Effect of Sub-T_g Annealing on Gas Transport in Polycarbonate

INTRODUCTION

Polymeric glasses such as polycarbonate exist in a nonequilibrium state; thus, their physical state and consequently their properties depend on past sample history. This is well illustrated by the effect annealing just below the glass transition has on density,[1] enthalpy,[2] creep,[3] stress relaxation,[4] and ultimate mechanical properties.[5] Recently, we reported that sub-T_g annealing reduces appreciably the solubility of gases in polycarbonate,[6,7] which is consistent with the envisioned collapse of free volume associated with a closer approach to an equilibrium state during annealing. Conversely, exposure of the glass to high-pressure CO_2 causes a dilation of its nonequilibrium state and increased gas solubility in subsequent sorption experiments.[8]

Results developed during the last 20 years indicate that the nonequilibrium nature of glassy polymers introduces additional mechanisms of gas sorption and transport[9,10] not found in polymers above their T_g. These effects can be well described by the dual-sorption–dual-mobility models that have evolved over the past two decades.[10] As a result of these mechanisms, the commonly reported parameters of transient permeation experiments, viz., the time lag (θ) and the permeability (P), depend on the upstream driving pressure in contrast to the case for rubbery polymers.

The present note reports briefly on experiments designed to determine how sub-T_g annealing of polycarbonate affects the transport parameters P and θ for simple gases.

EXPERIMENTAL

The film used was commercial samples of 5.0 mil melt-extruded Lexan supplied by the General Electric Company. The as-received film was annealed at 125°C for various periods of time in a forced-air oven. All specimens were uniformly conditioned by exposure to 20 atm of either N_2 or CO_2 for 24 hr at 35°C prior to transport measurements for reasons described earlier.[8] Transport measurements with either N_2 or CO_2 were made as a function of upstream gas pressure with equipment described previously[11] at 35°C.

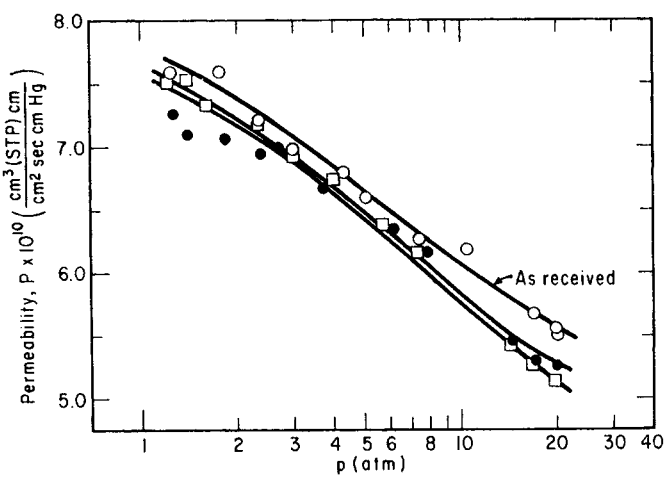

Fig. 1. Permeability of CO_2 in polycarbonate (at 35°C) as a function of upstream driving pressure and thermal history. Annealed at 125°C for (●) 2 hr and (□) 7 days.

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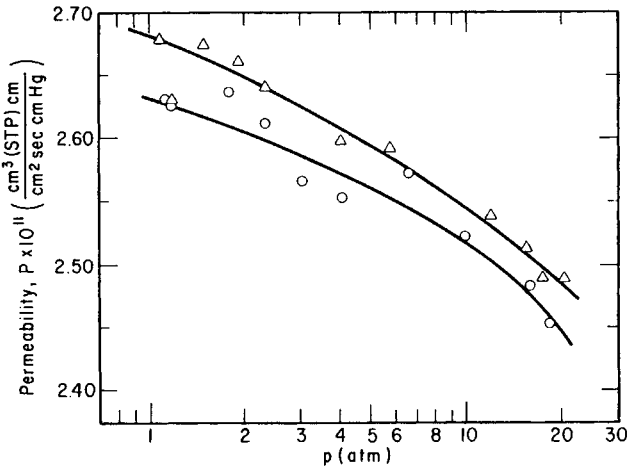

Fig. 2. Permeability of N_2 in polycarbonate (at 35°C) as a function of upstream driving pressure and thermal history. (○) as received; (△) annealed at 125°C for 1 week.

RESULTS

Figures 1–4 show the results obtained. Both P and θ decrease with upstream gas pressure as mentioned above; however, the main point of interest here is the effect annealing history has on the values of P or θ at any pressure. The effect of annealing on the permeability is quite small. After one week at 125°C, the N_2 permeability appears to be larger by about 2% while the CO_2 permeability seems to be about 5–6% lower. However, these changes are too near the experimental reproducibility of the measurements to attach much significance to them. The time lag on the other hand is clearly and significantly reduced by annealing. The latter observation may appear contrary to physical intuition at first glance; however, the following comments readily explain this effect.

Equilibrium sorption of gases in glassy polymers occurs by two separate mechanisms.[9,10] One mode follows Henry's law and is similar to the mechanism also observed when the polymer is above T_g. The other follows a Langmuir isotherm and is the result of the nonequilibrium nature of the glass apparently arising from "microvoids" trapped in the glassy structure. Gas molecules held by this mode are less mobile by about one order of magnitude than gas molecules sorbed according to the mode following Henry's law. Filling these less mobile sites during transient permeation prolongs the attainment of steady-state transport and thus causes an abnormally large observed

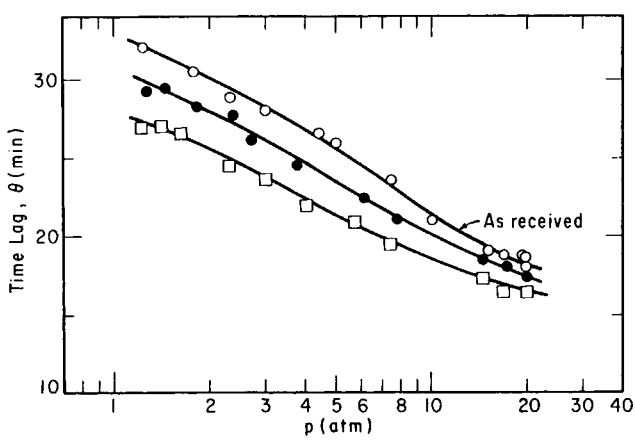

Fig. 3. Time lag (at 35°C) for CO_2 in polycarbonate. Annealed at 125°C for (●) 2 days and (□) 7 days.

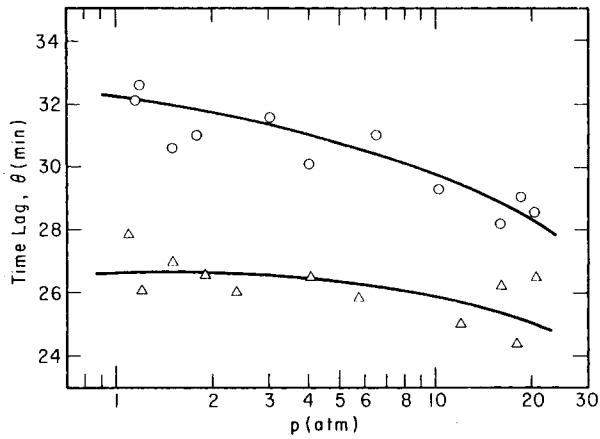

Fig. 4. Time lag (at 35°C) for N_2 in polycarbonate. (○) as received; (△) annealed at 125°C for 1 week.

time lag.[10] Sub-T_g annealing decreases the capacity of the Langmuir sites[6] evidently by collapsing the "microvoids" which give rise to this mechanism. Thus, by diminishing the magnitude of this "hole filling" process, sub-T_g annealing causes a decrease in the observed time lag. Application of the dual-sorption–dual-mobility model to the present data reveals a slight decrease in the mobility of the gas held by Henry's law and a slight increase in mobility of the gas held by the Langmuir mode as a result of this thermal treatment; however, the dominant effect on θ is by far the reduction in capacity of the Langmuir mode.

It is interesting to compare the present results with the effects caused by exposing glassy polycarbonate to high pressures of CO_2.[8] This treatment reduces the glassy state density, increases the gas sorption (primarily through an increase in the Langmuir capacity), has little effect on the permeability, and increases the observed time lag. These trends are exactly the opposite of those caused by sub-T_g annealing.

CONCLUSIONS

Sub-T_g annealing of glassy polymers decreases the capacity of the Langmuir mode of sorption and thereby reduces the "hole filling" time during transient permeation experiments and consequently reduces the observed time lag. In contrast, there is little effect on the steady-state permeation rate because the sorption and transport processes which are primarily responsible for this rate are not altered very much by this thermal treatment. The effects on P and θ could be considerably greater for penetrants larger than N_2 and CO_2.

Chen[12] reported that the apparent diffusion coefficients for methane and propane obtained by a gas-flow permeation apparatus decrease very slightly as the result of annealing glassy polymers. These trends are opposite of those reported here, and no rationalization of these differences can be offered at this time.

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