Solubility and Partial Molar Volume of Carbon Dioxide and Ethane in Crosslinked Poly(ethylene oxide) Copolymer

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ABSTRACT: Experimental solubility and sorptive dilation data are reported for carbon dioxide and ethane in a crosslinked poly(ethylene oxide) (XLPEO) rubbery copolymer. Five different temperatures ($253 \leq T (K) \leq 308$) were considered, with a maximum gas pressure of 2.09 MPa (20.6 atm). The polymer was prepared by photopolymerization of a solution containing 70 wt % poly(ethylene glycol) methyl ether acrylate (PEGMEA) and 30 wt % poly(ethylene glycol) diacrylate (PEGDA). Sorption isotherms were described by the Flory-Huggins model. For each gas, the Flory-Huggins interaction parameter was a decreasing function of temperature and did not show a composition dependence. Dilation and sorption data were combined to calculate the partial molar volume (PMV) of the gases in the polymer, which was an increasing function of temperature. Based on a comparison with literature data for a XLPEO homopolymer prepared from pure PEGDA over the same range of operating conditions, an effect of the network composition on both gas solubility and PMV was found. © 2010 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 48: 456–468, 2010

KEYWORDS: dilation; PEO; rubber; rubbery polymer; sorption; swelling

INTRODUCTION

Cross-linked poly(ethylene oxide)s (XLPEOs) constitute a promising material for the development of improved membranes to remove carbon dioxide from light gases. These rubbery materials are synthesized from acrylate-functionalized, low-molecular-weight oligomers, which can be cross-linked, for example, by exposure to UV light. They work as solubility-selective membranes, with high permeability and selectivity for CO$_2$ due to specific interactions of this acid gas with ether groups in the chains. Although these interactions have been known for a long time, high-molecular-weight PEO is semicrystalline at ambient conditions, which is deleterious for gas permeability. The short nature of the runs of ethylene oxide in these XLPEO materials, combined with cross-linking, suppresses crystallinity.

Most of the studies concerning XLPEOs have focused on the measurement of pure gas permeation properties of dense films prepared from either pure oligomers or their binary mixtures, with the purpose of correlating such properties with the architecture of the polymer network and eventually optimizing membrane performance for a given separation. In particular, copolymers synthesized by photopolymerization of different composition ratios of poly(ethylene glycol) diacrylate (PEGDA) and poly(ethylene glycol) methyl ether acrylate (PEGMEA) exhibited excellent separation performance for CO$_2$/hydrocarbon mixtures in permeation experiments performed with both pure gases and gas mixtures. Considering that XLPEO-based membranes are solubility-selective, extensive characterization of gas solubility in these materials is of considerable importance. Compared with gas permeation, gas sorption by XLPEOs has been given less attention. Solubility data for CO$_2$ and a few other gases at 35 °C are available for some materials, whereas systematic studies at other temperatures were reported by Lin and Freeman and Kelman et al. However, all these data were obtained without considering the effect of polymer dilation, which can lead to errors in the reported solubility data, since experimental methods for measuring gas solubility in polymers are sensitive to the volume of the polymer sample. These data confirmed that to obtain more accurate gas solubility values in XLPEOs by the pressure-decay method, the changes in the volume of the polymer sample due to gas sorption and thermal expansion should be taken into account.

In this study, pure-gas solubility and sorptive dilation data are reported for carbon dioxide and ethane in a XLPEO copolymer obtained by photopolymerization of a PEGDA(30 wt %)–PEGMEA(70 wt %) solution. This particular copolymer exhibits high CO$_2$ permeabilities and good selectivity values. Ethane was chosen as the model light gas in view of the large interest in the use of membranes to purify natural gas.
Apart from being the second major component of natural gas (after methane), ethane forms a maximum pressure azeotrope with CO$_2$ that can complicate effective natural gas treatment. In addition, because of their similar condensabilities, carbon dioxide and ethane are particularly interesting from a fundamental point of view for an investigation of gas solubility in rubbery polymers. Five operating temperatures ($-20 \leq T(\degree C) \leq 35$) were considered, with a maximum operating pressure of 2.09 MPa (20.6 atm). Pure gas dilation and sorption data were combined and used to determine partial molar volumes (PMVs) and Flory-Huggins interaction parameters for each gas in the polymer. To determine whether the network composition of the XLPEO rubber had any effect on either gas solubility or PMV, the values for the copolymer were compared with those reported in the literature for a homopolymer prepared from pure PEGDA.

**EXPERIMENTAL**

**Materials and Polymer Preparation**

Cylinders of ethane (99% purity) and carbon dioxide (99.999% purity) were purchased from Airgas Southwest Inc. (Corpus Christi, TX). Poly(ethylene glycol) diacrylate (PEGDA; nominal MW = 700 g/mol), poly(ethylene glycol) methyl ether acrylate (PEGMEA, nominal MW = 460 g/mol), and 1-hydroxy-cyclohexyl phenyl ketone (HCPK; 99% purity), the photoinitiator, were obtained from Aldrich Chemical Co. (Milwaukee, WI). All gases and chemicals were used as received. The chemical structures of PEGDA and PEGMEA, as well as a representative schematic of the XLPEO copolymer formed by them, are shown in Figure 1.

Following the same procedure adopted in previous studies, the copolymer was prepared by adding 0.1 wt % HCPK to a PEGDA(30 wt %)--PEGMEA(70 wt %) solution, stirring for 2 h, placing the resulting solution between two quartz plates, and finally exposing it to 312 nm UV light for 90 s at 3 mW/cm$^2$ in a UV-cross-linker (Fisher Scientific, model FB-UVXL-1000). The solid film thus obtained was immersed in an ethanol bath for 3 days to remove any residual components or low-molecular-weight species (i.e., sol), and then it was dried at room temperature for at least 7 days. The liquid bath was replaced daily with fresh ethanol. The final film thickness, measured with a digital micrometer (Mitutoyo, Model ID-C112E) readable to $\pm 1/\mu$m, was about 300 $\mu$m. At 23 $\degree$C, the density of the XLPEO film was $(1.153 \pm 0.001)$ g/cm$^3$, a value determined based on the difference between the weight of a polymer sample in air and in n-heptane. According to Lin et al., the glass transition temperature of this material is 216 K.

**Dilation Measurements**

In the dilation experiments, a strip of the polymer was placed in a temperature-controlled chamber, degassed overnight, and then exposed to a given pressure of gas. With the aid of a COHU (model 491-2000) CCD camera (San Diego, CA), the length of the polymer sample was monitored as a function of time until equilibrium was reached, at which point a further aliquot of gas was admitted into the chamber to reestablish equilibrium at a higher pressure. Detailed descriptions of the experimental setup and procedure are given elsewhere.

Let $\Delta L_n$ be the length increase due to gas sorption associated with an equilibrium pressure $P_n$, $L_0$ be the length of

![Figure 1](image-url)
the polymer sample under vacuum at the operating temperature, and \( V_0 \) the volume of the degassed polymer at the same temperature. Assuming isotropic dilation, the change in the polymer volume at \( P_n (\Delta V_n) \) was calculated by the following:

\[
\frac{\Delta V_n}{V_0} = \frac{V_n - V_0}{V_0} = \left(1 + \frac{\Delta L_n}{L_0}\right)^3 - 1
\]  

(1)

**Sorption Measurements**

Gas solubility in the polymer was measured by the barometric pressure-decay method with the same apparatus utilized by Raharjo et al.\(^27\) It consists of two interconnected chambers of known volume immersed in a temperature-controlled bath. A known amount of polymer was placed inside the sample chamber and degassed at least overnight before beginning an experiment. A given amount of gas was introduced into the sample chamber, whose pressure then decreased as sorption occurred. Once equilibrium was achieved, which could take from 90 min to 2 days depending on the operating temperature and on the gas under study, more gas was introduced into the sample chamber to determine solubility as a function of pressure. Detailed descriptions of a general setup and procedure for this experiment can be found elsewhere.\(^{28,29}\)

Pressure in each chamber was measured by a Super TJE transducer from Honeywell Sensotec (Columbus, OH) with a full scale reading of 500 psia and an accuracy of 0.05\% of full scale. The cell volumes, 11.58 and 15.19 cm\(^3\), were determined according to the method proposed by Burnett.\(^30\) A refrigerated bath circulator (Neslab RTE 140), operating with an aqueous solution containing 50 wt \% methanol as cooling fluid, provided temperature control. The changes in the gas phase volume of the polymer-containing cell due to sorptive and thermal dilation of the polymer sample were taken into account in the mass balances using data from dilation measurements. Blank runs without the polymer\(^19\) have proven that gas adsorption on the walls of the sorption cells makes a negligible contribution to the observed sorption over the pressure and temperature ranges considered.

The pressure-decay method relies on an equation of state to transform the pressure reduction observations into a sorption isotherm via mass balances.\(^{28,29}\) In this work, the virial equation of state truncated to three terms\(^31\) was adopted. The virial coefficients, listed in our previous work,\(^22\) were chosen from the literature\(^32\) based on a comparison of density predictions with experimental data for the temperature and pressure ranges of interest. In the case of carbon dioxide, 130 density data points\(^{33,34}\) were considered, and the mean prediction error was 0.012\%, whereas, for ethane, 112 data points\(^{34,35}\) were included in the comparison, and the mean prediction error was 0.045 \%.

**RESULTS AND DISCUSSION**

**Polymer Dilation**

Whenever different operating temperatures are considered, the first step in the study of sorptive dilation is the determination of the thermal expansion coefficient of the polymer, \( \beta \), defined as follows:\(^{36}\)

\[
\beta = \frac{1}{V} \frac{\partial V}{\partial T}_p
\]

(2)

where \( V \) is the volume of the polymer, \( T \) is the operating temperature, and \( P \) is pressure.

Assuming \( \beta \) to be temperature-independent, eq 2 can be integrated as follows:

\[
V(T) = V_{ref} \exp[\beta(T - T_{ref})]
\]

(3)

where \( V_{ref} \) is the known volume of the polymer at a given reference temperature \( T_{ref} \). In terms of volume change, \( \Delta V = V(T) - V_{ref} \), eq 3 can be rearranged as follows:

\[
\ln \left(1 + \frac{\Delta V}{V_{ref}}\right) = \beta(T - T_{ref})
\]

(4)

Using the dilation apparatus, changes in the length of the polymer sample as a function of temperature were measured under vacuum, and, with the aid of eq 1, the corresponding changes in volume were computed. The results, expressed in accordance with eq 4 for \( T_{ref} = 23 \, ^\circ C \), are plotted in Figure 2. The line shown in this figure represents the least-square fit of the data, from which \( \beta = (6.107 \pm 0.043) \times 10^{-4} \, K^{-1} \). This value is quite similar to the range reported by Van Krevelen\(^37\) for poly(ethylene oxide): \( \beta = (6.2 - 6.6) \times 10^{-4} \, K^{-1} \). The \( \beta \) found in this work for the XLPEO copolymer is somewhat smaller than the one obtained by Ribeiro and Freeman\(^22\) for a XLPEO prepared from pure PEGDA, that is, \((6.53 \pm 0.14) \times 10^{-4} \, K^{-1}\), which suggests that the inclusion of PEGMEA in the prepolymerization solution decreases the thermal expansion coefficient of XLPEO.

Once the thermal expansion coefficient was determined, the relative increase in the volume of the polymer sample due to gas sorption was measured at five different temperatures. The results are presented in Figure 3 as a function of gas
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FIGURE 3 Sorptive dilation of the XLPEO copolymer as a function of gas fugacity for carbon dioxide (a) and ethane (b) at different operating temperatures. The lines are drawn to guide the eye.

fugacity, whose value was computed with the virial equation of state, as described elsewhere. For each temperature, the penetrant-free volume, \( V_0 \), was obtained utilizing eq 3.

For both gases, the volume of the polymer always increases with increasing gas fugacity, an effect which becomes more pronounced as temperature decreases. As shown in "Gas Sorption", both trends are a direct consequence of changes in the amount of gas sorbed by the polymer at a given operating condition. In the case of CO\(_2\), because of its high affinity for the polymer, the dilation isotherms in Figure 3(a) are always convex to the fugacity axis, and the volume increase can be rather significant, especially at lower temperatures, for which dilation values as high as 25% can be observed. Ethane, on the other hand, has a much less pronounced effect. Within the investigated range of operating parameters, the dilation isotherms in Figure 3(b) are almost linear, with only a slight curvature, and the change in the volume of the polymer does not surpass 5%.

Gas Sorption

Sorption isotherms for pure carbon dioxide and ethane in the XLPEO copolymer at the different operating temperatures considered in this work are presented in Figure 4. The results are expressed as the concentration \( C \) of gas sorbed in the polymer per unit volume of the corresponding penetrant-free polymer at the operating temperature (given by eq 3).

Gas solubility in many polymers scales with some convenient measure of solute condensability, such as the critical temperature, \( T_c \). Considering that the \( T_c \) values of carbon dioxide (304.2 K) and ethane (305.3 K) are very close, small differences between the solubility of these gases in polymers can be expected. Nonetheless, a comparison between Figures 4(a) and 4(b) shows that, at a given fugacity, carbon dioxide concentrations in the polymer are always higher than those of ethane, confirming the preferential sorption of carbon dioxide in the XLPEO copolymer due to the specific interactions of this gas with the ether groups in the polymeric chain.

FIGURE 4 Sorption isotherms for carbon dioxide (a) and ethane (b) in the XLPEO copolymer as a function of gas fugacity at five different temperatures. The lines are the prediction of the Flory-Huggins model with the parameters fitted in this work.
At all temperatures, ethane isotherms only exhibit a slight curvature. However, in the case of carbon dioxide, the sorption isotherms become highly nonlinear at lower temperatures, with the typical shape associated with the sorption of highly soluble penetrants into rubbery polymers. A comparison between Figures 3 and 4 shows that, as expected, higher volume changes are associated with the dissolution of larger amounts of gas in the polymer. For this reason, the dilation and sorption isotherms bear a strong qualitative resemblance to each other.

The equilibrium concentration at a given fugacity increases with decreasing temperature for both gases, an effect which is particularly pronounced for CO$_2$. Gas solubility in polymers increases with decreasing temperature because, for the same fugacity, the gas is more condensable at lower temperatures, or, in other words, its activity is higher. In Figure 5, the same sorption data for C$_2$H$_6$ [cf. Fig. 5(a)] and CO$_2$ [cf. Fig. 5(b)] in the XLPEO copolymer are now plotted as a function of gas activity, which is defined as the ratio of fugacity to the saturation fugacity at the same temperature ($\alpha = f/f^{\text{sat}}$). The gas saturation pressure at a given temperature, required for the calculation of $f^{\text{sat}}$, was estimated using the expressions given by Liley et al. For both gases, these expressions were extrapolated above $T_c$ to obtain a pseudo-$f^{\text{sat}}$ value at 35 °C.

As seen in Figure 5, in the case of ethane (cf. Fig. 5(a)), the differences in activity are accounted for, the sorption data for different temperatures fall on a single master curve. Similar behavior was previously reported in the literature for $n$-butane in PDMS over an even wider range of operating temperatures (−20 to 50 °C). With regard to carbon dioxide (cf. Fig. 5(b)) although the isotherms for different temperatures come very close together, there is a slight increase in the concentration of gas dissolved in the polymer at a given activity as the temperature decreases, at least for $T \leq 0$ °C. This could be a result of an increase in the polymer-penetrant interaction for CO$_2$ at lower temperatures.

To model the sorption isotherms, the traditional Flory-Huggins equation was adopted:

$$\ln \frac{f}{f^{\text{sat}}} = \ln \phi + (1 - \phi) + \chi(1 - \phi)^2$$  \hspace{1cm} (5)

where $\chi$ is the Flory-Huggins interaction parameter, which has to be fitted for each polymer-penetrant system, and $\phi$ is the volume fraction of the penetrant in the polymer. The values of $C$ and $\phi$ can be related to each other with the aid of the partial molar volume of the gas in the polymer ($\bar{V}$) as follows:

$$\phi = \frac{C\bar{V}}{22,414 + CV}$$  \hspace{1cm} (6)

Partial molar volumes for each gas in the copolymer as a function of temperature were obtained in this work by combining results from gas sorption and dilation measurements, as detailed in “Partial Molar Volumes.” For each isotherm, the parameter $\chi$ was fitted by the maximum likelihood method with an objective function in terms of $C$ utilizing the software ESTIMA. The computed values for $\chi$ are listed in Table 1.

The inverse dependence of $\chi$ on temperature anticipated by the Flory-Huggins theory is observed for both gases. The individual values for carbon dioxide are always smaller than those of ethane at a given temperature, indicating the higher

### Table 1

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$\chi_{\text{CO}_2}$</th>
<th>$\chi_{\text{C}_2\text{H}_6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>35.0</td>
<td>0.8915 ± 0.0077</td>
<td>1.9604 ± 0.0046</td>
</tr>
<tr>
<td>25.0</td>
<td>0.9169 ± 0.0083</td>
<td>2.0699 ± 0.0022</td>
</tr>
<tr>
<td>0.0</td>
<td>0.9751 ± 0.0080</td>
<td>2.3056 ± 0.0057</td>
</tr>
<tr>
<td>−10.0</td>
<td>1.0499 ± 0.0073</td>
<td>2.4177 ± 0.0047</td>
</tr>
<tr>
<td>−20.0</td>
<td>1.069 ± 0.015</td>
<td>2.467 ± 0.011</td>
</tr>
</tbody>
</table>
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FIGURE 6 Solubility of carbon dioxide as a function of fugacity at different temperatures in XLPEOs prepared from pure PEGDA (PEGDA100, Ribeiro and Freeman\textsuperscript{22}) and a PEGDA(30 wt %)–PEGMEA(70 wt %) solution (PEGMEA70, this work): (a) 25, 0, and –20 °C; (b) 35 and –10 °C. All data were obtained taking the effect of polymer dilation into account.

solubility of the former in the polymer. The fitted isotherms, shown as continuous lines in Figure 4, are in good agreement with the experimental data, without the need of including a dependence of \( \chi \) on penetrant volume fraction. This differs from the findings of Kelman et al.,\textsuperscript{18} who worked with the same gases and polymer considered here and reported that an empirical dependence of \( \chi \) on both temperature and penetrant volume fraction was necessary to properly fit the sorption isotherms. The causes for this difference are believed to be twofold. First, since no information on the sorptive or thermal dilation of the XLPEO copolymer was previously available, both effects were not taken into account by Kelman et al.\textsuperscript{18} in the measurement of the sorption isotherms. Second, the partial molar volume of the gases was assumed to be independent of temperature, and an average of literature values reported for different rubbery polymers at 25 °C was utilized. As demonstrated later in “Partial Molar Volumes,” the partial molar volume is a function of temperature for the system under consideration in this contribution. Moreover, Ribeiro and Freeman\textsuperscript{22} have recently shown that the partial molar volume of a given gas dissolved in a rubbery polymer does depend on the chemical structure of the polymer, and therefore, the use of averages among different liquids and/or different polymers should be avoided whenever possible.

In a previous study over the same temperature range considered here, Lin et al.\textsuperscript{16} found very similar CO\textsubscript{2} and CH\textsubscript{4} solubility in polymers prepared from pure PEGDA and two PEGDA-PEGMEA solutions (9 and 30 wt % PEGMEA). On the other hand, working with polymers prepared from different solutions of PEGDA and short-chain acrylate monomers, Kusuma et al.\textsuperscript{17} observed an increase in the solubility of these gases in the polymer at 35 °C with decreasing PEGDA content for short-chain branches terminated with –OCH\textsubscript{3} and –OC\textsubscript{2}H\textsubscript{5} groups. In both studies, however, gas solubility was measured by the pressure-decay method without taking polymer dilation into account, and only infinite dilution solubility values were compared. Thus, to address the matter of gas solubility in XLPEO rubbers as a function of network composition, we decided to compare our isotherms with those previously obtained for the homopolymer prepared from pure PEGDA.\textsuperscript{22} To the best of our knowledge, these represent the only data sets currently available in the literature for gas sorption in XLPEOs which take the polymer dilation effect into account.

The sorption isotherms for CO\textsubscript{2} and C\textsubscript{2}H\textsubscript{6} in these two XLPEO rubbers are compared in Figures 6 and 7, respectively, in terms of the gas solubility, \( S \), defined as follows:

\[
S = \frac{C}{f}
\]  

(7)

It is evident from Figures 6 and 7 that the inclusion of PEGMEA in the prepolymerization solution leads to an increase in the solubility of both gases in the final XLPEO rubber, regardless of the operating temperature. Dynamic mechanical data\textsuperscript{16} indicate that the addition of PEGMEA into the prepolymer solution decreases crosslink density, which would favor higher sorption. In rubbery polymers, penetrant sorption involves the creation of molecular-scale gaps to accommodate the penetrant molecules into the polymeric matrix, which is normally an endothermic process due to the work required to separate polymer chains.\textsuperscript{43,44} Positron annihilation lifetime spectroscopy (PALS) results\textsuperscript{16} demonstrate that the average size of the free volume elements in XLPEO rubbers increases systematically as the PEGMEA content in the prepolymerization solution increases. In the specific case of the two polymers considered here, PALS results indicate that the addition of 70 wt % PEGMEA in the copolymer increases the mean size of free volume elements from 133 to 145 Å\textsuperscript{3}. Larger free volume elements imply a higher probability of finding a cavity large enough to accommodate a given penetrant molecule in the matrix and can thus lead to a higher (less negative) entropic contribution to the Gibbs energy of sorption.\textsuperscript{45} The
resulting reduction in the Gibbs energy of sorption could be the reason behind the higher gas solubility observed for the PEGDA-PEGMEA copolymer in Figures 6 and 7.

If this reasoning in terms of larger free volume elements is correct, it follows that the increase in solubility should be more pronounced for the larger molecule. This aspect of the reasoning can be tested by comparing the pure-gas solubility selectivity ($x_s$) of the two polymers, whose value is defined as follows:

$$x_s = \frac{S_{CO_2}}{S_{C_2H_6}}$$

(8)

Considering that gas solubility is a function of fugacity for the systems under consideration, the direct use of experimental values of $S$ in eq 8 is difficult. To overcome this problem, we adopted the Flory-Huggins model to calculate the solubility of each gas in the polymer at a given fugacity, and these values were then substituted into eq 8 to give the corresponding solubility selectivity. The final results are shown in Figure 8. Flory-Huggins interaction parameters were taken from Table 1 and from the work of Ribeiro and Freeman,22 for the PEGDA-PEGMEA and PEGDA polymers, respectively. At a given operating condition, it is seen in Figure 8 that the homopolymer prepared from pure PEGDA always gives a higher selectivity for carbon dioxide over ethane. From eq 8, this indicates that the addition of PEGMEA indeed led to a higher increase in the solubility of ethane, the larger molecule ($d_{LJ} = 3.941$ and 4.443 Å for CO$_2$ and C$_2$H$_6$, respectively).
This fact provides additional evidence in favor of the reasoning that the larger free volume elements are responsible for the higher gas solubility in the PEGDA-PEGMEA copolymer.

One last aspect that can be analyzed concerning the sorption data is the effect of temperature on gas solubility. Traditionally, using the solubility at the limit of infinite dilution, \( S_\infty \), an enthalpy of sorption \( \Delta H_S \) is defined as follows:\textsuperscript{38}

\[
S_\infty = S_0 \exp\left(-\frac{\Delta H_S}{RT}\right) \tag{9}
\]

where \( S_0 \) is a pre-exponential factor, and \( R \) is the universal gas constant.

In the limit of infinite dilution, when the concentration of sorbed gas is very low, the Flory-Huggins model reduces to Henry’s law, \( C = S_\infty f_c \), where the value of \( S_\infty \) is given by the following:\textsuperscript{55}

\[
S_\infty = \frac{22.414}{f_{sat} V} \exp[-(1 + \chi)] \tag{10}
\]

Using eq 10 and the values of \( \chi \) and \( V \) obtained in this work, the infinite dilution solubility of carbon dioxide and ethane in the XLPEO copolymer was computed at the different operating temperatures considered. These results were then fitted to eq 9 to calculate the corresponding enthalpies of sorption. The values of \( \Delta H_S \) for both gases are compared in Table 2 with literature data\textsuperscript{22,46–51} related to other rubbery polymers. In all these polymers, the sorption of carbon dioxide and ethane is an exothermic process. In the case of ethane, all polymers exhibit a similar value for \( \Delta H_S \). For carbon dioxide, on the other hand, the XLPEO rubbers exhibit the lowest \( \Delta H_S \) values (i.e., most exothermic). One could interpret this outcome as evidence for the strong interaction between \( \text{CO}_2 \) and these polymers. However, as highlighted in Table 2, most \( \Delta H_S \) values are associated with different temperature ranges, and to draw a comparison in a more appropriate basis, these temperature differences ought to be accounted for. This can be done by referring to the usual analysis of gas dissolution into a polymer as a two-step thermodynamic process as follows:\textsuperscript{38}

(i) condensation of the gas to a liquid-like state (or, in the case of supercritical gases, to a condensed density consistent with that of the polymer), and (ii) mixing of condensed gas with polymer segments. The enthalpy of sorption can now be decomposed into two terms, the enthalpy of condensation \( \Delta H_{\text{cond}} \), a temperature-dependent property of the gas, and the enthalpy of mixing \( \Delta H_{\text{mix}} \), which is a function of the polymer-gas pair as follows:

\[
\Delta H_S = \Delta H_{\text{cond}} + \Delta H_{\text{mix}} \tag{11}
\]

Based on the concept of the mean value of a function over a given interval of its domain, an average enthalpy of condensation for a temperature range \( T_1 \leq T \leq T_c \) can be defined as follows:

\[
\Delta H_{\text{cond}} = \frac{1}{T_2 - T_1} \int_{T_1}^{T_2} \Delta H_{\text{cond}}(T) \, dT \tag{12}
\]

Using the function \( \Delta H_{\text{cond}}(T) \) presented by Liley et al.,\textsuperscript{36} eq 12 was applied to each gas and temperature range considered in Table 2, and the resulting \( \Delta H_{\text{cond}} \) was substituted into eq 11 to yield the corresponding \( \Delta H_{\text{mix}} \). All studies covered temperatures higher than the critical temperature of the gases, but since \( \Delta H_{\text{cond}} \) is not defined for \( T > T_c \), all calculations were made using \( T_2 = T_c \). The final results are listed in Table 2. In particular, for EP, since the lowest temperature investigated by Tsuibo et al.\textsuperscript{51} was already higher than \( T_c \), the value of \( \Delta H_{\text{cond}} \) could not be evaluated.

In all cases, the contribution of \( \Delta H_{\text{cond}} \) to the total value of \( \Delta H_S \) is very significant, varying from 52 to 88%. For \( \text{CO}_2 \), the absolute values of \( \Delta H_{\text{mix}} \) in the XLPEO rubbers are at least twice as high as the values associated with the other rubbery polymers in Table 2. This result is evidence for the strong interaction between this acid gas and the ether groups in the XLPEO chains. Compared with the value reported for

### Table 2: Enthalpies of Sorption, Condensation, and Mixing at Infinite Dilution for the Sorption of Carbon Dioxide and Ethane in Some Rubbery Polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( \Delta H_S ) (kJ/mol)</th>
<th>T Range (°C)</th>
<th>( \Delta H_{\text{cond}}^\text{mix} ) (kJ/mol)</th>
<th>( \Delta H_{\text{mix}} ) (kJ/mol)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS</td>
<td>-10.8</td>
<td>-30 to 55</td>
<td>-9.51</td>
<td>-1.29</td>
<td>Kamiya et al.\textsuperscript{50}</td>
</tr>
<tr>
<td>PE-co-VA</td>
<td>-7.95</td>
<td>10 to 40</td>
<td>-6.19</td>
<td>-1.76</td>
<td>Kamiya et al.\textsuperscript{49}</td>
</tr>
<tr>
<td>PE</td>
<td>-8.37</td>
<td>15 to 80</td>
<td>-5.56</td>
<td>-2.81</td>
<td>Kamiya et al.\textsuperscript{48}</td>
</tr>
<tr>
<td>LDPE</td>
<td>-7.28</td>
<td>25 to 55</td>
<td>-3.80</td>
<td>-3.48</td>
<td>Hirose et al.\textsuperscript{47}</td>
</tr>
<tr>
<td>PEGDA100</td>
<td>-16.32 ± 0.06</td>
<td>-20 to 35</td>
<td>-8.85</td>
<td>-7.47 ± 0.06</td>
<td>Ribeiro and Freeman\textsuperscript{22}</td>
</tr>
<tr>
<td>PEGMEA70</td>
<td>-15.71 ± 0.22</td>
<td>-20 to 35</td>
<td>-8.85</td>
<td>-6.86 ± 0.22</td>
<td>This work</td>
</tr>
<tr>
<td>EP</td>
<td>-11.0</td>
<td>56 to 62</td>
<td>-6.18</td>
<td>-3.45</td>
<td>Tsuboi et al.\textsuperscript{51}</td>
</tr>
<tr>
<td>PE</td>
<td>-9.63</td>
<td>5 to 55</td>
<td>-6.18</td>
<td>-3.45</td>
<td>Michaels and Bixler\textsuperscript{46}</td>
</tr>
<tr>
<td>PEGDA100</td>
<td>-10.9 ± 0.4</td>
<td>-20 to 35</td>
<td>-7.93</td>
<td>-3.0 ± 0.4</td>
<td>Ribeiro and Freeman\textsuperscript{22}</td>
</tr>
<tr>
<td>PEGMEA70</td>
<td>-12.2 ± 1.5</td>
<td>-20 to 35</td>
<td>-7.93</td>
<td>-4.3 ± 1.5</td>
<td>This work</td>
</tr>
</tbody>
</table>
The Ostwald solubility coefficient is related to $S_\infty$ by the following equation:

$$\Omega_\infty = \frac{T S_\infty P^o}{T^o}$$  \hspace{1cm} (14)

where $T^o$ and $P^o$ are the standard temperature (273.15 K) and standard pressure (1 atm), respectively.

The infinite dilution solubilities given by eq 10 were substituted into eq 14 to obtain the corresponding values of $\Omega_\infty$, which are plotted as a function of the operating temperature in Figure 9. Both gases show a positive slope in Figure 9, and therefore, in agreement with the findings of the traditional analysis previously discussed, the sorption process is exothermic. The values of $\Delta H_5$ calculated from eq 13 are listed in Table 3. According to van der Vegt,\textsuperscript{44} these values are different from those obtained from the temperature dependence of the solubility coefficient (Table 2) because the latter must be corrected with a term $RT$ to obtain $\Delta H_5$, a correction that is ignored in the traditional analysis. The negative enthalpies of sorption in Table 3 indicate that the work required to create a molecular-sized cavity in the polymeric solvent was more than compensated for by the binding interactions of the gas with the polymer. In agreement with the specific interactions of carbon dioxide with the ether groups in the polymeric chain, the enthalpy of sorption associated with this gas is smaller (i.e., more exothermic) than the one for ethane.

For comparison, the enthalpy of sorption of the two gases in the homopolymer prepared from pure PEGDA was also calculated from the Ostwald solubility coefficients using the values of $\gamma$ and $\tilde{V}$ reported by Ribeiro and Freeman.\textsuperscript{22} These results are presented in Table 3. The other polymers listed in Table 2 were not considered to avoid any effects of different ranges of operating temperatures. According to the data in Table 3, ethane sorption in the homopolymer (PEGDA100) is less exothermic than in the copolymer (PEGMEA70). This result is in agreement with the previous explanation given for the higher gas solubility in the copolymer. The larger free volume elements in the copolymer would imply a lower degree of rearrangement of the polymeric chains to accommodate a given penetrant molecule in the matrix, thereby leading to a less endothermic contribution to the sorption process. In the case of carbon dioxide, the enthalpies of sorption in the two materials are very close to each other, but the absolute value in the copolymer is slightly smaller. This may seem a contradiction at first, but it should be born in mind that $\Delta H_5$ is less endothermic than in the homopolymer (PEGDA100) and a PEGDA(30 wt %)-PEGMEA(70 wt %) solution (PEGMEA70).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>CO$_2$</th>
<th>C$_2$H$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEGMEA70</td>
<td>$-13.38 \pm 0.21$</td>
<td>$-10.54 \pm 0.57$</td>
</tr>
<tr>
<td>PEGDA100</td>
<td>$-13.99 \pm 0.09$</td>
<td>$-8.54 \pm 0.45$</td>
</tr>
</tbody>
</table>

The XLPEOs were prepared from pure PEGDA (PEGDA100) and a PEGDA(30 wt %)-PEGMEA(70 wt %) solution (PEGMEA70).
also depends on the binding interactions between the gas and the polymer, which, in the end, are precisely responsible for the solubility selectivity of these XLPEO rubbers toward CO\textsubscript{2}. Because of a pre-selection of appropriate molecular weights of the acrylate oligomers used in the preparation of these two XLPEO rubbers, their networks have approximately the same ethylene oxide content (\textasciitilde 82 wt%). In contrast to PEGDA, PEGMEA has only one acrylate group, and its use leads to a decrease in the cross-linking density and to the introduction of pendant –OCH\textsubscript{3} groups along the network backbone (cf. Fig. 1). The flexible pendant branches introduced by PEGMEA cause a reduction in the glass transition temperature of the polymer, and for sufficiently high PEGMEA contents, the cross-linking density becomes too low to fully suppress PEO crystallization at lower temperatures.\textsuperscript{16,26} This indicates that, because of their greater conformational mobility, these EO-containing pendant branches are able to interact with each other to a larger extent than the EO-chains involved in the cross-linking. Thus, it could be argued that the ether groups in the chains responsible for the cross-linking are more readily available to interact with CO\textsubscript{2}, which would lead to a more exothermic accommodation of this gas in the polymeric matrix. However, further investigation with other XLPEOs, taking the polymer dilution effect into account, is necessary to reach a final conclusion on this matter.

**Partial Molar Volumes**

Upon combining sorption and dilation data for a given polymer-penetrant pair, one can estimate the partial molar volume (PMV) of the gas in the polymer, \(\bar{V}\). When polymer compression effects can be neglected, which is reasonable for XLPEO materials and the gases considered in this work under the adopted operating conditions,\textsuperscript{22} \(\bar{V}\) is computed as follows:\textsuperscript{49}

\[
\bar{V} = 22.414 \frac{d}{dc} \left( 1 + \frac{\Delta V}{V_0} \right)
\]

(15)

Since the 1980s, when data for PMVs of gases dissolved in polymers started to appear in the literature, the standard procedure has been to compare the value in the polymer with averages among different organic solvents and/or other polymers to check whether these are similar. However, Ribeiro and Freeman\textsuperscript{22} recently demonstrated that, for rubbers, the PMV of a given gas depends on the chemical structure of the polymer, a behavior which is also observed in the case of gases dissolved in liquids. To take this dependence into account, the PMV of a dissolved gas in different materials, either liquids or polymers, at a given temperature, ought to be compared as a function of the solubility parameter (\(\delta\)) of the solvents. Therefore, in Figure 10, our values for the PMV of carbon dioxide and ethane in the XLPEO copolymer at 25 °C, computed from eq 15, are compared with literature data for different liquids\textsuperscript{53–65} and rubbery polymers,\textsuperscript{47–50,66–72} all of which plotted as a function of the solubility parameter of the solvent. Solubility parameters were taken from the literature,\textsuperscript{37,73,74} apart from the value related to the XLPEO copolymer, which was estimated by the relation between the solubility parameters and the Flory-Huggins interaction parameter for a given polymer-penetrant pair:\textsuperscript{75}

\[
\chi T = \frac{\bar{V}}{R} (\delta_p - \delta_g)^2
\]

(16)

where \(\delta_p\) and \(\delta_g\) are the solubility parameters of the polymer and the gas, respectively. Despite its ability to represent the experimental sorption isotherms for both gases in the XLPEO copolymer, the Flory-Huggins model includes the assumption that penetrant molecules and segments of the polymer chain (each segment being of the same size as the penetrant, with the chain comprising \(N\) connected segments) can be moved in space without any changes in the interactions of neighboring particles,\textsuperscript{40} which is not strictly true, specially in the case of
carbon dioxide, for which a strong, specific gas-polymer interaction is known to take place. Taking that into account, the use of the data related to ethane ($\delta_p = 10.4 \pm 0.2$ MPa$^{1/2}$ at 25 °C$^{19}$) was regarded as more suitable to estimate $\delta_p$ for the XLPEO copolymer, which leads to $\delta_p = (19.6 \pm 0.5)$ MPa$^{1/2}$ at 25 °C. This value is in very good agreement with the experimental values of (19.9 ± 2.2) MPa$^{1/2}$ and (20.2 ± 2) MPa$^{1/2}$ reported by Grulke$^{73}$ for poly(ethylene oxide).

From Figure 10, the PMVs of both gases are a decreasing function of the solubility parameter of the solvent. Therefore, unless the solvents under consideration have similar solubility parameters, averaging the PMV of a gas dissolved in these solvents is actually a crude approximation. The PMVs determined in this work for ethane and carbon dioxide in the XLPEO copolymer compare favorably with the literature values for other solvents with $\delta = 20$ MPa$^{1/2}$. It is interesting to note that, overall, all but one data point related to polymers (ethane in poly-1,2-butadiene$^{48}$) lie very close to the corresponding data for liquids with a given solubility parameter, which supports, in a more formal way, the general idea of a similar thermodynamic state of the dissolved gas in liquids and in rubbery polymers.

The influence of temperature on the PMV of the gases dissolved in the XLPEO copolymer is shown in Figure 11. All PMVs were calculated utilizing eq 15 and the data in Figures 3 and 4. Both ethane and carbon dioxide show a decrease in the PMV as the operating temperature is reduced. In analogy with the framework adopted for gases dissolved in liquids, the effect of temperature on $\bar{V}$ was represented in terms of a thermal expansion coefficient for the gas dissolved in the polymer, $\beta_i^p$, whose definition is exactly the same as that used for pure species (eq 2), just replacing $V$ by $\bar{V}$:

$$\bar{V}_i(T) = \bar{V}_{i, \text{ref}} \exp[\beta_i^p (T - T_{\text{ref}})]$$

(17)

Equation 17 was fitted to our data, using $T_{\text{ref}} = 25$ °C and the experimental value of $\bar{V}_i$ as $\bar{V}_{i, \text{ref}}$. The resulting values of $\beta_i^p$ are given in Table 4, and the corresponding predictions are shown as continuous lines in Figure 11. In view of the slight scatter in the data set, eq 17 provides a good representation of $\bar{V}$ and its dependence upon temperature in this system. All Flory-Huggins interaction parameters fitted in this work (Table 1), and consequently the calculated isotherm in Figure 4, are associated with the PMVs predicted by eq 17.

In a recent work, Ribeiro and Freeman$^{22}$ reported PMVs for carbon dioxide and ethane in a XLPEO rubber prepared from pure PEGDA for the same temperature range covered in this study. For comparison, their data are also plotted in Figure 11. At 35 °C, the $\bar{V}$ value is the same in both XLPEO matrices, but as temperature is reduced, differences become evident, with both gases exhibiting higher values in the homopolymer prepared from pure PEGDA.

As previously mentioned, it was only very recently that a correlation between the chemical structure of rubbery polymers and the partial molar volume of dissolved gases was recognized,$^{22}$ and at this point, we cannot provide a definitive explanation for the lower $\bar{V}$ values associated with the XLPEO copolymer. In the discussion of the $\Delta H_S$ results, it was pointed out that the addition of PEGMEA reduced the cross-linking density in the network, with the inclusion of flexible pendant branches, and that for sufficiently high PEGMEA contents, the cross-linking density became too low to fully suppress PEO crystallization at lower temperatures. Thus, because of their greater conformational mobility, these EO-containing pendant branches are able to interact with each other to a larger extent than the EO-chains involved in the cross-linking. This last aspect, in particular, can be interpreted as an indication of a higher cohesive energy for the PEGDA-PEGMEA network, favored by the greater conformational mobility of the flexible pendant branches. A decrease in $\bar{V}$ of dissolved gases with increasing cohesive energy of the matrix is precisely the trend verified in Figure 10. Such reasoning is in agreement with an increasing difference between the two materials as temperature decreases, since the attractive interactions between molecules becomes stronger with decreasing temperature.

With the aid of eq 16, the consistency of this explanation with the data set for ethane can be checked, since the values of $\chi$ and $\bar{V}$ at each temperature can be combined to give the corresponding ($\delta_p - \delta_e$) for the two XLPEO rubbers. The results of these calculations are listed in Table 5. In agreement with the supposed explanation, the solubility parameter estimated for the homopolymer prepared from pure PEGDA is lower than the one for the copolymer at $T \leq 25$ °C. In addition, at 35 °C,
temperature at which the $\bar{V}$ values for ethane in both polymers agree within the experimental error; the data in Table 5 show the same solubility parameter for both XLPEO rubbers within the estimated uncertainty. Nonetheless, the differences in the cross-linking density could also play some role, or even be the main factor responsible for the differences between $\bar{V}$ values in the XLPEO rubbers, and more experimental data related to other polymers are necessary before a final conclusion can be reached.

### CONCLUSIONS

Sorption, dilation, and partial molar volumes of carbon dioxide and ethane in a crosslinked poly(ethylene oxide) (XLPEO) copolymer were experimentally determined at five different temperatures (253 $\leq T$(K) $\leq 308$) and with a maximum gas pressure of about 20 atm.

The Flory-Huggins equation is able to represent the sorption isotherms over the entire range of operating conditions investigated. The Flory-Huggins interaction parameters for each gas are a function of temperature, as theoretically expected, but do not depend on the amount of gas dissolved in the polymer. The polymer has a strong affinity for carbon dioxide, which leads to an unusually high enthalpy of mixing compared with other rubbery polymers. At a given operating condition, the solubility of both gases in the XLPEO copolymer is higher than the one reported in the literature for a XLPEO homopolymer, indicating an effect of the network composition of the XLPEO rubber on gas solubility, which can be explained in terms of differences in the average size of free volume elements.

The partial molar volume (PMV) of both gases in the copolymer decreases with decreasing temperature, and the values for each gas are similar to those reported in the literature for liquids and rubbery polymers with a solubility parameter close to the one associated with the XLPEO copolymer. Similar to what occurs for solubility, the PMV of the dissolved gas also depends on the composition of the XLPEO rubber, being higher in the XLPEO homopolymer.

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### REFERENCES AND NOTES


### TABLE 5  Effect of Temperature on the Difference between the Solubility Parameters of the XLPEO Rubber ($\delta_p$) and Ethane ($\delta_g$), as Predicted by eq 16

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>PEGDA100</th>
<th>PEGMEA70</th>
<th>$\left(\delta_p - \delta_g\right)$(MPa$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35.0</td>
<td>8.61 ± 0.03</td>
<td>8.64 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>25.0</td>
<td>9.01 ± 0.03</td>
<td>9.22 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>9.92 ± 0.04</td>
<td>10.65 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>−10.0</td>
<td>10.32 ± 0.04</td>
<td>11.30 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>−20.0</td>
<td>10.59 ± 0.07</td>
<td>11.81 ± 0.06</td>
<td></td>
</tr>
</tbody>
</table>

The XLPEOs were prepared from pure PEGDA (PEGDA100$^{23}$) and a PEGDA30 wt %–PEGMEA70 wt % solution (PEGMEA70). Uncertainties were estimated by propagation of errors.