Accelerated Physical Aging of Thin Poly[1-(trimethylsilyl)-1-propyne] Films

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ABSTRACT: We present results for physical aging of films made from a high free volume polymer (poly-[1-(trimethylsilyl)-1-propyne], PTMSP). Aging was tracked by gas permeation measurements of He and N_2. The intermediate and thin films (3 and 1 μm) showed a rapid loss of gas permeability with time while the thick film (85 μm) showed no significant permeability change over more than 200 h. The permeability loss accelerated with decreasing thickness. The films were carefully conditioned to imprint a reproducible history. We conclude that bulk PTMSP apparently exhibits stable permanent gas permeabilities, but thin films appear prone to accelerated physical aging. This complements our earlier observations on a number of polymers. The results further support the hypothesis that free volume from the glassy material is eliminated over time at the surface of the films in a diffusion-like process.

Introduction

Poly[1-(trimethylsilyl)-1-propyne] (PTMSP) is a glassy polymer with extremely high gas permeability[1] (see below, reported N_2 permeability of about 3700−7000 barrer at 25 °C, 1 barrer = 1×10^{-10} cm^3 (STP) cm/(cm^2 s cmHg)). The permeation properties of the polymer have been studied rather extensively (see below). We have attempted to standardize the thermal history of PTMSP films so that physical aging observations as a function of thickness would not be obscured by history-dependent behavior. The gas transport behavior (He and N_2 permeabilities) of thick and thin free (unsupported) polymer films of PTMSP *with identical thermal history* has apparently not yet been compared. The behavior of thin polymer layers is interesting for gas separation membranes and other thin film applications (microelectronics, coatings, xerographic photoconductors, sensors). The results presented here complement previous observations on accelerated physical aging of thin polymer films when compared with thick films.[2,3,26]

Molecular modeling of PTMSP has been performed.[4,5] However, both the time frame and the sample size for computer simulation of thin film aging experiments as described in our work apparently exceed by far the limits of available computational power.

Yampol'skii et al.[6] measured transport properties and macroscopic densities and performed differential scanning calorimetry (DSC), X-ray scattering, positron annihilation (PALS) spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy on PTMSP. The film thicknesses used were apparently on the order of tens of micrometers. Films that had aged for 4 years in air at room temperature were compared with freshly cast films. Initially colorless films showed a yellow tint after aging. The macroscopic density increase was 20−30%. Gas permeabilities dropped up to 27-fold during aging, and selectivities for O_2/N_2 and H_2/N_2 increased. Diffusivities reportedly decreased as much as 2 orders of magnitude. No crystallization was observed by wide-angle X-ray measurements, but the interchain distance was found to decrease with aging.

Takada et al.[7] investigated the gas permeability of PTMSP films (10−50 μm thickness). The films were used after casting and drying at room temperature. Single gas permeabilities of 2000 barrer for nitrogen and 4100 barrer for helium were reported. The O_2 permeability and the ideal O_2/N_2 selectivity both declined with declining weight-average molecular weight of PTMSP. Heat treatment of PTMSP at 100 °C for 15 h decreased the oxygen permeability quickly by a factor of 10, while the O_2/N_2 selectivity increased from below 2.0 to about 2.6. The response to the heat treatment was interpreted as a relaxation/densification of the polymer. The activation energies for O_2 and N_2 permeation were found to be slightly negative.

By studying the gas and vapor permeation and sorption of PTMSP and of poly(vinyltrimethylsilane) (PVTMS), Plate et al.[8] have shown that the free volume of these polymers is larger when the backbone is stiff (PTMSP) than when it is flexible (PVTMSP). The T_g of PTMSP was reported to be 230 °C. PTMSP film geometric densities were reported in the range 0.70−0.77 g/cm^3. The N_2 permeability of PTMSP was reported to be 1500 barrer. However, values between 1500 and 4970 barrer were cited in this reference from other sources. Plate et al. reported that aging should not have played a role in their permeability measurements since care was taken to eliminate this uncertainty.

Values of the density of PTMSP were published[9] with significant differences between beads (0.938 g/cm^3) and membranes (0.70−0.77 g/cm^3). However, the polymer was not from the same batch. Permeability coefficients were determined for films of 30−200 μm thickness at 30 °C. The films were dried under vacuum after casting from toluene and immersing in methanol. The reported N_2 permeability coefficient was 4970 barrer, while 2000 and 4050 barrer at 25 °C were cited for N_2 from other sources.

Morisato et al.[10] used solvent-cast PTMSP films of 20−30 μm thickness. The films were dried at ambient conditions for 24 h and under vacuum at 80 °C for 3 days. A permeability of about 7000 barrer for N_2 through PTMSP was found at 25 °C. No details were

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given on the precautions taken to address the issues of time dependence and contamination for the pure PTMSP measurements.

Srinivasan et al.[11] have carefully examined the mechanism of gas transport in PTMSP based on sorption and permeation experiments in films of 50−115 μm thickness. The exceptionally high gas permeability of PTMSP was attributed to very large diffusivities compared to those of other glassy polymers. Large voids (order of 5 Å) in the polymer with some interconnections were postulated. Others have proposed a similar structure.[12] The authors also propose a relatively large separation of the polymer chains in the dense areas of PTMSP based on an analysis of activation energies of gas molecules of different size. They observed that PTMSP shows an increase in the permeability when the temperature decreases. Gas transport through PTMSP was suggested to be more similar to transport in a zeolite than in a typical glassy polymer.

Masuda et al.[13] have investigated the stability of polyacetylenes, including PTMSP. Weight loss of PTMSP was found to start at 250 °C in air and was also found to depend on the presence of oxygen. In our work the PTMSP is heated to 250 °C in a He atmosphere to remove solvents, standardize the thermal history, and avoid chemical reactions.

Langsam and Robeson[14] determined the stability of PTMSP by thermogravimetry and thermal spectroscopy. Film samples cast from a toluene solution (dried at room temperature for 24−48 h) had a thickness of about 50 μm. No second-order transitions were discovered below 200 °C. The polymer was reported stable in N_2 up to 300 °C. It was also suggested that a permeability loss of PTMSP films observed by others might be due to contamination with hydrocarbon vapors from the environment (for example from vacuum pumps) rather than to physical aging. No flux decline was reported at room temperature under 20 psig of O_2 for at least 23 days. The N_2 permeability was reported to be about 6400 barrer at 25 °C.

Consolati et al.[15] reported thermal stability of PTMSP to 300 °C. Permeability measurements on films (10−100 μm thickness) showed a significant permeability decrease over 30 days, but no details were given on precautions to avoid contamination. A significant density increase over 30 days was reported, but the sample storage conditions were not given in detail.

The T_g of PTMSP was reported to be 230 °C[16] (differential thermal analysis in a vacuum).

Savoca et al.[17] investigated a number of poly(silylpropynes) and report the T_g of PTMSP in excess of 300 °C. They report an N_2 permeability of 6700 barrer for PTMSP. It was reported that heat treatment up to 250 °C in a vacuum did result in lowered O_2 permeabilities and discolored the PTMSP films. However, the original permeability was recovered upon redissolving and casting of the polymer. It was therefore concluded that discoloration was due to changes in the chain packing during heat treatment but that no serious polymer degradation took place.

In summary, it appears that the history of the PTMSP samples that are tested is often not entirely well defined. Films are generally cast from solution at various concentrations and different evaporation conditions and dried far below T_g in air, under vacuum, or with a combination of drying procedures. It is therefore not easy to say how the polymer entered the glassy state. It may not be entirely surprising that the gas permeability coefficients for a high free volume polymer such as PTMSP are then somewhat inconsistent if the work from different laboratories is compared. It appears important to us to define the history of the glass to be measured as well as possible. We have attempted to standardize the sample histories in our work by identical high-temperature thermal treatment in inert gas without an attached support.

The issue of aging of thick PTMSP films seems somewhat controversial in the literature. While some workers report physical aging, others report no significant aging over similar times. Contamination is raised as an issue. The reactivity of the polymer with O_2 may be another issue. We have struggled to exclude all conceivable sources of condensable materials that could be absorbed into the polymer.

No work was discovered in the literature dealing with comparative permeation measurements and aging of thick and relatively thin PTMSP films (3 μm or below, as investigated here).

Aging in Glassy Polymers with Special Consideration of Thin Films. Aging of glassy polymers[18,19] seems to still defy a generally accepted and universal description. This is despite the very considerable amount of work in this area. Nevertheless, a reduction in the sample volume (volume recovery) of a pure polymer sample in the absence of chemical reactions and as a function of time could probably be seen as acceptable evidence of physical aging.[20] The references on aging of glassy polymers given above are by no means meant to be exhaustive for a field of such breadth and depth. The work referenced above can only serve as an introduction to the field. Further review of the general literature on aging is omitted here for the sake of brevity. We will concentrate on thin film behavior that is documented in the literature.

Some of the excess free volume will be eliminated from glassy polymer samples of any thickness.[21] If a volume reduction takes place during physical aging, then this can be probed by a number of techniques. However, the small amount of material and the handling issues for very thin films are serious obstacles. Permeation measurements with permanent gases as we employed them here can be applied to probe both thick and thin films. The free volume in the films has a strong influence on sorption and diffusion of gases. A volume reduction by aging can therefore be tracked by gas permeation.[3]

Braun and Kovacs[22] concluded that aging of glassy polymer samples of 1 mm thick sheets and powders with 0.1−1 μm particle size was not different. The nature of the polymer and the experimental conditions may have prevented the observation of accelerated aging in thin films that we report here and elsewhere.[3]

McCaig and Paul[23] have reported experiments on physical aging in thin glassy polymer films of a polyarylate. Qualitatively similar results as reported earlier[3,26] were found. An important additional experimental proof of accelerated thin film aging was an experiment where aging was reversed by reheating of the thin film above T_g. The accelerated aging process in the thin film that was originally observed was essentially reproduced after reheating. This confirms the physical nature of the observed aging process.

McCaig et al.[24] have reported on a mathematical model to capture the phenomena of aging of thin glassy

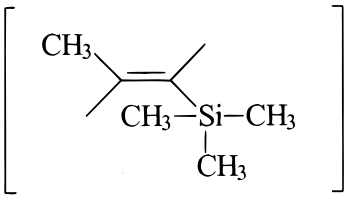

Figure 1. Repeat unit of poly[1-(trimethylsilyl)-1-propyne] (PTMSP).

polymer films. McCaig et al.'s model and graphical data representations (permeability as a function of time over square of the film thickness) assume among other conditions a constant film thickness. The accelerated volume recovery of thin polymer films during aging has been shown previously directly by densitometry.[26] This significant thickness decrease of thin films during aging may be an issue in the model development, the choice of plots, and the calculation of absolute gas permeabilities by McCaig et al.

On the basis of our observations, we postulate a diffusion-like mechanism of free volume elimination at the surface of the samples as was suggested earlier.[26] This mechanism only becomes important when the sample thickness is reduced sufficiently. This has been proposed conceptually,[25] but no experimental evidence was available. The first explicit experimental proof of this concept for several polymers with a variety of methods (gas permeation, densitometry, X-ray diffraction) and a new model (incorporating thickness-dependent glass transition temperatures) were published previously by the coauthors of the work presented here.[2,26]

Experimental Section

Materials. The repeat unit of PTMSP is shown in Figure 1. The polymer was supplied by Air Products and Chemicals, Inc. All polymer films were cast from solutions of the same batch of polymer in toluene (Aldrich, 99.9% purity, used as received). After heat treatment and cooling (see below) films for permeation tests were prepared by adhering aluminum foil masks to the polymer films[3] with an epoxy adhesive (Duro Master Mend). All gases (minimum purity 99.9%) were obtained from Air Products and Chemicals, Inc., and used as received.

Film Preparation. The films were cast from toluene solutions containing approximately 3.6 and 0.07 wt % of polymer (85 μm films and 3 and 1 μm films, respectively). The solutions were filtered through a 0.45 μm Teflon syringe filter and cast directly into a stainless steel casting ring on a leveled mirror. A second glass plate was placed across the top of the casting ring to slow evaporation. The initial evaporation was performed in a glovebag in toluene-enriched air. After 48 h, the films were removed from the mirror by immersion in water. The films were further dried under vacuum at 100 °C to a constant weight. The vacuum system was equipped with a trap to prevent oil vapor back-diffusion.

The history of the samples used here must be well defined and as uniform from sample to sample as possible. We used a controlled procedure described in detail elsewhere.[26] A He stream (about 100 cm^3 (STP)/min) is purged continuously through a preheating coil into a steel sample chamber inside of a gas chromatograph oven chamber (GC). This removes residual solvent, prevents buildup of contaminants, and prevents chemical reactions with oxygen. The films are suspended in the sample chamber on rings so that the area to be used in permeation experiments is not in contact with a solid. This eliminates issues of polymer chain orientation near polymer−solid interfaces. The GC oven is programmed for heating to 250 °C, holding (15 min), and cooling to room temperature at 5.0 °C/min.

Film Thickness and Area. After drying and imprinting of the thermal history the film thicknesses were measured. For thick films a known area was weighed, and using the measured density,[8] the film thickness was calculated. The accuracy as determined by repeated measurements was estimated to be within 2% of the reported value. The thickness of the thick films is 85 μm.

The thickness of the thin films is determined by mass balance, using the concentration and amount of the casting solution. The same macroscopic density as for the thick films is assumed. This assumption may lead to an error of on the order of several percent of the calculated thickness compared to the actual thickness, due to density differences between thick films and thin films. This error is likely time dependent since the thin films physically age and thereby densify. The calculated thickness of the thin film was about 1 μm. Overall, considering the significant differences in permeabilities that were found (see below), the error introduced by assuming a constant density for all films is not sufficient to explain the observed permeability differences. Furthermore, the shape of the permeability vs time curves is not influenced by errors in the assumed thickness.

The permeation area was determined by successively magnified xerographic images of the masked permeation area taken after the end of the permeation experiments. The size of the permeation area was then determined gravimetrically from the enlarged images. The average permeation area determined by the above procedure is 0.06 cm^2 for the thin film with an error of about 1%.

Permeation Measurements. The permeability was studied by single-gas permeation using a constant-volume/variable-pressure apparatus. The permeation cell was maintained at 35.0 ± 0.1 °C. The feed pressure was 2 psia. A slow purge stream was maintained on the feed side of the film. On the permeate side of the film, the gas pressure was less than 10 Torr and considered negligible.

A liquid nitrogen trap was used both in the gas line to the permeation cell (feed) and also upstream of the vacuum pump (permeate side). The vacuum pump was equipped with an adsorbent-type foreline trap.

The leak rate into the vacuum system introduced an error for the permeability measurement of less than 0.01% for the slowest gas. These techniques have been described in greater detail for example by Koros.[27]

The initial N_2 permeability of the films was also checked as a function of feed gas pressure (2, 3, and 4 psia) to detect any defects in the films. The permeability did not change significantly as a function of pressure.

Results and Discussion

It is important to note that defects (pinholes, etc.) are probably more likely in thin films. Such defects would *increase* the calculated permeability coefficient values and decrease calculated gas selectivities. Overall, small defects in the thin films would counteract any evidence of accelerated aging of thin films and could not be responsible for the results discussed below. Significant defects would also be easily detected by low gas selectivities for the thin films compared to thick films.

Figures 2 and 3 present the time dependence of the He and N_2 permeability coefficients for thin and thick films. It is apparent that the aging process is accelerated for the thin films while the thick films do not age significantly. The aging also progressively accelerates as the film thickness declines. This behavior is consistent with a diffusion-like process of excess free volume elimination at the surface of the films.

Since both N_2 and He are not highly sorbing gases, one could interpret the ideal He/N_2 selectivity (the ratio of the single gas permeabilities) as governed mostly by the diffusivity of the gases. The ideal gas selectivities for both films are presented in Figure 4. This figure

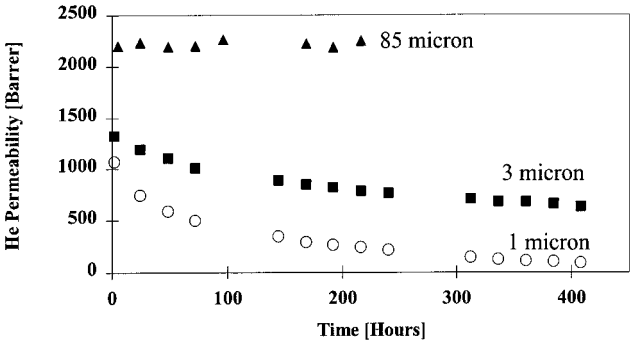

Figure 2. He permeability coefficients as a function of aging time for thin, intermediate, and thick PTMSP films (35 °C, feed pressure 2 psia). 1 barrer = 10^{-10} cm^3 (STP) cm/(cm^2 s cmHg).

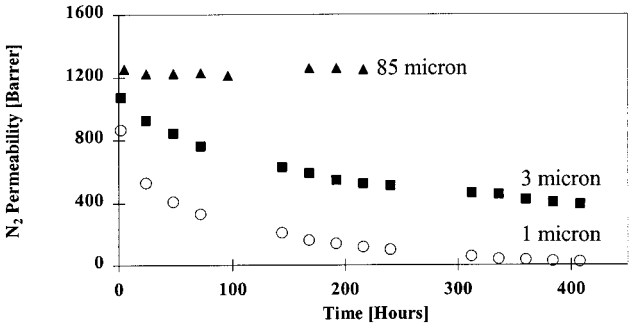

Figure 3. N_2 permeability coefficients as a function of aging time for thin, intermediate, and thick PTMSP films (35 °C, feed pressure 2 psia). 1 barrer = 10^{-10} cm^3 (STP) cm/(cm^2 s cmHg).

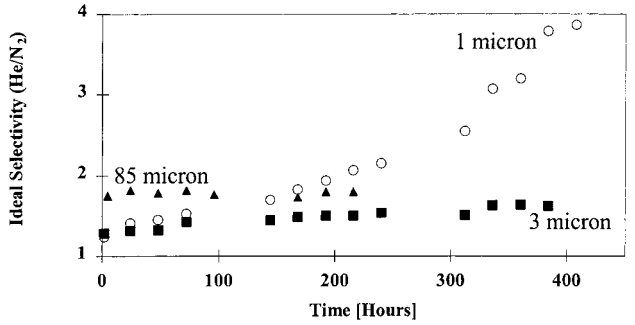

Figure 4. Ideal He/N_2 selectivity as a function of aging time for thin, intermediate, and thick PTMSP films (35 °C, feed pressure 2 psia).

shows that the aging process does not affect the selectivity of the thick film. The intermediate thickness film shows a stable or slightly increasing selectivity. A clear increase in the selectivity coefficient for the thin film is observed. Small defects in the thin films are likely responsible for the initially lower selectivity compared to that of the thick film. In respect to the permeabilities shown before, defects will however only *increase* the permeability coefficients. The accelerated physical aging seen in Figures 2 and 3 can therefore not be interpreted as being due to defects.

Interpretation and Modeling

The hypothesis that physical aging in glassy polymers proceeds by two mechanisms (a bulk mechanism and a surface related mechanism) was put forward several years ago and supported by a number of characterization methods applied to two glassy polymers.[26] The elimination of free volume at the film surface becomes important as the surface-to-volume ratio decreases. Drawing on published data, a critical range for the film thickness where the surface-related aging of glassy polymers becomes important appears to be a few micrometers and below.[2,3,23,26] Interestingly, the high free volume polymer investigated here ages rapidly already at a film thickness of about 3 μm. This is at the high limit of film thicknesses reported to show rapid aging. A polymer with high free volume such as PTMSP may be expected to show rapid aging at rather high film thicknesses since aging is expected to be self-retarding with respect to the amount of free volume.

We have previously put forward a phenomenological model for aging of thin glassy polymer films.[2] We chose this path over the development of a free volume diffusion model[24] since the time- and location-dependent size distribution of free volume packets in a film is not easily accessible. Free volume packets may coalesce or divide before being eliminated. In addition, film thickness changes with time especially in rapidly aging thin films tend to complicate the boundary conditions needed to solve a diffusion model.

An attractive point of our model[2] may be that we combine both the classical results on volume recovery of bulk polymeric glasses[20] and the more recent discovery of thickness-dependent glass transition temperatures of glassy polymers.[28] Combining these two phenomena, we were able to qualitatively arrive at results that confirm a third independent observation: our time-dependent gas permeation measurements on thin and thick films.

Concluding Remarks

The reduction of gas permeabilities of a glassy polymer (PTMSP) with time deep within the glassy state is strongly accelerated as the film thickness is reduced to the low micrometer range. No significant gas permeability decline was found for thick films, while thin films showed a rapid drop in permeability that is accelerated with reduced thickness. We interpret the permeability loss as due to physical aging since the history of the films was well-defined and standardized. The physical aging of PTMSP is therefore thickness-dependent. This is further evidence for the previously postulated diffusive removal of free volume from the polymer glass as a mechanism for physical aging[25,26] that is very significant in thin glassy polymer structures while it is not easily observed on a practical time scale in thick films. The critical thickness for rapid aging of thin glassy polymer films seems to be the highest for the high free volume polymer PTMSP (about 3 μm) compared to other more conventional polymers.

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