3 for M_t/M_∞ values between 0.4 and 0.8 over a range of activities and, therefore, penetrant concentrations. To establish a consistent basis for comparison, infinite dilution diffusion coefficients were estimated by extrapolating semi-logarithmic plots of D versus C as shown in Figure 10.

The infinite dilution diffusion coefficients, characterizing propane transport kinetics in the various

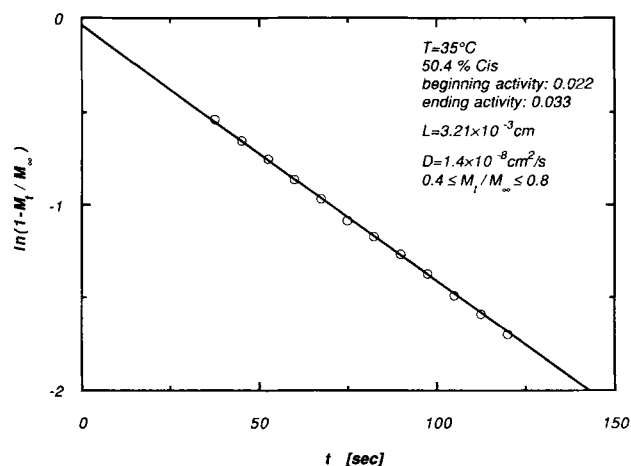


Figure 9 The diffusion kinetics in PTBA (long time analysis).

PTBA samples, are presented in Figure 11. The diffusion coefficients decrease with increasing *cis* content at *cis* contents greater than 50%. The results of Figures 3 and 6 suggest that the packing efficiency of the polymer structure becomes greater as the *cis* content is increased.

Lee²⁶ has proposed that penetrant diffusion coefficients in polymers could be correlated with fractional free volume in the manner suggested by Doolittle:

$$D_o = A \exp \left[\frac{B}{f} \right] \quad (4)$$

where A and B are constants, and f is the fractional free volume in the polymer system. The fractional free volume is defined as:²⁷

$$f = \frac{V_g - V_o}{V_g} = \frac{V_{\text{free}}}{V_g} \quad (5)$$

where V_g is the total specific volume of the polymer, V_o is the so-called "occupied volume," which cannot assist in penetrant transport, and V_{free} is the specific free volume of the polymer. Maeda and Paul,²⁸ Min and Paul,²⁹ and Muruganandam et al.³⁰ have used eq. (4) to rationalize the dependence of gas diffusion coefficients on fractional free volume in a variety of glassy polymers. In polymers sufficiently far below their glass transition temperature, Muruganandam et al.³⁰ have suggested that the free volume is equal to the nonequilibrium excess volume of the glass. For many glassy polymers, the Langmuir capacity parameter from the Dual Mode Sorption Model, C'_H , can be related to the nonequilibrium excess volume of the glass by eq. (6)²²:

$$C'_H = \frac{V_g - V_L}{V_g} \rho^* = \frac{V_e}{V_g} \rho^* \quad (6)$$

where V_L is the total specific volume of the liquidus or rubbery polymer if vitrification were kinetically precluded, V_e is the excess specific volume of the glassy polymer, and ρ^* is the condensed density of the penetrant at the experimental conditions. The specific free volume in eq. (5) can be replaced by the excess specific volume in eq. (6) to give the following expression for the diffusion coefficient:

$$D_o = A \exp \left[\frac{B\rho^*}{C'_H} \right] \quad (7)$$

Two scenarios motivate the replacement of the spe-

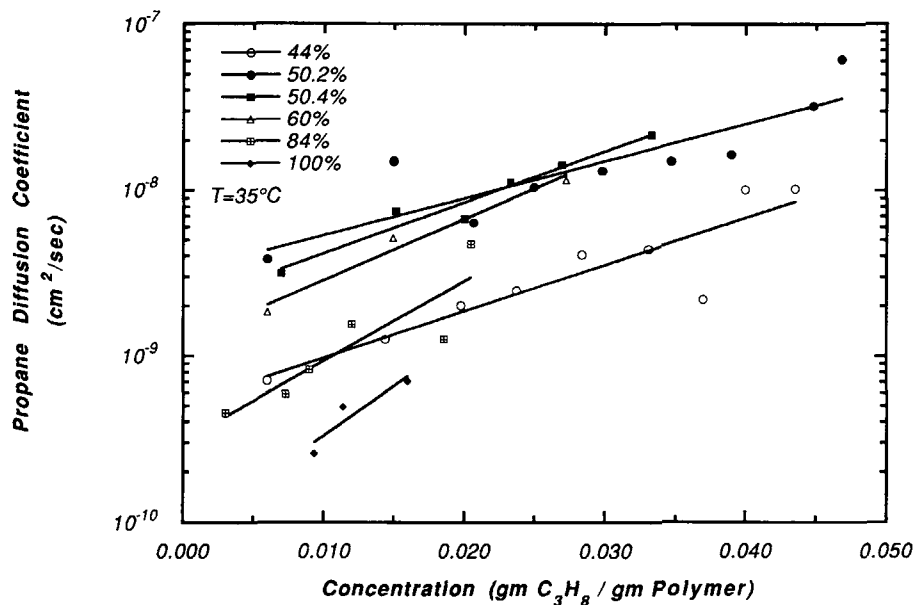


Figure 10 Propane diffusion coefficients calculated from long time data.

cific free volume in eq. (5) by the excess specific volume. First, if the polymers in this report are studied at temperatures sufficiently below their glass transition temperature, then the excess specific volume will be the dominant contribution to the specific free volume. To a good approximation, the specific free volume could, therefore, be equated to the excess specific volume. The glass transition temperature of PTBA is believed to be high, although it has not been reported since the polymer decomposes before undergoing a glass transition detectable by calorimetry. In the second scenario, the specific free volume

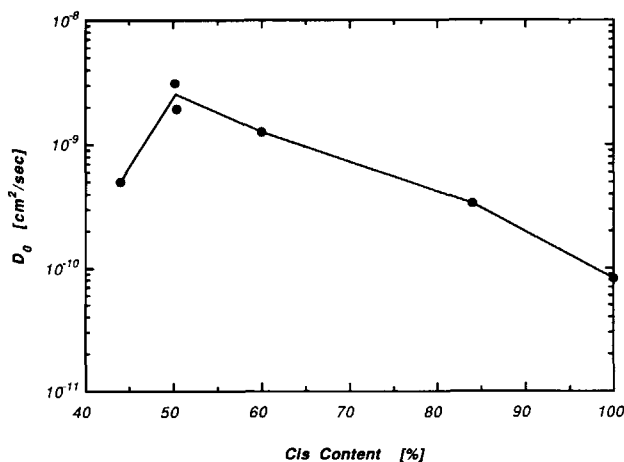


Figure 11 Relationship between infinite dilution diffusion coefficient and *cis* isomer content in PTBA.

in eq. (5) should be replaced by the excess specific volume if, at infinite dilution, penetrant molecules partition preferentially into the nonequilibrium excess volume of the glassy polymer. If most of the penetrant molecules are restricted to the excess volume, then it is the fractional free volume associated with the excess volume which should enter eq. (4).

The Dual Mode model provides the following estimate of the fraction of penetrant molecules which are present in the nonequilibrium excess volume of the glass, N_e :

$$N_e = \frac{C_H}{C_D + C_H} = \frac{C'_H \frac{bP/P_o}{1 + bP/P_o}}{k_D P/P_o + C'_H \frac{bP/P_o}{1 + bP/P_o}} \quad (8)$$

where C_H is the concentration of penetrant molecules in the excess volume of the glass, and C_D is the penetrant concentration in the densified matrix of the polymer. The total penetrant concentration, C , is the algebraic sum of C_D and C_H . In the infinite dilution limit, eq. (8) reduces to:

$$N_e|_{P \rightarrow 0} = \frac{C'_H b}{k_D + C'_H b} \quad (9)$$

Using average values of k_D (0.19 gm C_3H_8 /gm poly/activity) and b (95 activity⁻¹), the values of C'_H reported in Figure 6 lead to N_e values ranging from

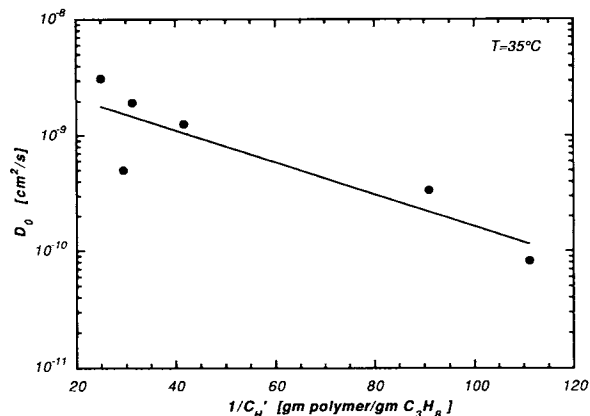


Figure 12 The relationship between infinite dilution diffusion coefficient and reciprocal Langmuir capacity in glassy PTBA.

0.83 to 0.95, suggesting that the vast majority of penetrant molecules are in the nonequilibrium excess volume of the glass at low penetrant activities. These two scenarios, while not mutually exclusive, both suggest that the appropriate free volume to use in the expression for the infinite dilution diffusion coefficient is the specific excess volume. The infinite dilution diffusion coefficient data are, therefore, plotted vs. $1/C_H^*$ in Figure 12. The linearity of this plot suggests that both static sorption data and dynamic diffusion data support the notion that varying the *cis* content of PTBA results primarily in changes in the packing efficiency of assemblies of chains, manifested principally by variations in the nonequilibrium excess volume of the glassy polymers.

CONCLUSIONS

The composite observations from this study suggest that variations in the *cis/trans* content of PTBA can systematically influence the fundamental sorption and transport properties of PTBA, which, in turn, determine the permeability of PTBA. Increasing the *cis* content of PTBA from 44% to 100% leads to a pronounced reduction in the sorption capacity of PTBA, more than an order of magnitude reduction in the diffusivity of propane in PTBA, and a 16% decrease in *d*-spacing. These changes are consistent with the hypothesis that increasing the *cis* content of PTBA leads to more efficient chain packing and, in turn, lower penetrant solubility and diffusivity. While the effects of chemical structure have been widely exploited to vary polymer sorption and transport properties, the current study suggests that chain configuration and, in turn, supermolecular

structure may also play important roles in determining the sorption and transport properties of synthetic polymers.

The authors would like to thank the Plastics Institute of America for providing fellowship support for Mr. Nathanael R. Miranda during the course of his Ph.D. program at North Carolina State University. Thanks are also due to Mr. G. Zannoni (ICM-CNR Milano) for recording ^{13}C NMR solution spectra. Financial support by CNR Progetto Bilaterale and Progetto Finalizzato Chimica Fine II is gratefully acknowledged.

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Received June 30, 1992

Accepted January 15, 1993