complexes, while the discrete components behave in aqueous alkaline solution as appreciably expanded random coil molecules. The intermolecular associative effects are apparently governed by nonbonded orbital interactions,[4] presumably between the aromatic moieties in the components. On the other hand, the overall rates of association are determined by the conformational changes that lead to component conformations which are complementary to one another.[4] A thickness of 1.6 nm for monomolecular lignin films[32] would certainly accommodate the requirement for a perpendicular disposition of the benzene rings with respect to the surface of the associated complex. Consistent with this working hypothesis is the evident lack of a hydrodynamic effect arising from long-chain branching: such a factor in the individual components would have rendered associated complexes with the proposed configuration difficult to envisage. A more detailed understanding of the associative mechanism between the components should serve to reduce the apparent complexity that presently typifies the physicochemical properties of byproduct lignins.

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Effect of Polystyrene Molecular Weight on the Carbon Dioxide Sorption Isotherm

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ABSTRACT: Sorption isotherms for CO_2 at various temperatures were measured for several nearly monodisperse polystyrenes with molecular weights ranging from 3600 to 850 000 and for one commercial polydisperse polystyrene. Extent of sorption decreased with increasing temperature but increased as the molecular weight increased. The results were interpreted in terms of the dual-sorption model. The Langmuir capacity term was observed to increase with molecular weight of the polystyrene because of the corresponding increase in the glass transition. A quantitative analysis of this effect is presented.

Introduction

Information about the solubility of solute molecules in polymers is essential for quantifying transport processes such as permeation. When the solubility is quite small, as for gases, it has been common practice to infer this information from transport measurements, owing to the difficulties of direct measurement. For simple systems, the Henry's law solubility coefficient can be computed from experimentally observed diffusion time lags and the permeability coefficient as has been the practice for gases in polymers above their glass transition temperature. However, when the mechanism for sorption and transport deviates from simple linear models, as occurs in glassy polymers,[1] inference of sorption isotherms from transport observations becomes less reliable and direct measurement is essential. The recent results reported by Toi et al.[2]

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Table I
Polystyrene Samples

source	designation	mol wt	$\bar{M}_w/\bar{M}_n$
Pressure Chemical Co.	batch 61110	$\bar{M}_v$ = 3600	<1.06
Pressure Chemical Co.	batch 80314	$\bar{M}_v$ = 9100	<1.06
Pressure Chemical Co.	batch 41220	$\bar{M}_v$ = 17 400	<1.06
Pressure Chemical Co.	batch 80323	$\bar{M}_v$ = 850 000	<1.10
Cosden Oil and Chemical Co.	Cosden 550	$\bar{M}_n$ = 90 000	2.8

illustrate one approach to the indicrect method referred to above. This work raises the interesting question of what effect polymer molecular weight has on gas solubility. One other paper[3] has examined the influence of polymer molecular weight on the diffusion of gases in polystyrene, but no solubility information was given.

The purpose of this paper is to examine by direct measurements the influence of polymer molecular weight, or the concentration of chain end defects,[4] on equilibrium gas sorption. The availability of nearly monodisperse polystyrenes covering a broad range of molecular weights made this an ideal choice for such a study. Carbon dioxide was selected as the gas. All sorption observations were made below the polymer's glass transition, where the relationship between concentration and pressure is expected to follow the dual-sorption model[1,5]

$$C = k_D p + \frac{C_H' b p}{1 + b p} \qquad (1)$$

with k_D, C_H', and b being model parameters.

Experimental Section

The polystyrene samples used in this work are described in Table I. One is a polydisperse material typical of commercial grades and serves as a reference to other work on polystyrene reported in the literature.[6,7] Films were cast on a clean mercury surface from filtered solutions containing 20% polystyrene in trichloroethylene. After 1 week or more of air-drying at room temperature, the films were removed from the mercury surface and placed in a vacuum oven for several days at about 5 °C above the glass transition to remove the remaining solvent. Completeness of solvent removal was monitored by thermal analysis.

Glass transitions were measured by a Perkin-Elmer DSC-2 instrument. The details of the sorption equipment and its operation have been described elsewhere.[8,9] Prior to determination of the sorption isotherms of CO_2 in these films, they were conditioned for 1 day at 24 atm of CO_2.

Results

Sorption isotherms were measured at 35 °C for all of the polymers in Table I and at 45 and 55 °C for the two lowest molecular weights and for the commerical material. Figures 1–3 show representative results from these measurements. Figure 1 clearly demonstrates that the extent of CO_2 sorption at any pressure *increases* as the polystyrene molecular weight increases. As expected, the magnitude of sorption *decreases* for all molecular weights as temperature is raised (see Figures 2 and 3).

The sorption isotherms are well described by eq 1, and values for the three model parameters were obtained by nonlinear regression of each isotherm data set. These parameters at 35 °C are plotted in Figure 4 against the number-average molecular weight of the polystyrene sample along with the observed glass transition temperature. The affinity parameter, b, does not vary greatly with molecular weight but there does appear to be a slight decrease with increasing $\bar{M}_n$. The Henry's law coefficient, k_D, and the Langmuir mode capacity, C_H', both increase with $\bar{M}_n$ and then appear to approach an asymptotic limit near $\bar{M}_n \sim 10^5$, similar to the well-known manner in which T_g does.[4] Within experimental limits, the commercial polystyrene fits into the pattern established by the nearly monodisperse samples.

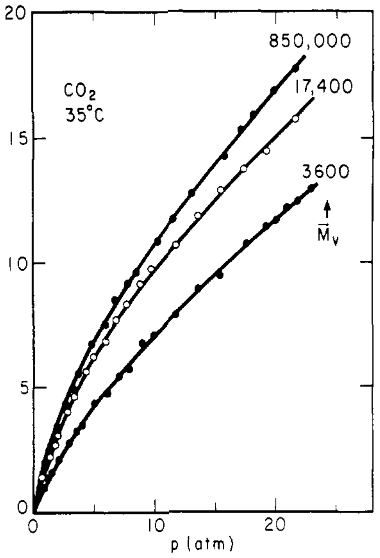

Figure 1. Sorption isotherms for CO_2 in various monodisperse polystyrenes at 35 °C.

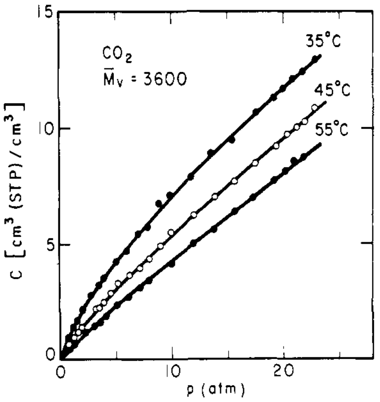

Figure 2. Effect of temperature on sorption of CO_2 in monodisperse polystyrene with $\bar{M}_v$ = 3600.

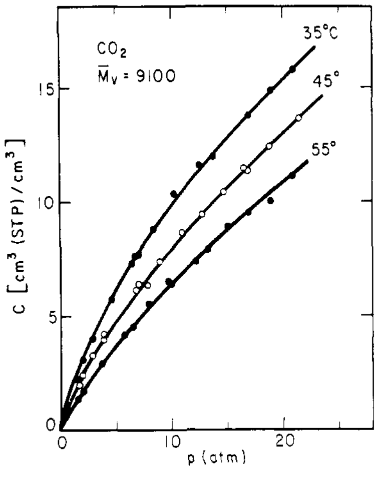

Figure 3. Effect of temperature on sorption of CO_2 in monodisperse polystyrene with $\bar{M}_v$ = 9100.

All three sorption parameters decreased as the temperature was raised, paralleling behavior seen for other systems.[10]

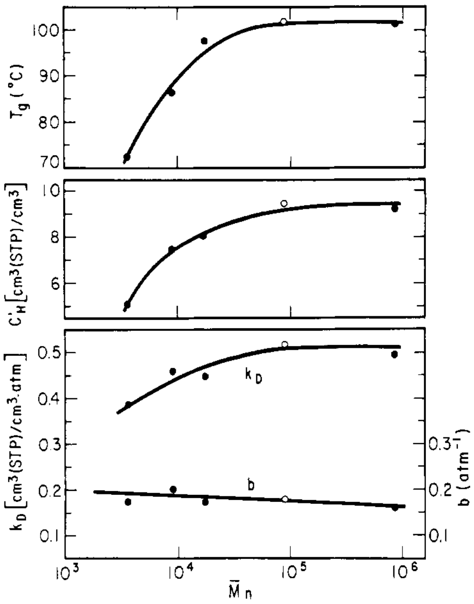

Figure 4. Effect of polystyrene molecular weight on the glass transition temperature and dual-mode sorption parameters for CO_2 at 35 °C. Solid points are for monodisperse samples while the open circles are for a polydisperse commercial material.

Discussion

It was suggested earlier[10-15] that the Langmuir sorption mode stems from the nonequilibrium nature of the glassy state, and its capacity, C_H', is related to the excess volume of the glassy state relative to the extrapolated equilibrium liquid volume, i.e., $V_g - V_l$, by

$$C_H' = 22414\left(\frac{V_g - V_l}{V_g}\right)/\tilde{V}_{CO_2} \tag{2}$$

where the numerical factor expresses the result in the units normally employed, V_g is the specific volume of glass at T, and V_l is the specific volume of equilibrium liquid at T as determined by extrapolation from volumetric behavior above T_g. Equation 2 implies that the Langmuir sorption involves filling this excess volume with CO_2 in a liquid-like state. The molar volume of CO_2 in the condensed state, $\tilde{V}_{CO_2}$, has been estimated to be 55 cm^3/mol.[10-15] One might wonder how free volume associated with chain ends fits into this picture, especially since Figure 4 shows C_H' to increase with $\bar{M}_n$. The latter is contrary to estimates made earlier by indirect methods.[2]

Fox and Flory[4] found that the specific volume of polystyrene at a fixed temperature above the glass transition increased linearly with $1/\bar{M}_n$ and interpreted this to mean that end groups contribute a volumetric packing defect or free volume proportional to their concentration. On the other hand, they found that the specific volumes of polystyrenes below their glass transition do not behave similarly but are independent of the molecular weight. They also concluded that the thermal expansion coefficients above and below T_g were independent of molecular weight. From these observations it may be deduced that the fractional "excess" free volume of glassy polystyrene at temperature T as defined earlier and employed in eq 2 is given by

$$\frac{V_g - V_l}{V_g} = (\alpha_l - \alpha_g)(T_g - T) \tag{3}$$

where α_l and α_g are the volumetric thermal expansion coefficients above and below T_g, respectively. Note that the only effect of molecular weight, or chain ends, on this quantity stems from the influence on T_g. According to the iso-free-volume view of the glass transition, this effect is quantified by

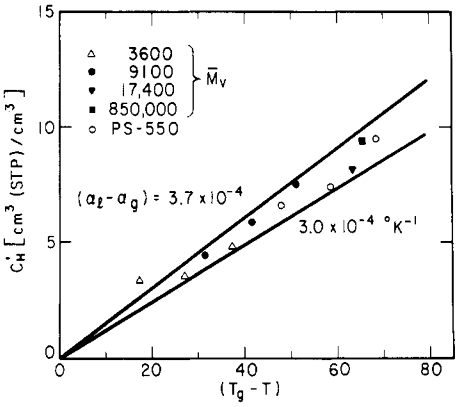

Figure 5. Correlation of C_H' with $T_g - T$ as suggested by eq 2 and 3 and from which solid lines were calculated. Note that both T_g and T vary.

$$T_g = T_g^{\infty} - \frac{2\mu}{V_g(\alpha_l - \alpha_g)\bar{M}_n} \tag{4}$$

where T_g^{∞} is the glass transition of an infinite molecular weight polymer and μ is the unoccupied volume associated with a mole of chain ends.

The above discussions suggest that the influence of temperature and molecular weight on C_H' observed here could be unified by plotting vs. $T_g - T$. This has been done in Figure 5, using the T_g values for each polystyrene shown in the upper part of Figure 4. The solid lines were calculated from eq 2 and 3, with $\tilde{V}_{CO_2}$ = 55 cm^3/mol and the values of $\alpha_l - \alpha_g$ shown. The two numerical choices for the latter span the range of values reported for polystyrene.[16] As can be seen, the calculated results embrace the experimental observations very well and would be in excellent accord with the average value of $\alpha_l - \alpha_g = 3.38 \times 10^{-4}$ K^{-1} used previously.[15] It is quite clear that the increase in C_H' with molecular weight as shown in Figure 4 is due to the increase in T_g.

We may conclude that eq 2 plus the volumetric model of chain end defects from Fox and Flory gives a good accounting of the effect of polystyrene molecular weight on the Langmuir capacity for CO_2 sorption. This picture does not implicitly require the validity of the iso-free-volume concept of the glass transition. We might also note that k_D appears to increase as the polystyrene molecular weight goes up in a manner that parallels the increase in excess free volume of the glass due to the change in T_g as expressed by eq 3 and 4. However, it is quite speculative to relate one response to the other, and other investigations will be needed to ascertain any physical significance or interpretation of this observation. The very slight effect of molecular weight on the affinity parameter shown in Figure 4 is of the same order as the experimental uncertainty and should not be interpreted seriously.

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Scaling Concepts and the Spinodal and Binodal Curves in Polymer Solutions

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ABSTRACT: After summarizing the Daoud–Jannink scaling theory, which suggests that the binodals in polymer solutions should obey a corresponding-states principle, we show that this result may be approximately derived for both the binodals and spinodals from Flory–Huggins thermodynamics, keeping constant the interaction parameter χ.

This paper is concerned with a corresponding-states property for the spinodals in polymer solutions. This is a family of curves depending on the polymerization number N of the polymer. The binodals are examined subsequently.

Let us first briefly summarize the Daoud–Jannink theory,[1] which, to our knowledge, was the first theory to point out a corresponding-states property for the binodals in polymer solutions, using scaling arguments near a critical point.[2] Following the observation by de Gennes[3] that the Flory Θ temperature should be a tricritical point, Daoud and Jannink elaborated a diagram dividing the concentration–temperature space into four distinct regions, as shown in Figure 1. Regions 1–4 are respectively called the dilute, critical semidilute, tricritical semidilute, and collapsed regions. One may add the biphasic region 5. Included in the dilute range is region 1′, the dilute tricritical or "Θ" region. When one crosses the straight line

$$\tau = (1/\phi^*)\phi \tag{1}$$

where ϕ is the volume fraction of the polymer, $\tau = (T - \Theta)/\Theta$ is the reduced temperature, and ϕ^* is a constant defined below, then, following Daoud and Jannink, a second-order phase transition occurs, which, however, may not be sharp, as a result of a crossover region of finite width. In eq 1, ϕ^* is the volume fraction of the polymer where chains begin to "overlap", or, more precisely

$$\phi^* = N/R_g^{\,3} \tag{2}$$

where $R_g^{\,3}$ is the radius of gyration of the macromolecule. In Θ solvents ϕ^* is proportional to $N^{-1/2}$. If now one crosses the line

$$\tau = -(1/\phi^*)\phi \tag{1′}$$

a first-order transition occurs, and therefore the above authors conclude that this should be an asymptote to the phase equilibrium curves, or binodals (for $\tau N^{1/2} \gg 1$). Since the phase equilibrium curves have two asymptotes, the τ axis and the straight line (1′), Daoud and Jannink guessed that these curves should be hyperbolas. Using scaling arguments, they found that the critical reduced temperature $\tau_c = (T_c - \Theta)/\Theta$ and the critical volume fraction of the polymer ϕ_c should obey

$$\tau_c \sim N^{-1/2} \tag{3}$$

$$\phi_c \sim N^{-1/2} \tag{4}$$

One may notice that relations 3 and 4 follow also from Flory's relations[4,5]

$$\phi_c = \frac{1}{1 + N^{1/2}} \simeq \frac{1}{N^{1/2}} \tag{5}$$

and

$$\frac{1}{T_c} = \frac{1}{\Theta}\left[1 + \frac{1}{\psi}\left(\frac{1}{N^{1/2}} + \frac{1}{2N}\right)\right] \tag{6}$$

where ψ is the entropic parameter, if some evident approximations are made. Knowing the asymptotes and the location of the critical point, Daoud and Jannink wrote the equation of the hyperbola as

$$\frac{\tau N^{1/2}}{-\alpha} = \phi N^{1/2} + \frac{1}{\phi N^{1/2}} \tag{7}$$

where α is some positive constant. This yields a universal curve independent of polymerization number N if one shifts to the new variables $\tau' = \tau N^{1/2}$ and $\phi' = \phi N^{1/2}$.

Daoud and Jannink proceeded by saying that near the critical point the curve should not be a hyperbola, because in this region the polymer system is equivalent to an Ising system and therefore Ising exponents should appear. They, however, assumed a universal form for the binodals as

$$\tau N^{1/2} = f(\phi N^{1/2}) \tag{8}$$

where $f(\phi N^{1/2})$ is some unknown function. On the other hand, Daoud, in his Ph.D. dissertation[6] showed that the spinodals should take such a form and concluded, apparently without further proof, that the same should also hold for the binodals.

We now want to show that equivalent results may be obtained from Flory–Huggins thermodynamics, with the sole assumption that the Flory–Huggins χ parameter is concentration independent.

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