

Time-Dependent Permeation of Carbon Dioxide Through a Polyimide Membrane Above the Plasticization Pressure

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SYNOPSIS

The time-dependent permeation behavior of a glassy polyimide is studied above and below the plasticization pressure with carbon dioxide as the permeating gas. The work particularly focuses on the quantification of the slow increase in permeability at feed pressures above the plasticization pressure. Significant differences in permeation behavior were found for membranes with and without permeation history. Introducing the quantity "conditioning time" allows one to compare the results obtained for membranes with different permeation history. The concept of conditioning time furthermore allows one to quantify the aging of a membrane plasticized during previous permeation. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polymer films are frequently applied as barrier materials in food-packaging applications and as selective layers in membrane gas separation.¹ The mass-transport behavior depends strongly on the state of the polymer.² In the rubbery state, the permeability of a polymer is independent of the applied pressure difference across the polymer film. The permeability is very reproducible since the polymer matrix responds elastically to the sorption of the permeating species. In the glassy state, the permeability decreases with increasing feed pressure because the solubility decreases with increasing pressure. After passing through a minimum, the permeability-vs.-pressure curve increases. This is often referred to as plasticization and the pressure at the minimum permeability is called the plasticization pressure p_{pl} . Above the plasticization pressure, the permeability of a polymer is very hard to quantify due to the nonequilibrium state of the glassy polymer.

In the literature, the phenomenon of plasticization during permeation has frequently been addressed.⁴⁻¹⁰ In particular, the following phenomena were observed:

- The permeating molecules decrease the glass transition temperature of the polymer.¹¹⁻¹⁴
- Above the plasticization pressure, the permeability increases in time for increasing feed pressure steps.¹⁵⁻¹⁸
- Above and below the plasticization pressure, the permeability decreases when the feed pressure decreases from a pressure higher than the plasticization pressure.¹⁵
- A significant hysteresis exists in the permeability-vs.-pressure curve when the curve is determined by increasing or decreasing incremental pressure steps.¹⁵
- The permeability-vs.-pressure curves of two subsequent pressurization/depressurization cycles are not reproducible.¹⁵

These effects are often described as the result of polymer conditioning by the sorbed penetrant molecules. The phenomena can be attributed to the swelling stresses exerted by the penetrant molecules on the polymer network.^{18,19} In this contribution, we focus on the time-dependent permeability above the plasticization pressure. We introduce the concept of conditioning time to quantify the dynamic permeability and relate the obtained results to the history of the polymer.

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EXPERIMENTAL

Polymer Synthesis and Characterization

The permeation experiments were carried out with the aromatic polyimide 6FDA-MDA. The polymer is based on the dianhydride 6FDA ([4,4'-(2,2,2-trifluoromethyl) ethylidene]-bis[1,3-isobenzofurandione]) and synthesized following the procedure described in Ref. 20. The completion of the imidization reaction was observed by $^1\text{H-NMR}$ and IR spectroscopy. Homogeneous membranes were prepared by casting a 10–15 wt % solution of the synthesized polyimide in dimethylacetamid (DMAc) on a glass plate. The membrane was dried for 2 days under a stream of nitrogen. After solvent evaporation, the membranes were released from the glass plate by immersion in a water bath. Samples were dried for at least 2 weeks in a vacuum oven at 150°C to remove the residual solvent. After drying, no characteristic solvent peaks could be found in the IR spectra. The membranes used were about 25–35 μm thick. The glass transition temperature T_g was obtained by DSC measurements performed on a Perkin-Elmer DSC-4 calorimeter at a heating rate of $20^\circ\text{C}/\text{min}$. The polymer density was measured using a setup in which the weight of a polymer sample is measured in air and in a liquid (water or isooctane). The chemical structure and physical properties are listed in Table I.

Permeation Experiments

The permeation setup consists of two permeation cells as shown in Figure 1. The experimental technique is based on the principle that molecules permeating through a membrane into an evacuated constant volume will increase the pressure in this volume. The measurement volume V_m was calibrated

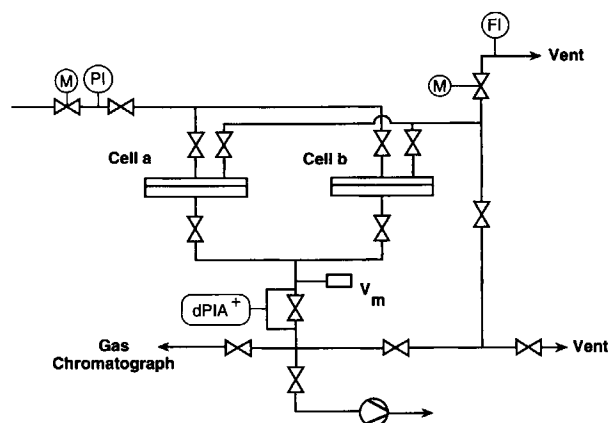


Figure 1 High-pressure permeation setup containing two permeation cells.

using a standard membrane obtained from the U.S. National Bureau of Standards/Colorado. The setup can measure pure gases as well as gas mixtures. Particularly for repetitive experiments above the plasticization pressure, the system was automated with a programming logic control unit (PLC). The permeability at time t is determined by measuring the pressure increase in the permeate volume for a small time period (<5 min). This period is negligibly small with respect to the total experimentation time. At feed pressures below the plasticization pressure, the permeability stays constant after the concentration profile in the membrane has been established (time lag). Above the plasticization pressure, the permeability continues to increase. Normalizing the permeability by the permeability at the time lag results in Figure 2, showing schematically the change in relative permeability as a function of time. In the following, this methodology will be used for all experiments.

Table I Chemical Structure and Physical Properties of Polyimide Synthesized

Polymer Name	6FDA-MDA
Chemical structure	
Glass transition temperature ($^\circ\text{C}$)	330
Density (g/cm^3)	1.382

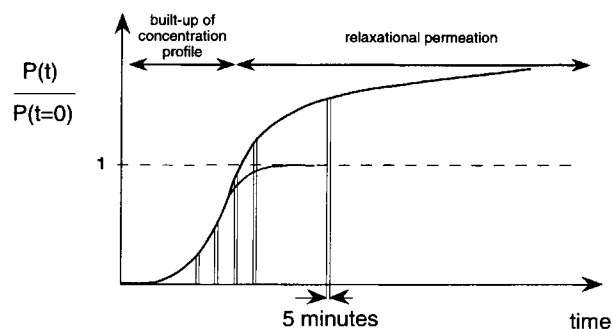


Figure 2 Schematic representation of the measurement principle for the normalized permeability as a function of experimentation time.

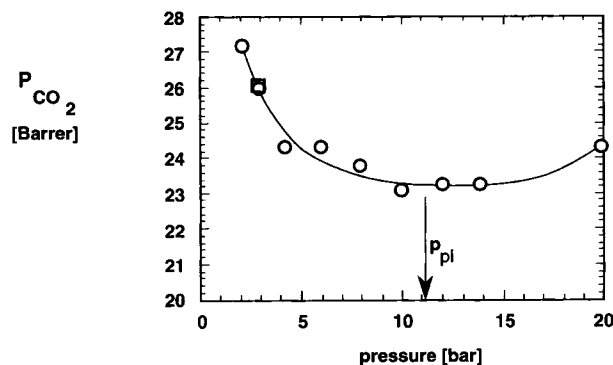


Figure 3 Carbon dioxide permeability of the polyimide 6FDA-MDA as a function of the feed pressure; rectangle data point represents a second polymer batch.

RESULTS

The permeability-vs.-pressure curves are normally determined by increasing the feed pressure by incremental steps. A typical result of such an experiment is shown in Figure 3. Below the plasticization pressure of about 11 bar, the permeability is independent of time. Above the plasticization pressure, the permeability increases slowly. A new experiment starts at a higher pressure after a pseudoequilibrium has been reached. We determined the dynamic permeability above the plasticization pressure at 20 bar feed pressure with two different experiments:

1. The feed pressure increases from 0 to 20 bar; the membrane has never been in contact with CO_2 .
2. The feed pressure was increased incrementally and the permeability at 20 bar feed

pressure was determined for a pressure step from 17 to 20 bar; the membrane, therefore, has a certain history.

Figure 4 shows the permeability as a function of time for experiment (1), a pressure step from 0 to 20 bar. Figure 5 shows the permeability as a function of time for experiment (2), a pressure step from 17 to 20 bar. In both figures, the permeability $P(t)$ at a time t is normalized for the permeability P_0 at the time when the concentration profile has been built up due to Fickian diffusion. A logarithmic time scale allows one to distinguish small changes in permeability at long times. The time scale is normalized for the squared membrane thickness to compensate for the influence of membrane thickness on the initial concentration buildup in the membrane.²¹ Both figures clearly show that the dynamic permeability response upon an increase in driving force is significantly different.

For experiment (1), a drastic increase in the relative permeability, ranging from 0.1 to 1, can be observed. This increase is related to the buildup of the concentration profile in the membrane (time lag). In the case of a polymer which is not "plasticized," no relaxational response of the permeability was measured, and after the time lag, the permeability remained constant. (This was experimentally verified for pressures lower than 11 bar.) However, for a pressure step from 0 to 20 bar, the permeability increases linearly on a logarithmic time scale after passing the time lag. This linear increase cannot be found in the experiment for a pressure step from 17 to 20 bar, as shown in Figure 5. For a feed pressure step from 17 to 20 bar, shown in Figure 5, the permeability is almost constant for $\log(t/d^2)$ values of

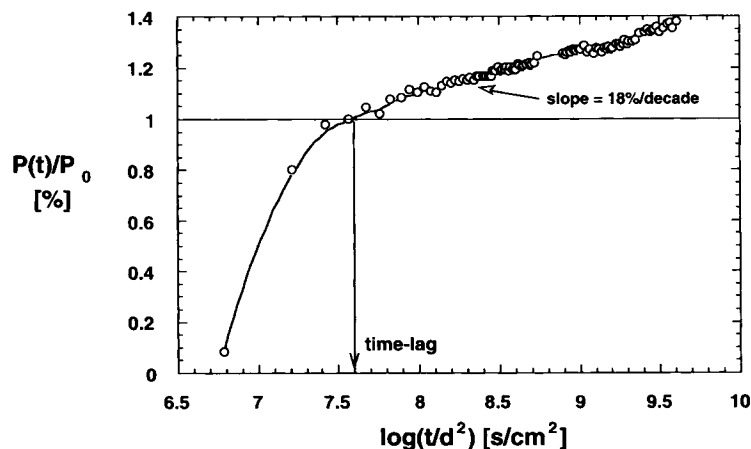


Figure 4 Normalized permeability of carbon dioxide through 6FDA-MDA as a function of time for a pressure step from 0 to 20 bar feed pressure.

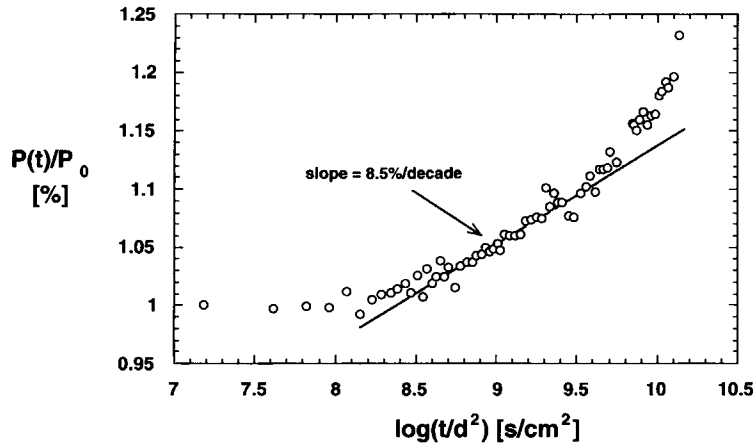


Figure 5 Normalized permeability of carbon dioxide through 6FDA-MDA as a function of time for a pressure step from 17 to 20 bar feed pressure.

7–8. For the decade from 8.5 to 9.5, the relative permeability increases only by about 8.5% per decade. Comparing the slope of the permeability for the two experiments, a significant difference can be observed: 8.5% (decade 8.5–9.5) for the pressure step from 17 to 20 bar and 18% (decade 7.5–9.5) for the pressure step from 0 to 20 bar.

To obtain more insight in these differences, new experiments were carried out with virgin membranes at 14 and 17 bar feed pressures. The curves obtained show the same characteristic shape as found in Figure 4. In Figure 6, the main characteristic, the slope of the relaxational permeability curve, is plotted vs. the feed pressure. Clearly, the slope of the relaxational permeability increases with increasing feed pressure. The swelling stresses in the polymeric matrix induced by the sorbed penetrant molecules become larger as the penetrant concentration in-

creases, leading to more pronounced relaxation processes, and they become faster and more pronounced as the feed pressure, and, hence, the penetrant concentration, increases. Since no equilibrium value is reached within the experimentation time, no conclusion can be drawn about the absolute value of the permeability increase due to relaxations. One can also conclude from Figure 6 that there will be no time-dependent permeation at feed pressures below 11 bar, since the extrapolated slope will be equal to zero at $p = 11$ bar. This, indeed, agrees well with the experiments shown in Figure 3. In Figure 3, as long as the permeability decreases with increasing pressure, no time dependence was observed. As soon as the permeability increases with increasing feed pressure, mass transport across the membrane is time-dependent.

The open question about the origin of the differ-

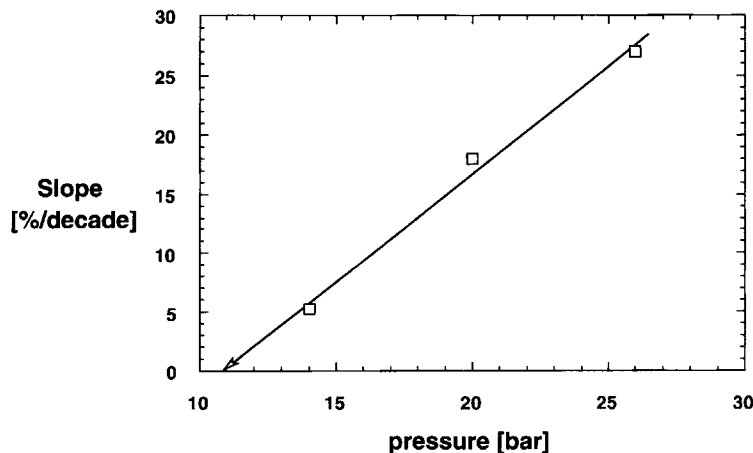


Figure 6 Slope of the time-dependent normalized permeability of carbon dioxide at different feed pressures for membranes without permeation history.

ence between experiments (1) and (2) can be answered by considering the experimental protocol. The membrane which was investigated for the pressure step from 17 to 20 bar had already a certain relaxation history at pressure steps of 14 and 17 bar. However, this additional time is not considered when resetting the time to zero for each new experiment at a higher pressure. This problem will be worked out in more detail below.

A property y which is a function of time obeying eq. (1),

$$y(t) = at + b \quad (1)$$

can be shifted along the time axis into a new time frame $t' = t - t_0$ obeying eq. (2):

$$y(t' + t_0) = a(t' + t_0) + b = at' + b' \quad (2)$$

without changing its slope a . Only the intercept with the y -axis varies upon shifting. However, this is not valid for a property that changes linearly with the logarithm of time [as empirically found in experiment (1) for a virgin membrane].

For a membrane without history, the time $t = 0$ is, in fact, the beginning of the experiment. For membranes which have been characterized by consecutive pressure steps above the plasticization pressure, the time $t = 0$ is not known at all. One may assume that the time at which the membrane was characterized at lower pressures must be added to the experimentation time. However, this neglects the fact that the penetrant-induced stresses are smaller at smaller pressures compared to the actual experimental situation.

Assuming the general validity of the empirically found linear relationship between the permeability and the logarithmic time, only a certain percentage of the experimentation times at lower pressures was added to the actual experimental time until a linear relation was obtained. To correct the time scale of experiment (2), 10% of the experimental time for the 14 bar experiment and 25% of the 17 bar experiment was added to the actual experimental time. The obtained slope for the relaxational permeability is 20%, as shown in Figure 7. The same procedure can be applied to the results of the permeation experiment from 14 to 17 bar feed pressure. Here, only the history for the permeation experiment from 11 to 14 bar must be taken into account. The result is shown in Figure 8. The slopes in both figures agree well with the slope expected from a permeation experiment carried out with a virgin membrane as shown in Figure 8.

DISCUSSION

The choice of the absolute value of shifting the starting point appears arbitrary; however, the extent of shifting has to fulfill a few general conditions as discussed below.

Mathematical Formulation of Boundary Conditions

The data treatment described above can be defined mathematically: The time-dependent permeability of a virgin membrane [experiment (1)] at a certain pressure p can be expressed for times larger than the time lag (see Fig. 4) as

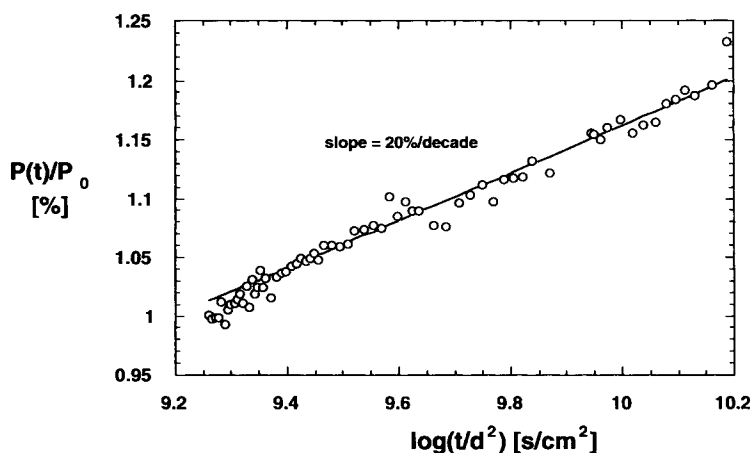


Figure 7 Normalized permeability as a function of the history-corrected permeation time for a permeation experiment with a feed pressure step from 17 to 20 bar.

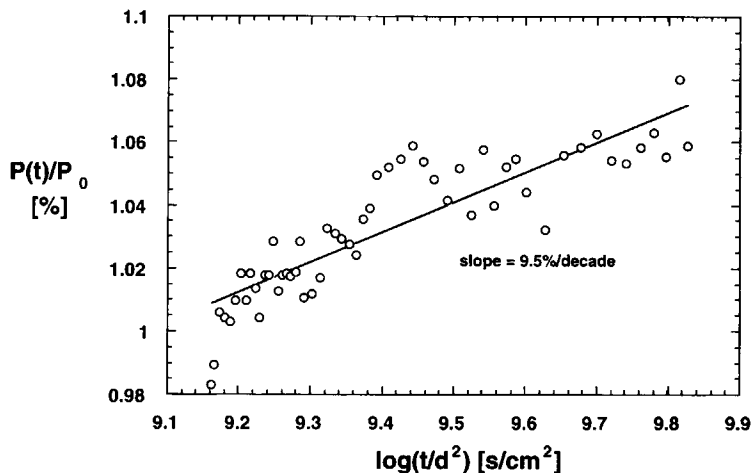


Figure 8 Normalized permeability as a function of the history corrected permeation time for a permeation experiment with a feed pressure step from 14 to 17 bar.

$$\frac{P(p, t)}{P_0(p)} = 1 + a \log\left(\frac{t}{d^2}\right) \quad (3)$$

Considering an experiment with consecutive pressure steps [experiment (2)] with m previous permeation experiments at lower pressures p_m , the experimentation time t for the permeation experiment at $p > p_m$ can be corrected according to eq. (4):

$$\frac{P^*(p, t^*)}{P_0^*(p)} = 1 + a^* \log\left(\frac{t + \sum_{n=1}^m x_n t_n}{d^2}\right) \quad (4)$$

so that the slopes a and a^* of both figures are equal.

x_n is the percentage of the experimentation time t_n used for the experiment at the pressure p_n . No definite statement can be made at this moment regarding the absolute values of the permeabilities $P_0(p)$ and $P_0^*(p)$ which are not influenced by the relaxation phenomena. However, since the permeability alterations seem to stem from irreversible or very slowly reversible morphology alterations, different experimental procedures in the sequence of pressure and vacuum application on the feed side of the membrane may cause variations in the initial values of P_0 . The sum of the effective experimentation times $x_n \cdot t_n$ of low-pressure experiments will be called the "conditioning time."

Using the following rules, the conditioning time can be determined:

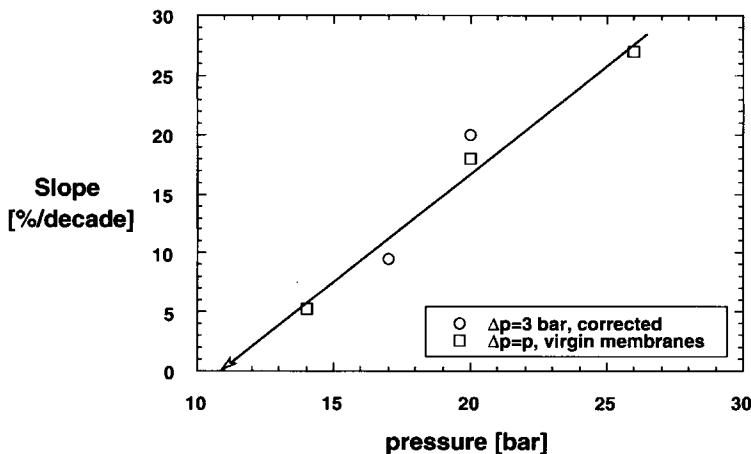


Figure 9 Slope of the time-dependent normalized permeability of carbon dioxide at different feed pressures for virgin membranes and membranes with permeation history where the conditioning was added to the experimentation time.

- The conditioning times must be chosen such that the slopes of the time-dependent permeability on a logarithmic time scale are equal for the virgin and the conditioned membrane.
- For a membrane history of only one experimental run at a feed pressure lower than the actual experimental feed pressure and the same experimental time t , the conditioning time $x_1 \cdot t$ cannot be equal to or larger than the actual experimentation time t . Therefore, x_1 is smaller than 1.
- For a membrane history with various consecutive pressure steps and equal experimentation times per step, the conditioning time at a low pressure must be smaller than is the conditioning time at any higher pressure. This is because swelling stresses are smaller at lower pressures than at higher pressures.
- At pressure steps causing linearly increased swelling stress steps in the polymer matrix and equal experimentation times t , the conditioning time can be calculated from

$$\sum_{n=1}^m x^n t \quad (5)$$

Physical Significance of the Conditioning Time

The physical significance of the conditioning time for permeation was tested by the following experiment: The membrane which was earlier used for permeation experiments at 14, 17, and 20 bar feed pressure was left for 4 weeks at ambient atmosphere. The time-correction procedure resulted in a total conditioning time of 32 h (10% of the experimentation time at 14 bar, 25% of the experimentation time at 17 bar, and the full experimentation time at 20 bar feed pressure). After 4 weeks of storage at an ambient condition, a new permeation experiment was carried out for a pressure step from 0 to 20 bar. For all experiments carried out from 0 to a certain pressure above the plasticization pressure, virgin membranes showed a linear relation between the normalized permeability and the logarithmic time scale. The membrane used in this experiment, with the permeation history at 14, 17, and 20 bar feed pressure, did not show this linear relation. However, adding 11 h of experimentation time gives the empirical linear relationship. The conditioning time of 11 h is considerably smaller than is the conditioning time of 32 h obtained after the first, consecutive permeation experiments.

On a molecular level, the difference in condition-

ing times can be attributed to physical aging.^{22,23} As the carbon dioxide desorbs from the membrane, the internal stress on the polymer matrix vanishes. The polymer matrix can consolidate back into a morphology similar to the virgin membrane and the observed conditioning time is smaller than is the conditioning time determined directly after the initial permeation experiment.

CONCLUSIONS

1. For membranes without a permeation history and feed pressure steps from 0 to a pressure above the plasticization pressure, the relaxational permeability of carbon dioxide is linearly related to the logarithmic experimentation time.
2. For incremental feed pressure steps above the plasticization pressure, the linear relation cannot be observed. Adding the conditioning time to the experimentation time, however, results in the linear relation.
3. The slope of the relaxational permeability increases with increasing feed pressure due to the increased swelling stresses exerted by the sorbed carbon dioxide on the polymer matrix.
4. The slope of the relaxational permeability equals zero at the pressure where the permeability-vs.-feed pressure curve shows the minimum.
5. Consolidation and aging of the polymer matrix after permeation experiments and storage of the membrane can be quantified as a decrease in conditioning time.

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