Effect of Various Preexposure Agents on Methane Sorption and Dilation in Tetramethyl Polycarbonate

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ABSTRACT: The effects caused by preexposure of tetramethyl polycarbonate (TMPC) to CO_2, C_2H_4, and C_3H_8 on subsequent apparent equilibrium CH_4 sorption and dilation are explored. Three exposure histories are studied: (i) no preexposure (unconditioned), (ii) preexposure to CO_2, C_2H_4, and C_3H_8, respectively, followed by depressurization to vacuum (conventionally conditioned), and (iii) preexposure to high swelling levels, with the same three agents, followed by exposure to CH_4 without depressurization (exchange conditioned). The unconditioned samples exhibit the lowest CH_4 sorption and dilation levels while the exchange-conditioned samples exhibit the highest CH_4 sorption and dilation levels. The increases above the unconditioned levels for the exchange-conditioned samples depend only on the swelling level achieved during the conditioning step and are independent of the conditioning agent. On the other hand, the increases seen for the conventionally conditioned samples show a slight dependence on the conditioning agent possibly due to the occurrence of an effective "templating" of the free volume distribution during the conditioning procedure.

Introduction

Unlike rubbery polymers, the sorption, dilation, and transport properties of glassy polymers depend upon the previous history of the particular polymer sample. Thermal treatments such as annealing normally tend to lower the gas sorption and permeation through a glassy sample,[1] while preexposure to a highly sorbing gas tends to raise the gas sorption and permeation through a sample.[2-4] Most of these preexposure experiments have been performed using CO_2 as the swelling agent. It was the purpose of this study to compare the conditioning ability of CO_2 with that of other highly sorbing gases at similar levels of dilation.

Tetramethyl polycarbonate (TMPC) was chosen as the glassy polymer for this study since high sorption levels can be attained in this material in the presence of several gases under convenient conditions. Propane and ethane were chosen as the conditioning agents to compare with CO_2. Both of these gases have high sorption levels in TMPC and were expected to provide a high swelling of the sample. Methane was used as the secondary penetrant to probe the effect of the conditioning agent since its sorption level is high enough to be accurately measured under convenient pressure conditions without running the risk of inducing conditioning effects in the glass itself.

The selection of these gases also played a practical role since each is found in natural gas streams where knowledge of the extent and persistence of conditioning of a typical glassy polymer like TMPC is critical for the use of membrane-based separations. By understanding fundamentally how the various gases interact with glassy polymer matrices, selection of structures which can either take advantage of, or be immune to, the conditioning effect may be feasible. For example, by analogy to doping a material to achieve semipermanently altered electrical properties, it might be possible to tailor the long-lasting effects of conditioning with a properly chosen swelling agent to provide increased production without a loss in product quality. In contrast, a membrane immune to the conditioning effect might be desired in order to prevent changes in a separation during the accidental introduction of a highly condensible penetrant. Thus, while the focus of the present study is fundamental, practical implications of the results are clear in the emerging field of membrane-based gas separation.

Background

In an earlier study, three sample exposure histories were described by the following definitions:[5]

(1) The term "unconditioned" refers to samples with no prior gas exposure history other than normal atmospheric storage.

(2) The term "conventionally conditioned" refers to the case in which a highly sorbing penetrant is equilibrated at a predetermined pressure with the sample and then evacuated completely before exposure to the secondary penetrant.

(3) Finally, the term "exchange conditioned" refers to a sample which has been exposed to a highly sorbing penetrant at a predetermined pressure; however, instead of evacuating the sample, the secondary penetrant is swept through the sample chamber to completely replace the conditioning agent at a constant pressure. Purging is continued until all of the conditioning agent has been removed from the polymer sample as well as the surrounding gas space.

Each of these exposure histories provides a unique sorption and dilation isotherm due to the ability of glassy polymers to "remember" perturbations in the segmental packing configurations induced by such penetrant exposure protocols.

In order to understand the isotherm differences, it is useful to visualize the sorption process on a molecular scale. The molecule sorbing into the unconditioned sample encounters a relatively well-packed matrix, and, on the average, a relatively large amount of energy is needed to dilate the matrix to generate a "sorbed cage" to accommodate the penetrant. The molecule sorbing into a conventionally conditioned sample ideally faces a matrix which has been disturbed somewhat due to a previous swelling step. Depending upon the magnitude of the previous swelling exposure and the time of aging since the exposure, the segmental packing is thought to be disrupted to varying degrees, thereby providing easier sorption for the penetrant. Finally, the molecule sorbing into an exchange-conditioned matrix faces a completely different

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environment, since the matrix is still swollen with the conditioning agent. As the exchange of gases occurs, the penetrant is able to sorb into the sites vacated by the desorbing conditioning agent, allowing the penetrant to reach a relatively high sorption level. Since the conditioning agent has been chosen to be able to dilate the glass more than the probe agent, based on intrinsic properties, the probe finds an environment totally unlike that which would exist naturally in its interaction with the glass. In each case, therefore, the polymer matrix has been disrupted to a different degree, thereby changing the energetics of sorption. While equilibrium constraints may dictate a tendency to relax toward a unique sorption level at a given external penetrant activity, the rates of any such relaxations are negligible under the conditions considered here.

To compare the conditioning ability or ability to disrupt the polymer matrix of the three conditioning agents, CO_2, C_2H_4, and C_3H_8, it was necessary to establish a common conditioning level. The conditioning level was selected to be at a pressure which caused a 7.8% volume dilation of the sample. This dilation was chosen to correspond with the value obtained for 900 psia of CO_2 in polycarbonate, since earlier studies have considered this system, and comparisons between polymers is best done under controlled dilation conditions.

Experimental Section

Materials. The polymer used in this study was tetramethyl polycarbonate (TMPC) provided by Dow Chemical Co. The polymer was cast on a glass plate from a 5 wt % solution in methylene chloride at room temperature. The casting was performed in a glovebag to prevent rapid evaporation of the solvent. After approximately 3–4 h, the film was removed and placed in a vacuum oven. The film was dried over 3 days by gradually increasing the temperature to approximately 10 °C above the glass transition temperature. After 4 h, the oven was turned off, and the film was allowed to cool to room temperature over a period of approximately 5 h. The resulting films had thicknesses of approximately 5 mil with a T_g of 203 °C as measured by DSC and a density of 1.08 g/cm^3 as measured by an aqueous density gradient column.

The CO_2, C_2H_4, C_3H_8, and CH_4 were supplied by Linde, Inc., at purities of at least 99.998%, 99.5%, 99.0%, and 99.97%, respectively. The gases were used as received.

Equipment and Procedures. Sorption measurements for the unconditioned and conventionally conditioned samples were made by a mass balance technique using a pressure decay cell. This type of measurement has been described in detail elsewhere.[6] Sorption measurements for the exchange-conditioned sample required using a gravimetric technique which employed a quartz spring suspended in a high-pressure Jerguson liquid level gauge. The two methods give comparable results (±2%) under equivalent conditions. The quartz-spring experimental setup allowed a flow of gas past the polymer during the gas exchange. The polymer sample was placed directly on the spring, and by using a high-accuracy filar eyepiece the displacement of the spring was measured at various pressures. After the buoyancy of the spring and sample was accounted for, the gas sorption level was determined. For all sorption measurements, equilibrium was determined to occur when less than a 0.1% change occurred in the sorption level over 4 h. Additionally, in order to assure that the sorption level was at equilibrium after the various gas exchanges, up to 5 days was allowed to elapse after the apparent equilibrium level was achieved. During this time, no further change in the sorption level was observed. The procedure for using this technique has also been described in detail previously.[7–9]

Dilation measurements were conducted by first suspending strips of polymer between brass guides which were machined to allow free movement of the sample but still prevent curling. The assembly was then placed in a high-pressure Jerguson gauge where the sample length was measured optically with a cathetometer. The Jerguson gauge was constructed with two openings to allow for the gas-exchange process. As with the sorption, sufficient time was allowed for the sample to reach equilibrium. A sample with a change of less than 0.05% in the overall volume over 8 h was considered to be at equilibrium. Also as with the sorption, for exchange-conditioned samples, up to 5 days was allowed to elapse after the apparent equilibrium was reached to assure that no further consolidation of the matrix was occurring. The experimental procedure has been described in more detail previously.[5]

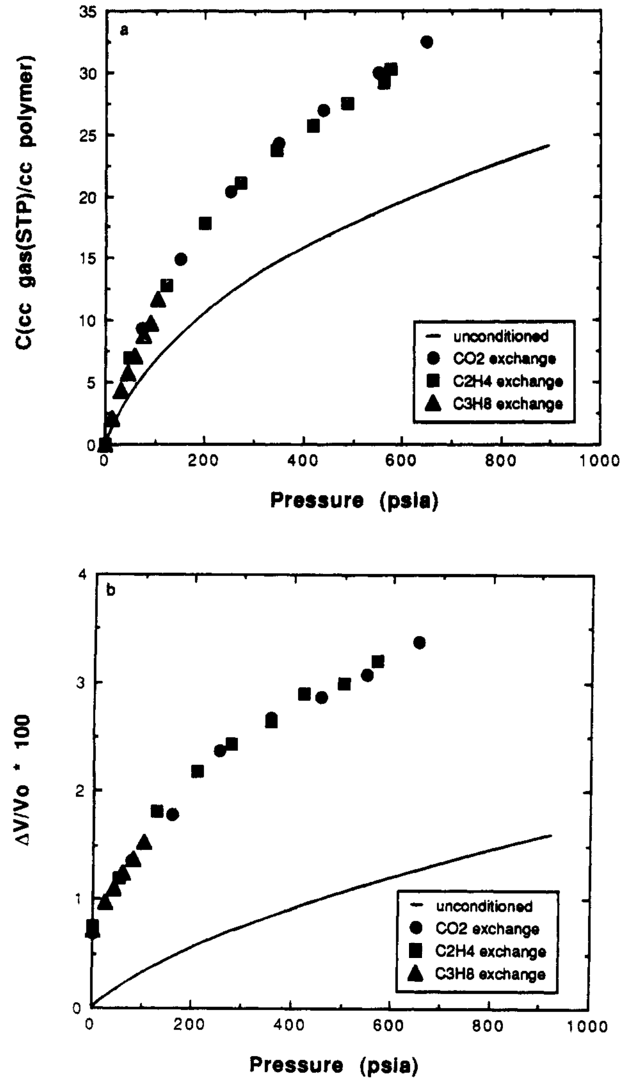

Figure 1. (a) Exchange-conditioned sorption isotherms of CH_4 in TMPC using different conditioning agents at 35 °C. (b) Exchange-conditioned dilation isotherms of CH_4 in TMPC using different conditioning agents at 35 °C.

Measurements of all sorption and dilation isotherms were performed at 35 °C.

Results and Discussion

Data are first presented for CH_4 sorption and dilation in the exchange-conditioned samples of TMPC as shown in parts a and b of Figure 1. In both plots, the solid line represents the unconditioned as-received CH_4 sorption and dilation levels while the solid points represent the sorption and dilation data for the exchange-conditioned samples. In this series of experiments, each sample was exposed to the conditioning agent at a pressure which produced an equilibrium volume dilation of 7.8%. This conditioning pressure was approximately 650 psia for CO_2, 575 psia for C_2H_4, and 100 psia for C_3H_8. Once the 7.8% volume dilation was achieved, the conditioning agent was exchanged for CH_4 at a constant pressure. In each case, a complete gas exchange was confirmed by analyzing the gas surrounding the sample by gas chromatography. Fresh samples were used to obtain each isotherm to avoid any previous exposure effects.

The resulting depressurization isotherms show significant increases in both sorption and dilation when compared to the unconditioned levels. These increases have been discussed before[6] and will only be briefly reviewed here. At the conditioning level used in these experiments, the polymer matrix has undergone a significant amount of swelling due to the high sorption level of the conditioning penetrant. Accompanying this swelling is a large amount of excess free volume which allows freer movement of the polymer chains. This more open and mobile structure creates, in effect, a new material with a lowered cohesive energy density. The matrix is held open during the gas-exchange procedure by the conditioning penetrant, thereby allowing the CH_4 to take advantage of the lowered energy requirement for sorption.

The major focus of this study, however, was to determine if these increases depended upon the nature of the conditioning agent. It is apparent from parts a and b of Figure 1 that the CH_4 sorption and dilation increases over unconditioned levels are identical for the CO_2-exchange-conditioned, C_2H_4-exchange-conditioned, and C_3H_8-exchange-conditioned samples. We may therefore hypothesize that the increases in sorption and dilation observed for the exchange-conditioned samples *do not* depend on the conditioning agent that is used as long as the same dilation level is reached with each conditioning agent. One can rationalize this line of thinking if we consider what is physically occurring during the conditioning and subsequent exchange process.

At the 7.8% dilation level, the conditioning penetrant molecules reside within the polymer matrix and contribute a certain amount of free volume in addition to the volume that they occupy. The important point to realize is that at a given dilation each sample has been expanded by an equivalent amount independent of the conditioning agent. As the exchange process begins, the CH_4 is able to take advantage of the still highly swollen matrix and displace the conditioning agent while rearranging polymer chains to better suit its local volume requirements. Since the exchange is performed at the same dilation level with each conditioning penetrant, the CH_4 finds the same amount of volume available and apparently makes no distinction between the CO_2-swollen sample, the C_2H_4-swollen sample, and the C_3H_8-swollen sample. We may therefore conclude that, at a given dilation, the energy required to place a CH_4 molecule within the polymer matrix has been lowered by the same relative amount regardless of the dilating agent.

Data are next presented for CH_4 sorption and dilation in TMPC samples which were conventionally conditioned with CO_2, C_2H_4, and C_3H_8. Whereas the explanations for the exchange-conditioned results were relatively straightforward, the explanations regarding the conventionally conditioned isotherms are somewhat more complex. The CH_4 sorption and dilation isotherms are shown in parts a and b of Figure 2,, respectively. Fresh TMPC samples were used for each experimental run to avoid any complications that might arise from exposure to more than one of the conditioning agents. Each sample was again exposed to a pressure of the conditioning agent to produce an equilibrium volume dilation of 7.8%. The sample was then slowly depressurized in increments of approximately 50–100 psia for CO_2 and C_2H_4 and 15–20 psia for C_3H_8 over several days. Each sample was then held under vacuum until all of the conditioning penetrant had desorbed, which could be confirmed by monitoring the space surrounding the sample with an extremetly sensitive pressure transducer. Methane was then introduced to the sample to produce the isotherms presented in Figure 2. The isotherm for the C_3H_8-conditioned sample shows data for the second CH_4 exposure as will be discussed in more detail later.

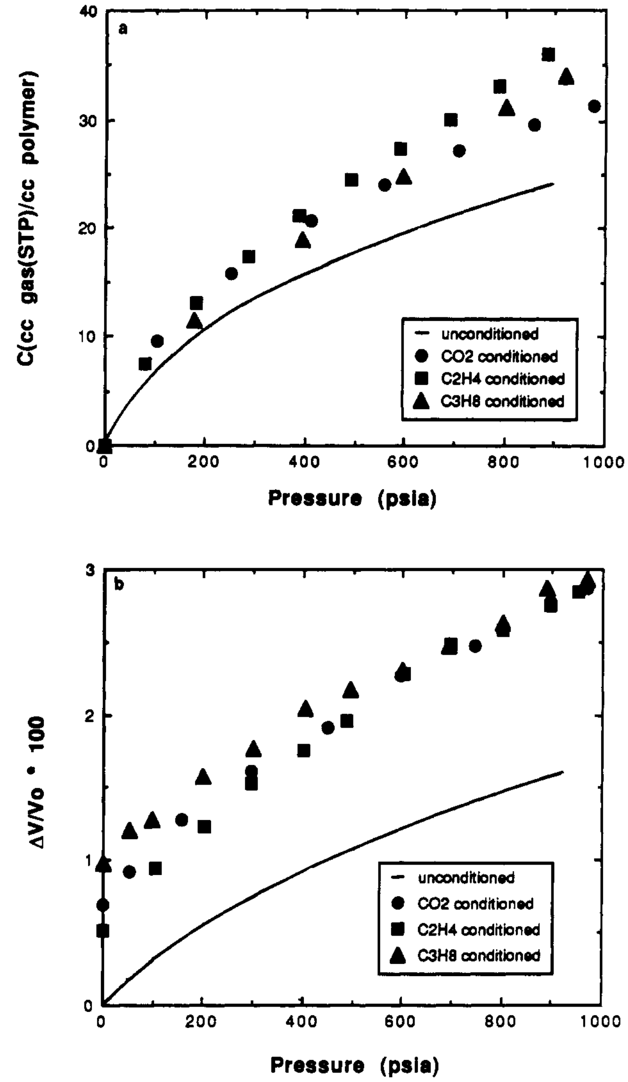

Figure 2. (a) Conventionally conditioned sorption isotherms of CH_4 in TMPC using different conditioning agents at 35 °C. (b) Conventionally conditioned dilation isotherms of CH_4 in TMPC using different conditioning agents at 35 °C.

From Figure 2a, it is seen that all of the conventionally conditioned isotherms lie above the unconditioned level. These increases have been explained previously by suggesting that subtle packing disruptions are introduced during the conditioning procedure which serve to lower the energy required for subsequent CH_4 sorption.[5] Since each of the samples in this study exhibited an increase in sorption over unconditioned levels, we may hypothesize that all three conditioning agents were able to introduce these disruptions. However, it is seen from Figure 2a that although the isotherms initially fall along the same curve, some divergence is noted above 600 psia. We may therefore suggest that although the matrix has been disrupted by each conditioning agent, the manner in which the chains have been reordered is different.

To help explain these differences, the conventional conditioning procedure is compared to the exchange-conditioning procedure. In the exchange-conditioning procedure, the CH_4 molecules enter a highly swollen and more mobile matrix due to the presence of the conditioning agent. The chains are therefore better able to conform to the specific volume and shape characteristics required by the CH_4 molecule. In contrast, the conditioning penetrant has been completely removed from the conventionally conditioned sample. The evacuated matrix may therefore retain certain packing conformations which were formed specifically to accommodate the conditioning penetrant. Hence, unlike the exchange-conditioned samples, we speculate that CH_4 may encounter a different environment in the conventionally conditioned samples depending on the conditioning agent. Another possible explanation for the different environments could be due to the different intrinsic desorption rates of the various conditioning agents. In extreme cases where the gas is rapidly removed from the sample, the different desorption rates could indeed play a factor. However, the samples used in this study were depressurized over long periods of time to avoid this complication. Additionally, if the different rates of desorption of the conditioning agents were a factor, differences in sorption levels between the various exchange-conditioned samples would also be expected, which, however, have already been shown to be identical.

Some physical evidence of these different environments in the conventionally conditioned samples may be seen from Figure 2b. The dilation of TMPC by CH_4 is shown for samples conventionally conditioned by CO_2, C_2H_4, and C_3H_8. As with the sorption isotherms, all of the conventionally conditioned dilation isotherms lie above the unconditioned dilation isotherm, presumably due to the lowered energy requirement for penetrant placement within the matrix. It is also seen that each of the conventionally conditioned isotherms begins with a nonzero dilation due to a residual volume dilation left by the conditioning agents. This residual dilation is most likely made up of both subtle packing disruptions caused by rotations of polymer segments and more substantial new penetrant scale defects caused by the coalescing of free volume during conditioning penetrant exposure. Although each conditioning agent produces a residual dilation, the values are somewhat different. These differences in residual dilation for the conventionally conditioned samples demonstrate that CH_4 encounters a different environment depending on the conditioning agent and therefore should not necessarily follow the same sorption or dilation isotherm for each sample.

It might be reasoned that the sample which displays the largest residual dilation should also display the largest increase in CH_4 sorption over unconditioned levels. However, as seen from Figure 2a, this is not necessarily the case since the C_3H_8 conventionally conditioned sample shows CH_4 sorption increases approximately the same as the C_2H_4 conventionally conditioned sample. We can rationalize these observations if we consider what may be happening to the chain packing and configurations.

Shown in Figure 3 are three CH_4 sorption isotherms in TMPC. The solid line again shows the unconditioned sorption level, while the other curves represent TMPC which has been conventionally conditioned with 100 psia C_3H_8 as described earlier. We see that the initial exposure of CH_4 to the conditioned sample produces an isotherm which is actually significantly *lower* than the second or third CH_4 exposures. In fact, below about 400 psia, the initial exposure to CH_4 gives sorption values that are even *lower* than the unconditioned sorption values. These unusual results were confirmed by running the series of exposures in two different sorption cells using two different samples. The effects observed are definitely beyond the small experimental error in the method employed (±2%) for samples with truly identical histories. Additionally, in order to confirm that all of the propane had desorbed, each sample was held under vacuum for 10 days. The pressure of the chamber containing the TMPC sample was then monitored to check for any residual propane desorption. In each case, it was found that all of the propane had been removed.

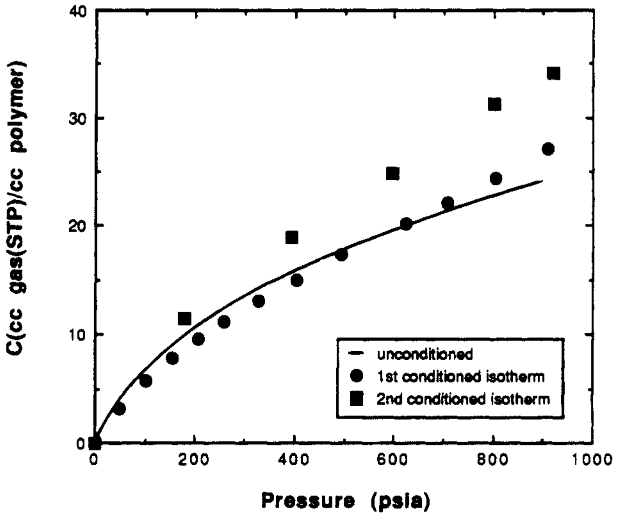

Figure 3. Comparison of first and second CH_4 exposure for CH_4 sorption in C_3H_8 conventionally conditioned TMPC at 35 °C.

These results may be explained by considering the possible action of C_3H_8 on the matrix during the conditioning procedure and evacuation step. As C_3H_8 resides in the matrix at high concentrations, it may be able to rearrange the polymer chains into a most favorable packing conformation which presumably creates a space appropriate for accommodating a C_3H_8 molecule. The sorbed cage size in dissolved environments has been shown earlier to be approximated well by the van der Waals volume of the penetrant, approximately 84 cm^3/mol (139 $Å^3$/molecule) for C_3H_8.[10] As C_3H_8 is removed, a slowly fading "memory" of these packing conformations may remain since a rearrangement would require a significant amount of energy and time. When CH_4 then enters the matrix, the molecules may possibly encounter some spaces which are much larger than they require for equilibrium accommodation. The molecules sorbing into these voids would then be left with an excess of volume which at low concentrations is unavailable to the other sorbed molecules. Such a situation corresponds to an inefficient usage of the excess free volume introduced by the conditioning agent which apparently outweighs the effect of disruptions and lowers the overall sorption level. As the concentration of CH_4 increases, the molecules appear to be able to rearrange the polymer chains over observable time scales in order to redistribute the excess free volume introduced by C_3H_8. Thus, on subsequent exposures, the sorption level has increased as originally expected by making better use of the residual volume introduced by prior exposure to the conditioning agent. These effects apparently occur only when the size of the conditioning agent is significantly larger than that of the secondary probe penetrant. These effects were not expected or seen with the CO_2- and C_2H_4-conditioned samples since the molecular sizes of both CO_2 (71 $Å^3$/molecule) and C_2H_4 (95 $Å^3$/molecule) are similar to that of CH_4 (71 $Å^3$/molecule) and would therefore tend to leave environments of a suitable size for CH_4 to use without significant local rearrangements.

Conclusions

Through this study, it has been shown that penetrants other than CO_2 are able to condition a glassy polymer matrix. Preexposure of TMPC to C_2H_4 or C_3H_8 produced increases in the subsequent CH_4 sorption and dilation isotherms as compared to an as-received sample. These increases in sorption were similar at low pressures but diverged slightly at high pressures, presumably due to the different conditioning penetrants altering the polymer matrix in subtly different ways. It was hypothesized that CH_4 was initially not able to take complete advantage of the increase in free volume produced by C_3H_8 conditioning since the newly created voids were larger than needed. However, upon reaching a higher concentration, CH_4 appeared to be able to redistribute the volume in the C_3H_8-conditioned sample to some degree. These hypotheses were supported by the dilation data.

In contrast, the increases in the CH_4 sorption and dilation isotherms produced by the exchange-conditioning procedure were identical for each of the conditioning agents. The identical isotherm increases were due to equivalent amounts of volume available to the incoming CH_4 molecules independent of the dilating penetrant. At the conditioning level employed in this study, the matrix is highly swollen and mobile during the exchange procedure. This mobility allows the available volume to conform to the needs of the CH_4 molecule and is not complicated by templating from the conditioning penetrant.

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References and Notes

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Registry No. TMPC (copolymer), 52684-16-9; TMPC (SRU), 38797-88-5; CH_4, 74-82-8; CO_2, 124-38-9; C_2H_4, 74-85-1; C_3H_8, 74-98-6.