dently, a penultimate gauche bond affords a more compact molecular shape, but a visualization of a reduction of nearly 1 Å^3 in molecular volume by means of mechanical molecular models is not easily achieved.

With the exception of the end effect, the results described above show the conformer population is essentially unaffected by pressure densification. Even the gauche enhancement of penultimate bonds becomes noticeable only at densities in absolute units greater than 0.9 g/cm^3 for 10-segment chains and 1.0 g/cm^3 for 20 segment chains, which are realized at pressures greater than ca. 5.0 kbar.[12] Accordingly, for most purposes, the statistical characteristics of chain conformation should be considered a function of temperature only. Figure 9 shows the temperature dependence of trans conformer population for chains with 10, 20, and 30 segments (evaluated during stepwise cooling/compression runs at constant average pressure of 3.0 reduced units). These simulation results are compared with the prediction from the rotational isomeric state model. The pair of dashed line curves in each figure was obtained with the parameter E_σ taken equal to the trans–gauche energy difference 679.3 cal/mol used in the torsional potential energy function for the simulation and with the E_ω values equal to 1500 and 2500 cal/mol, which represent the range of values normally quoted for this parameter. The solid lines were calculated with a value of E_σ equal to 790 cal/mol and E_ω again equal to either 1500 or 2500 cal/mol. The dashed lines, calculated with the use of the "true" trans–gauche energy difference, fail to reproduce the conformer population correctly, but the solid lines calculated with the use of "effective" energy difference are able to represent the population faithfully at temperatures greater than 3.5 reduced units. The rotational isomeric state model in effect neglects all intermolecular interactions and all intramolecular interactions beyond those involving a four-bond sequence. Despite such simplification, it is gratifying to see that the model is capable of predicting the conformer populations correctly, provided a suitably adjusted numerical value is used to represent the effective trans–gauche energy difference.

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Volumetric Behavior of Glassy Polymer–Penetrant Systems

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ABSTRACT: A model is proposed for predicting the volumetric behavior of the glassy polycarbonate–carbon dioxide system. This model is based on the hypothesis that the molecular structure of a glassy polymer changes with changing penetrant concentration. The predictions of the model are in reasonably good agreement with experimental data.

Introduction

When a low molecular weight penetrant is added to a polymer melt, the volume of the mixture at a particular temperature can be determined by using the following equation, if volume change on mixing effects are negligible:

$$\frac{V_m}{V_0} = \frac{\omega_1}{1 - \omega_1} \frac{\hat{V}_1^0}{\hat{V}_2^0} + 1 \tag{1}$$

Here, V_m is the total volume of the mixture, V_0 is the volume of the pure polymer, ω_1 is the mass fraction of penetrant, $\hat{V}_1^0$ is the specific volume of the pure penetrant, and $\hat{V}_2^0$ is the specific volume of the pure equilibrium liquid polymer. If a penetrant is added to a glassy polymer, it would appear reasonable to suppose that the volume of the system could be determined by using the following relationship:

$$\frac{V_m}{V_0} = \frac{\omega_1}{1 - \omega_1} \frac{\hat{V}_1^0}{\hat{V}_{2g}^0(\omega_1{=}0)} + 1 \tag{2}$$

Here, $\hat{V}_{2g}^0(\omega_1{=}0)$ is the specific volume of the pure glassy polymer which would be used in volumetric calculations in the limit of zero penetrant concentration. It has been suggested,[1] however, that eq 2 can seriously overestimate the volume of the mixture, and consequently, it has been postulated that only a fraction of the penetrant leads to volume dilation for a glassy polymer–penetrant system. The rest of the penetrant molecules participate in a hole-filling process and thus do not contribute to any volume expansion. This so-called dual mode sorption model distinguishes between dissolved penetrant and penetrant which is used to fill gaps in the polymer matrix.

The purpose of this paper is to propose an alternative explanation for the volumetric behavior of glassy poly-

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mer–penetrant systems which does not introduce the concept of two different modes of sorption and the idea that not all penetrant molecules lead to volume expansion. The theoretical basis of the model is described below, and the equations of the model are used to predict the volumetric behavior of the glassy polycarbonate–carbon dioxide system at 35 °C.

Theory

A model has been proposed elsewhere[2] for describing the volumetric behavior of glassy polymer–penetrant mixtures. This model is based on the hypothesis that the molecular structure of a glassy polymer is different at different values of the penetrant concentration. For a glassy polymer–penetrant mixture, it is assumed that there is volume additivity at each value of penetrant concentration in the sense that volumes contributed by the pure penetrant and by the glassy polymer can be added together. However, the structure of the nonequilibrium liquid system changes as the concentration of penetrant is increased, and $\hat{V}_{2g}{}^0$, the specific volume of the pure glassy polymer which is used in volume calculations, is thus a function of penetrant concentration. The concentration dependence of $\hat{V}_{2g}{}^0$ is a consequence of the fact that the molecular structure of the glassy polymer is different at each concentration.

The precise nature of the equations which must be used to perform volumetric calculations for a glassy polymer–penetrant system will depend on how the polymer–penetrant mixture is prepared because of the history dependence of the properties of glassy polymers. Equations have been derived elsewhere[2] for the description of volumetric behavior for a glassy polymer–penetrant mixture which is formed by first mixing the materials at some temperature above the glass transition temperature of the system and then cooling the mixture to the desired temperature, using a conventional experimental time scale. The equations for this model are restricted, in the strictest sense, to the description of the volumetric behavior for systems prepared only in this manner. However, the predictions of the model were compared previously[2] to volumetric data for glassy polymer–diluent systems prepared by a solvent-casting procedure. Since there was reasonably good agreement between theory and experiment in this case, it would appear that experimental volumetric data may not be overly sensitive to the exact nature of the sample preparation history in some cases. Consequently, the equations developed previously will be used to attempt to predict published volumetric data[1] for the glassy polycarbonate–carbon dioxide system, even though the glassy polymer–penetrant samples were obtained by using a different sample preparation history than the one used in the theoretical development. The volumetric data reported for the polycarbonate–carbon dioxide system were measured on samples prepared in the following manner: the original polymer was taken to 35 °C and the carbon dioxide was added by increasing the pressure in 50 psi steps up to 900 psia.

From the results of the model proposed previously, it can be shown that the total volume of the glassy polymer–penetrant mixture can be calculated from the equation

$$\frac{V_m}{V_0} = \frac{\frac{\omega_1}{1-\omega_1}\hat{V}_1{}^0 + \hat{V}_{2g}{}^0(\omega_1)}{\hat{V}_{2g}{}^0(\omega_1=0)} \tag{3}$$

with

$$\hat{V}_{2g}{}^0(\omega_1) = \hat{V}_2{}^0(T_{gm})[1 + \alpha_{2g}(T - T_{gm})] \tag{4}$$

Here, $\hat{V}_{2g}{}^0(\omega_1)$ is the appropriate specific volume of the glassy polymer at penetrant mass fraction ω_1 and temperature T, T_{gm} is the glass transition temperature of the polymer–penetrant mixture, $\hat{V}_2{}^0(T_{gm})$ is the specific volume of the equilibrium liquid polymer at T_{gm}, and α_{2g} is the thermal expansion coefficient which is measured for the glassy state as the pure polymer is cooled below T_{g2}, its glass transition temperature. It is often convenient to introduce a linear approximation for the concentration dependence of T_{gm}

$$T_{gm} = T_{g2} - A\omega_1 \tag{5}$$

where the coefficient A depends on the nature of the penetrant used to depress the glass transition temperature for a particular polymer.

The parameters T_{g2} and α_{2g} are available for most common polymers, and the quantity A can be evaluated if data are available for the depression of the glass transition temperature. The quantity $\hat{V}_2{}^0(T_{gm})$ can be computed by effectively extrapolating volumetric data for the melt below T_{g2}. Clearly, then, the variation of V_m/V_0 with ω_1 at a particular temperature can be determined if an estimate for $\hat{V}_1{}^0$ is available. In the previous study,[2] values of $\hat{V}_1{}^0$ were taken to be the specific volumes of the pure diluents, since all of the diluents studied were liquids at the temperature of the experiment. For the glassy polycarbonate–carbon dioxide system, it is reasonable to assume that $\hat{V}_1{}^0$ for carbon dioxide is approximately constant (independent of pressure), but there is of course no value of $\hat{V}_1{}^0$ available for the liquid state at 35 °C.

For the calculations carried out here, the quantities T_{g2}, α_{2g}, and $\hat{V}_2{}^0(T_{gm})$ were taken from data presented by Zoller,[3] and the data of Chiou et al.[4] for the depression of the glass transition temperature of polycarbonate by carbon dioxide were used to determine A. Fleming and Koros[1] carried out volumetric calculations for the polycarbonate–carbon dioxide system using $\hat{V}_1{}^0 = 1.045$ cm^3/g. They noted that this value was consistent with volumetric data for carbon dioxide in low molecular weight liquids and in rubbery polymers. We believe a more direct method can be used to estimate $\hat{V}_1{}^0$ for carbon dioxide. This method, which involves only some data extrapolations, can be summarized as follows. At 35 °C, it follows from eq 5 and the data of Chiou et al.[4] that the polycarbonate–carbon dioxide system becomes an equilibrium liquid at $\omega_1 = 0.104$. Hence, the volumetric properties of the mixture can be estimated by using the equation

$$\hat{V} = \omega_1\hat{V}_1{}^0 + (1 - \omega_1)\hat{V}_2{}^0 \tag{6}$$

where $\hat{V}$ is the specific volume of the equilibrium liquid mixture. A value of $\hat{V}_2{}^0 = 0.8135$ cm^3/g for the equilibrium liquid polymer at 35 °C can be obtained by extrapolating data for the polycarbonate melt to 35 °C by using an equation presented by Zoller.[3] Finally, from a slight extrapolation of the specific volume data presented by Fleming and Koros,[1] it is reasonable to conclude that the value of $\hat{V}$ for the polymer–penetrant mixture at $\omega_1 = 0.104$ should be less than 0.8175 cm^3/g. Hence, from eq 6, it follows that a reasonable estimate for $\hat{V}_1{}^0$ is 0.85 cm^3/g.

Results and Discussion

Predictions of the proposed theory are compared with the experimental data of Fleming and Koros[1] in Figure 1. Curve A in this figure is a representation of the data of Fleming and Koros, curve B is the prediction based on eq 3 with $\hat{V}_1{}^0 = 0.85$ cm^3/g, and curve C is the prediction based on eq 2 with $\hat{V}_1{}^0 = 0.85$ cm^3/g. It is clear that eq 2 significantly overestimates the volume of the mixture, whereas eq 3 yields estimates for the volume expansion

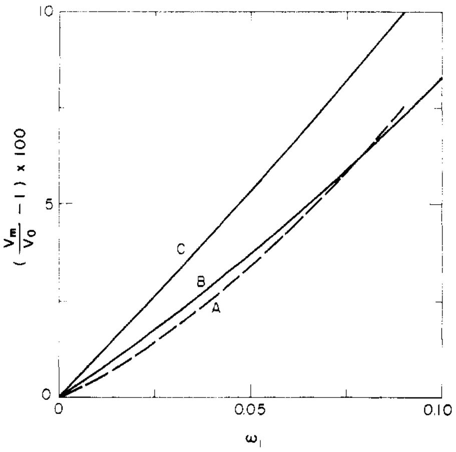

Figure 1. Volumetric behavior of glassy polycarbonate–carbon dioxide system at 35 °C: (A) experimental data of Fleming and Koros;[1] (B) prediction of eq 3 with $\hat{V}_1^0 = 0.85$ cm^3/g; (C) prediction of eq 2 with $\hat{V}_1^0 = 0.85$ cm^3/g.

which are in reasonably good agreement with the experimental data. This agreement is obtained even though the sample preparation histories for the theory and experiment are different and even though there may be some error introduced by the assumption that the volumetric behavior of the carbon dioxide is described by a constant specific volume, $\hat{V}_1^0$. We believe it is fair to conclude that the present approach provides a reasonable alternative to the dual-mode sorption model. However, no firm conclusions about the applicability of the two models can be made for the description of the volumetric behavior of the glassy polycarbonate–carbon dioxide system until a definitive value for $\hat{V}_1^0$ is available.

We conclude by commenting on the basic assumptions and possible limitations of the proposed theory for volumetric behavior in glassy polymer–penetrant systems. As noted above, the model of volumetric behavior is based on the premise that the molecular structure of the system is modified as a penetrant or antiplasticizer is added to the glassy polymer. The glassy polymer is in a nonequilibrium liquid configuration with extra hole free volume which is effectively frozen into the polymer. As a diluent is added to the polymer, there is a change in molecular structure in the sense that the system generally tends toward an equilibrium liquid configuration. The addition of diluent essentially leads to an eventual elimination of the extra hole free volume for the system. The premise that the structure of a glassy polymer changes as diluent is added is implied, for example, in a paper by Wyzgoski and Yeh.[5]

The determination of the exact nature of this volume relaxation involves the solution of a complex problem in volume viscoelasticity. In this and a previous paper,[2] the need to determine a solution to this complex problem is circumvented by assuming that the samples for the polymer–penetrant system are prepared in a simple manner. Although the predictions of the model are thus restricted, strictly speaking, to samples prepared in this manner, it is evident from the results presented here and in an earlier paper[2] that the above theory can also be used to provide reasonably good predictions for volumetric behavior for other sample preparation histories. It, of course, will not be possible to obtain useful predictions for all sample preparation histories by the above simple approach, but that does not necessarily mean that the premise that the addition of diluent leads to a modification in the molecular structure is incorrect. In such cases, a solution of a problem in volume viscoelasticity will have to be obtained to predict the volumetric behavior.

Finally, we note that the prediction of volumetric behavior for glassy polymer–penetrant systems is somewhat more difficult when the penetrant is a gas rather than a liquid at the temperature of interest, since a good estimate for $\hat{V}_1^0$ is generally not available for gaseous penetrants. Since both the present model and the model of Fleming and Koros[1] require a good estimate for $\hat{V}_1^0$, there is clearly no advantage of one model over the other in this regard.

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Electron Transport and Carrier Generation Characteristics of Poly[2-((3,5-dinitrobenzoyl)oxy)ethyl methacrylate]

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ABSTRACT: A methacrylate containing a 3,5-dinitrobenzoyl group (DNB), as an aromatic electron acceptor, was synthesized and polymerized. A radically initiated polymerization of this monomer, 2-((3,5-dinitrobenzoyl)oxy)ethyl methacrylate, gave a polymer with $\bar{M}_w$ of 2.1×10^4. Electron transport characteristics of the polymer were investigated by the time-of-flight technique, revealing that this polymer has photoconductivity. The electron drift mobility for the polymer was determined to be ca. 1.4×10^{-6} cm^2/(V s) at 10^5 V/cm. The apparent carrier injection efficiency of the polymer from a-Se and the carrier generation efficiency of a charge transfer complex of the polymer with poly(2-*N*-carbazolylethyl acrylate) were studied by the photodischarge technique.

Introduction

Electron-acceptor polymers are of interest from standpoints of an electronic property of polymers with an application to electronic devices. Although there are many reports on such electron-donor polymers as poly(*N*-vinylcarbazole), few studies about electronic properties of electron-acceptor polymers have been reported. For instance, the polymers containing 2,4,7-trinitro-9-fluorenone

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