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Free Volume Expansion of Poly[1-(trimethylsilyl)-1-propyne] Treated in Supercritical Carbon Dioxide As Revealed by Positron Annihilation Lifetime Spectroscopy

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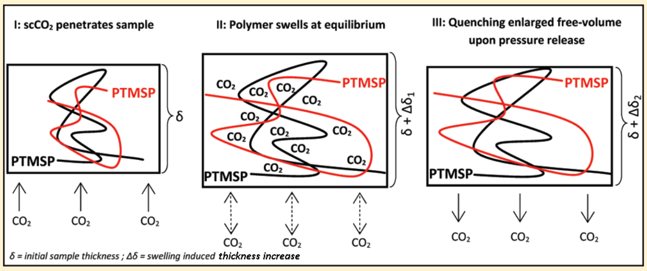
ABSTRACT: The free volume changes of poly[1-(trimethylsilyl)-1-propyne] (PTMSP) treated in supercritical CO_2 ($scCO_2$) were investigated with positron annihilation lifetime spectroscopy (PALS). CO_2 is known to plasticize and increase the free volume size of a broad range of polymers. In this work dense PTMSP films were treated with $scCO_2$ under different pressures and temperatures, resulting in the enlargement of the characteristic channel-like holes (R_3) and the larger free volume cages (R_4) up to 39% and 19%, respectively. The free volume enlargement was found to have a relaxation time of ∼30 years. At higher temperatures (110−150 °C), the *o*-Ps intensities and gel permeation chromatography (GPC) data revealed chemical changes of the $scCO_2$-treated polymer due to the onset of PTMSP's degradation. However, at lower temperatures (40−70 °C), significant free volume cavity size increases to 25% for R_3 and 9% for R_4 were also observed.



1. INTRODUCTION

Poly[1-(trimethylsilyl)-1-propyne] (PTMSP) is a substituted polyacetylene that combines a rigid backbone chain with bulky trimethylsilyl side groups. The latter restrict rotational mobility and limit the ability of the polymer chains to closely pack. As a result of inefficient chain packing due to the bulky pendant groups and poor interchain cohesion, neat PTMSP is understood to exhibit an extremely high free volume fraction and inherent nanoporosity.[1] Its free volume shows a bimodal distribution, with cavities having a main radius in the order of 0.3 and 0.5 nm according to the spherical cavity model.[2] It has been postulated that these small and larger cavities create a series of interconnected free volume pathways, thus giving PTMSP unique high-permeability characteristics.[3] Moreover, PTMSP materials exhibit a reverse-selective behavior due to the fact that relatively large organic molecules adsorb on the walls of the free volume elements, thereby hampering the transport of smaller, permanent gases.[4] Thanks to its intrinsic nanoporosity, glassy nature (T_g > 300 °C), reverse selectivity, and pronounced hydrophobicity, PTMSP has received much attention in the literature as a promising membrane-forming material. Since Masuda synthesized the polymer for the first time,[5] PTMSP still remains the most permeable polymer for gas separation[6−12] and pervaporation applications.[13−15] Several researchers have successfully attempted to increase the inherent high free volume of neat PTMSP even more by incorporating inorganic nanofillers in the polymer matrix.[7−13,16]

In this work, an alternative method consisting of a supercritical CO_2 ($scCO_2$)-treatment is proposed to increase the inherent high free volume and large permeability of neat PTMSP. Supercritical (T_c = 31.1 °C, p_c = 7.37 MPa) or compressed CO_2 has been extensively studied as an alternative solvent to water or organic solvents due to its environmentally benign character and tunable properties.[17−20] By varying the pressure or temperature, the solubility of CO_2 can be modified. Pressurized or supercritical CO_2 is known to swell and plasticize glassy polymers, leading to a depression of their T_g to almost the same extent as solvents or vapors.[21,22] The effect of $scCO_2$ or compressed CO_2 on the physical properties, free volume, or crystal structure of several polymers has been reported,[21−33] but high free volume polyacetylenes have hardly been investigated. Mohsen et al. studied the free volume parameters of PTMSP after sorption and desorption of CO_2 and CH_4 gases.[34] However, the authors only reported data of PTMSP samples treated at mild conditions, i.e., 1 bar and room temperature.

In the present work, the free volume changes of PTMSP films under the influence of a $scCO_2$-treatment have been studied by positron annihilation lifetime spectroscopy (PALS). First, the influence of pressure and temperature on the free volume changes is discussed. Subsequently, the long-term stability, the

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Table 1. ScCO$_2$ Treatment Conditions Used in This Study

	temperature (°C)			
pressure (MPa)	40	70	110	150
12	X		X	
16		X		X
20	X		X	
24		X		X

relaxation of the free volume, the reproducibility of the method, and the thermal stability of the treated PTMSP films are reported.

2. EXPERIMENTAL SECTION

2.1. Materials. Poly[1-(trimethylsilyl)-1-propyne] (PTMSP, $M_w \sim 4.49 \times 10^5$ g mol^{-1}) was purchased from Gelest, Inc., and dissolved in analytical graded toluene, obtained from Merck (Belgium). Technical grade liquid carbon dioxide was purchased from Air Products (Belgium).

2.2. Sample Preparation. Dense PTMSP films were prepared from toluene solutions containing 3 wt % of polymer. The polymer solutions were magnetically stirred for 4 days until complete dissolution, after which they were cast in a Petri dish. After casting, the films were dried for 10 days at ambient conditions and subsequently annealed for 2 h at 80 °C in a nitrogen atmosphere.

2.3. ScCO$_2$ Treatment. A high-pressure reactor from Premex Reactor Ag (Switzerland) with an internal volume of 1 L was used in combination with a ProMinent Orlita MhS 30/10 diaphragm pump (Belgium). Circular disks with a thickness of ~100 μm and a diameter of about 9 cm were cut from the PTMSP films and placed in the reactor, which was then sealed. First, the reactor vessel, pump, and piping were flushed with CO$_2$ until liquid CO$_2$ was obtained at the outlet. Subsequently, the reactor was filled with liquid CO$_2$ prior to heating. As the pressure increases upon heating due to phase transition and expansion of the liquid CO$_2$, a regulation valve was needed to prevent the pressure from crossing the set point pressure. In the present study, apart from a reference untreated PTMSP sample, PTMSP samples were treated at eight different conditions (Table 1), at pressures between 12 and 24 MPa and temperatures between 40 and 150 °C. Once the desired temperature and pressure were reached, the reactor was kept for 6 h under stable scCO$_2$ conditions. After, the CO$_2$ pressure was slowly released at 0.15 MPa s^{-1} as higher rates of depressurization can lead to foaming of the polymer. To prevent CO$_2$ from liquefying during depressurization, the reactor temperature was kept above 35 °C.

2.4. Positron Annihilation Lifetime Spectroscopy. The free volume of dense scCO$_2$-treated and untreated PTMSP films was measured by positron annihilation lifetime spectroscopy (PALS), which is a nondestructive technique that allows to probe solid structures at an atomic scale. By measuring the lifetime of orthopositronium (o-Ps) prior to annihilation ($\tau_{\text{o-Ps}}$), the size of the free volume cavities can be deduced, according to the Tao–Eldrup model (eq 1):

$$\tau_{\text{o-ps}} = 0.5\left(1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\frac{2\pi R}{R_0}\right)^{-1} \qquad (1)$$

This equation models the free volume in polymers as spherical cavities with a radius R. An o-Ps in a spherical free volume cavity is described as a particle in a spherical potential well with a radius $R_0 = R + \Delta R$, where ΔR represents the electron layer with a thickness of 1.66 Å. The free volume cavity sizes can be calculated according to eq 2:

$$\nu = \frac{4}{3}\pi R^3 \qquad (2)$$

Together with each o-Ps lifetime (τ) a relative intensity (I) is obtained from the PALS measurements, which expresses the relative probability of o-Ps formation.

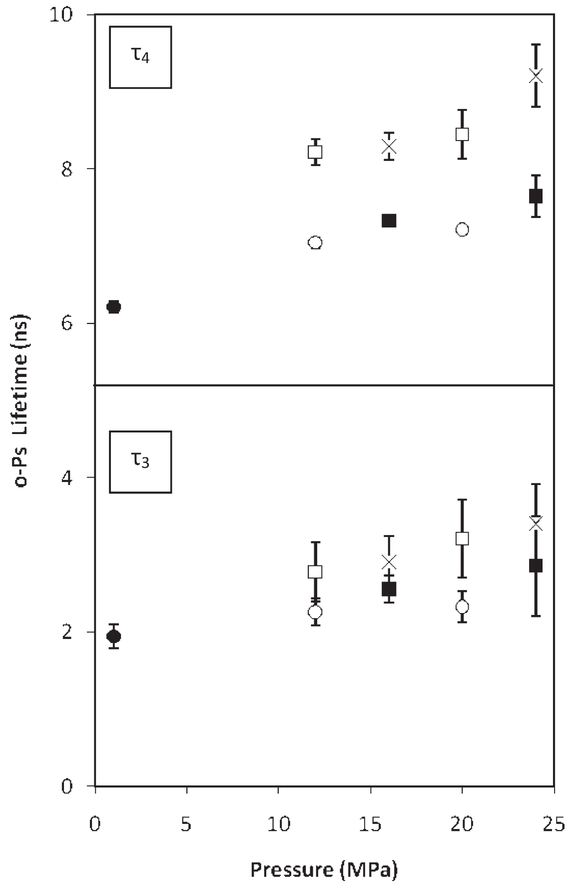


Figure 1. o-Ps lifetimes as a function of pressure and temperature of the scCO$_2$ treatment. Different treatment temperatures are represented by the following symbols: (●) room temperature, (○) 40 °C, (■) 70 °C, (□) 110 °C, and (×) 150 °C.

A ^{22}Na salt, encapsulated between two sheets of Kapton polyimide foil, was used as positron source. The samples were applied in a sandwich configuration with the PTMSP film being stacked at a total thickness of 1 mm on either side of the source. During the measurements, a count rate of ~700 s^{-1} was achieved, and each spectrum was built up of 2.5 million counts. The spectra were recorded on a fast–fast coincidence spectrometer system equipped with CsF crystals. Each sample was measured five times, and the spectra were analyzed with PALSFIT 1.54 software. This evaluation method extracts τ and I values from the recorded spectra with a model function consisting of a sum of decaying exponentials convoluted with the resolution function of the lifetime spectrometer plus a constant background. The PTMSP samples were analyzed with a four-component analysis. The variance of fit was close to unity (1.0–1.1) for all performed analyses.

To determine the thermal stability of the scCO$_2$-treated PTMSP films, PALS measurements at increasing temperatures in the range 30–170 °C (increments of 20 °C) were performed on selected scCO$_2$-treated samples as well as on a reference untreated sample. At each measuring temperature, the samples were kept isothermally for 240 min and four PALS spectra, each built up of ~2.5 million counts were recorded. During cooling, the samples were measured at the same temperatures as in the heating sequence. In all cases, the first of the four spectra was discarded to correct for temperature stabilization of the polymer sample at the start of each new measurement.

2.5. Gel Permeation Chromatography. The thermal effect of the scCO$_2$ treatment on the molecular mass (M_w) of the polymer was investigated by gel permeation chromatography (GPC). The samples

Table 2. o-Ps Lifetime (τ), Intensities (I), and Free Volume Radii (R) of the scCO$_2$-Treated Samples and Standard Deviations on the Measurements (Five Spectra)[a]

	τ_2 (ns)	I_2 (%)	τ_3 (ns)	I_3 (%)	R_3 (nm)[b]	τ_4 (ns)	I_4 (%)	R_4 (nm)[b]
reference	0.44 ± 0.01	44.7 ± 0.9	1.95 ± 0.16	7.2 ± 0.5	0.28	6.21 ± 0.08	33.0 ± 0.7	0.53
40 °C, 12 MPa	0.44 ± 0.01	47.5 ± 1.3	2.26 ± 0.18	8.0 ± 0.2	0.31	7.05 ± 0.07	30.8 ± 0.5	0.56
40 °C, 20 MPa	0.45 ± 0.02	43.6 ± 1.6	2.33 ± 0.21	8.3 ± 0.4	0.31	7.22 ± 0.05	32.4 ± 0.6	0.57
70 °C, 16 MPa	0.46 ± 0.01	42.8 ± 1.3	2.56 ± 0.17	8.6 ± 0.5	0.33	7.33 ± 0.06	31.3 ± 0.6	0.57
70 °C, 24 MPa	0.47 ± 0.01	42.7 ± 1.0	2.86 ± 0.65	9.7 ± 2.1	0.35	7.65 ± 0.27	29.7 ± 2.7	0.58
110 °C, 12 MPa	0.46 ± 0.02	43.0 ± 1.5	2.78 ± 0.38	9.2 ± 0.8	0.35	8.22 ± 0.17	30.1 ± 1.2	0.60
110 °C, 20 MPa	0.47 ± 0.02	42.8 ± 1.7	3.21 ± 0.51	10.6 ± 1.8	0.38	8.45 ± 0.32	28.4 ± 2.2	0.61
150 °C, 16 MPa	0.47 ± 0.01	42.5 ± 1.3	2.91 ± 0.33	9.1 ± 0.7	0.36	8.29 ± 0.17	29.9 ± 1.0	0.60
150 °C, 24 MPa	0.47 ± 0.01	46.9 ± 1.3	3.40 ± 0.51	11.1 ± 1.8	0.39	9.21 ± 0.41	26.2 ± 2.2	0.63

[a] τ_1 is fixed at 0.26 ns, and $I_1 = 1 - I_2 - I_3 - I_4$. [b] Calculated from average τ values.

were annealed in an oven at 160 °C for 1.5 and 8 h in a nitrogen atmosphere. The cured and reference samples were dissolved in THF and injected on a TSP GPC column with a Shodex RI-71 refractometer.

3. RESULTS AND DISCUSSION

3.1. Free Volume Changes in PTMSP Induced by scCO$_2$.

The PALS spectra of high free volume polyacetylenes like PTMSP are typically analyzed with a four-component analysis.[7,10,11,34] The third lifetime (τ_3) represents the channel-like holes interconnecting the larger cages which are in turn represented by the fourth lifetime (τ_4). The effect of the scCO$_2$ treatment of the PTMSP films on the *o*-Ps lifetimes τ_3 and τ_4 is shown in Figure 1. Treating the films with pressurized CO$_2$ clearly induces an increase of the initial free volume, as reported for other polymers.[24,26,27,34] For the present PTMSP system, both lifetimes τ_3 and τ_4 significantly increase compared to the untreated reference sample. For the scCO$_2$-treated samples in the temperature range of 40−110 °C, increasing the treatment pressure has no significant effect on τ_3 and τ_4. At higher temperatures (150 °C), however, the effect of the pressure is more pronounced. The effect of the scCO$_2$ treatment on the channel-like cavities, represented by τ_3, is clearly larger than the effect on τ_4, representing the large cages. Increases up to 74% for τ_3 and 48% for τ_4 are observed for the samples treated at the most extreme pressure/temperature conditions. These values are much larger than those reported in the literature for a similar PTMSP system treated in a CO$_2$ atmosphere at mild conditions. Mohsen et al. observed a 7.4% increase of both lifetimes τ_3 and τ_4 for PTMSP after desorption of CO$_2$ at 1 bar and room temperature,[34] thus demonstrating the large effect of pressure and temperature on the free volume expansion of scCO$_2$-treated PTMSP. For other polymers like poly(ethylene naphthalate)[24] and syndiotactic polystyrene,[27] *o*-Ps lifetime increases up to ~10% were reported after scCO$_2$ treatments of 6 h at 20 MPa and 100 °C and 3−10 h at 16 MPa and 40 °C, respectively. PALS does unfortunately not reveal any information about the number of free volume cavities. However, information on the homogeneity or distribution of the distinct lifetime components τ_3 and τ_4 can be deduced from the standard deviation on the five spectra obtained for each of the samples. As not all standard deviations are clearly visible in Figure 1, Table 2 gives an overview of the errors on the different τ values. It can be seen that the deviation on the τ_3 lifetimes is large compared to those on the τ_4 values. The larger deviation on τ_3 suggests a broader distribution of the free volume cavities corresponding to the channel-like holes. In general, Figure 1 and Table 2 show a clear increase of the error on the lifetimes of the treated samples compared to the reference, indicating the broadening effect of the scCO$_2$ treatment on the free volume distribution. At more intense pressure/temperature conditions, the standard deviations are even higher.

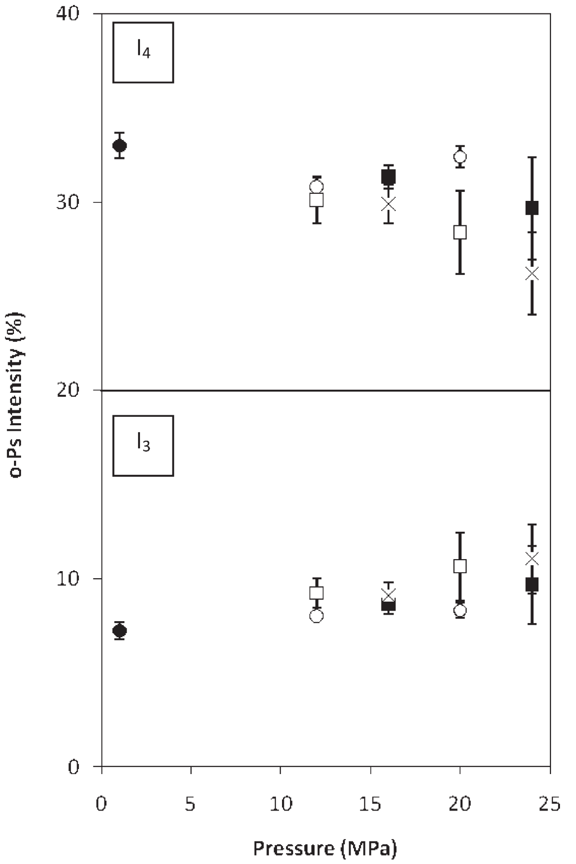
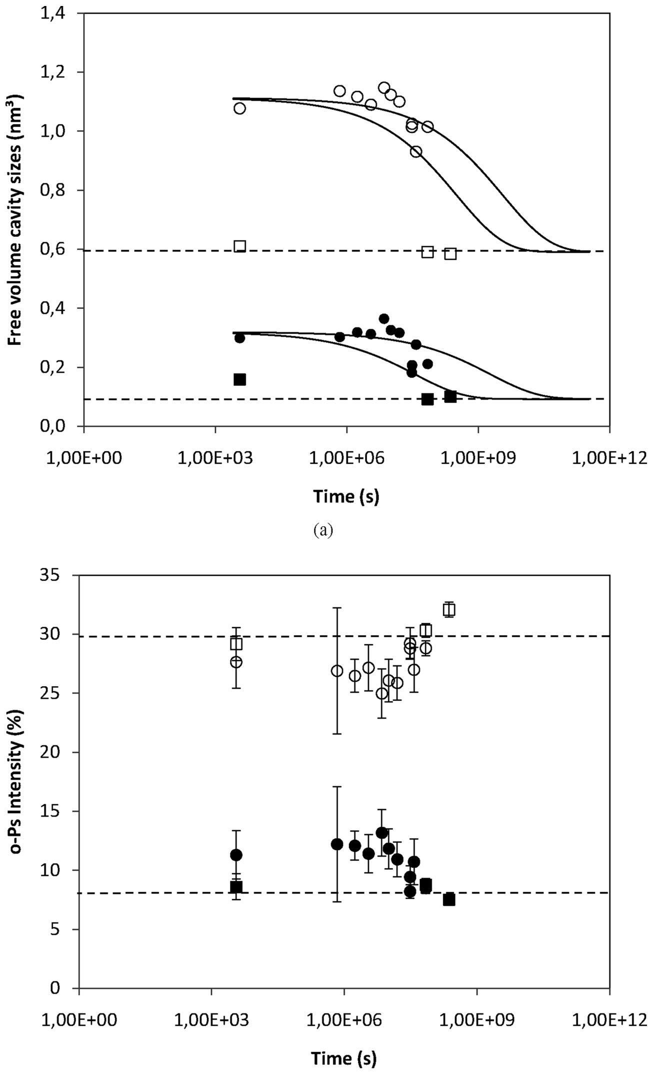


Figure 2. o-Ps lifetime intensities as a function of pressure and temperature of the scCO$_2$ treatment. Different treatment temperatures are represented by the following symbols: (●) room temperature, (○) 40 °C, (■) 70 °C, (□) 110 °C, and (×) 150 °C.

Each *o*-Ps lifetime results in a corresponding intensity (I), which provides information about the relative probability of *o*-Ps formation and indirectly about the chemical structure of the material. Figure 2 shows the intensities of scCO$_2$-treated and

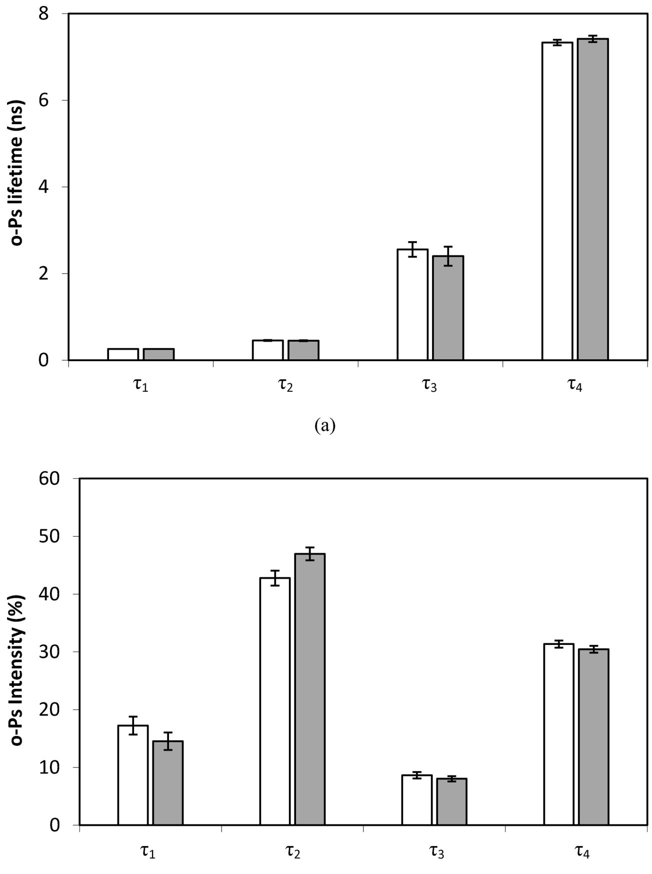


(a)

(b)

Figure 3. Long-term measurements of untreated (■, □) and scCO$_2$-treated (●, ○) PTMSP (16 MPa, 150 °C): (a) free volume ν_3 (filled symbols) and ν_4 (unfilled symbols) and (b) *o*-Ps lifetime intensity I_3 (filled symbols) and I_4 (unfilled symbols). The dotted lines represent the free volume and *o*-Ps lifetime intensity of the untreated samples, whereas the solid lines represent the relaxation curve estimated from the minimum and maximum t_ν.

untreated PTMSP samples. For τ_3 no significant change in intensity is observed, while I_4 clearly decreases with increasing treatment pressure and increasing temperature. This change of intensity may be attributed to the chemical degradation of the polymer under these conditions. The thermal effect of the scCO$_2$ treatment on the M_w distribution was investigated by GPC. A drop of 75% in M_w and a concomitant decrease in polydispersity of 35% were observed for a PTMSP sample that was not subjected to the scCO$_2$ treatment but was instead treated for 1.5 h at 160 °C in a nitrogen atmosphere. The onset of thermal degradation of PTMSP, investigated by thermogravimetrical analysis at a heating rate of 5 °C min^{-1}, is reported to occur around 155 °C.[10] For scCO$_2$-treated samples that have been subjected for 6 h to temperatures in the range of this degradation temperature (110−150 °C, isothermally), chemical modification of the polymer can be anticipated, thus explaining the observed change of the lifetime intensity. Similar to the lifetimes, the standard deviations on the *I* values clearly increase with the intensity of the scCO$_2$ treatment (Figure 2, Table 2).



(a)

(b)

Figure 4. (a) *o*-Ps lifetimes and (b) corresponding intensities of scCO$_2$-treated PTMSP (16 MPa, 70 °C). The open bars represent the sample made in the first run and the filled bars the newly prepared sample.

3.2. Long-Term Stability and Reproducibility of PTMSP Free Volume Enlarged by scCO$_2$.

Oka et al. reported the relaxation of the enlarged free volume of scCO$_2$-treated polystyrene as a function of time.[26] The *o*-Ps lifetime decreased from an initial value of 2.40 to 2.20 ns approximately 250 h after the scCO$_2$ treatment. Thus, a decrease in lifetime of ∼8% was noticed in this relatively short time frame, even though the lifetime remained higher than the initial 2.06 ns of untreated polystyrene. Figure 3a shows the free volume relaxation of a PTMSP sample subjected to a sCO$_2$ treatment at 16 MPa and 150 °C and of a reference PTMSP sample. It can be observed that the enlarged free volume is still present at all times; the relaxation of the excess free volume is expected after 10^7−10^8 s for the characteristic channel-like holes (ν_3) and 10^8−10^9 s for the large cages (ν_4). The relaxation of the free volume of amorphous polymers can be fairly described with eq 3:[35,36]

$$\nu - \nu_\infty = (\nu_0 - \nu_\infty)\mathrm{e}^{-(t/t_\nu)^m} \qquad (3)$$

with ν the free volume at time t, ν_0 the initial free volume, ν_∞ the free volume at infinitely long times, t_ν the characteristic free volume relaxation time, and m equal to 0.4.[35,36] Figure 3a shows the plotted eq 2, using the minimum and maximum characteristic volume relaxation times t_ν estimated from the experimental data. Since the relaxation curve is just at the onset of its decay, fitting

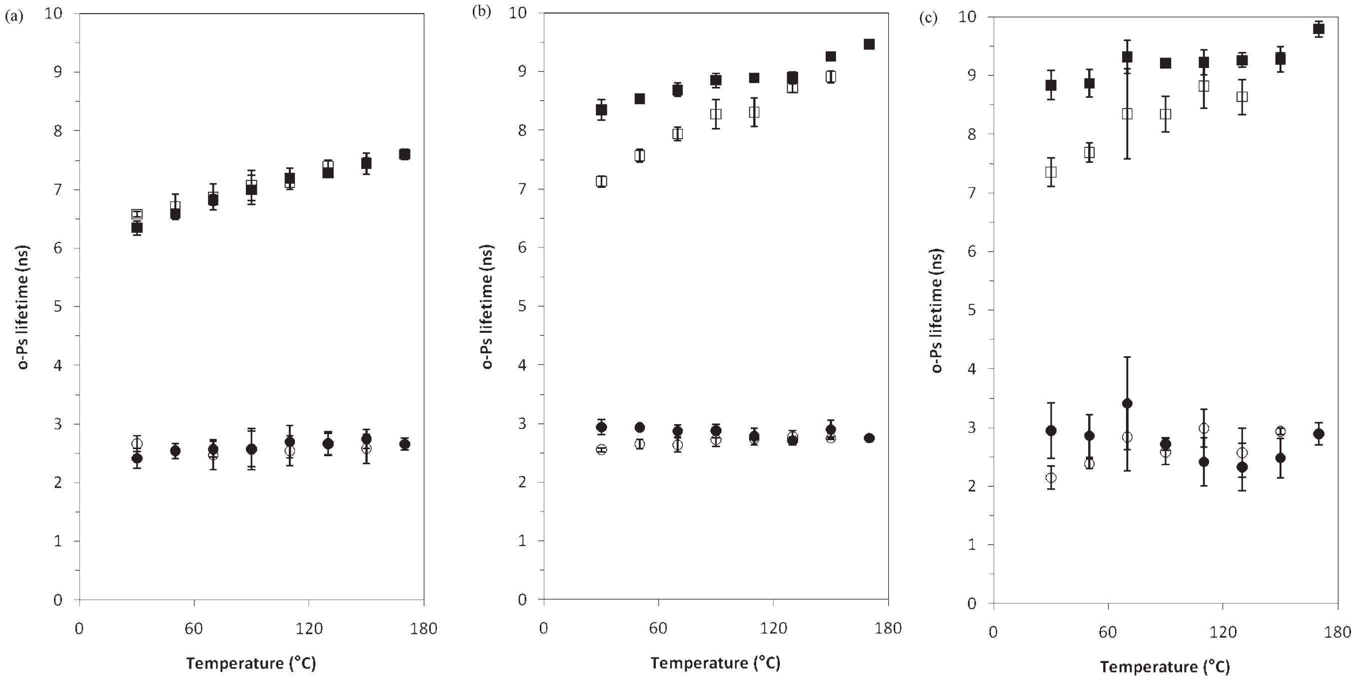


Figure 5. Changes of *o*-Ps lifetime τ_3 (●, ○) and τ_4 (■, □) during a heating (filled symbols) and cooling (open symbols) sequence: (a) untreated PTMSP, (b) PTMSP $scCO_2$-treated at 20 MPa and 110 °C, and (c) PTMSP $scCO_2$-treated at 24 MPa and 150 °C.

the model through these data is too ambitious. However, the order of magnitude of t_v for both lifetimes can be deduced from the curves. A characteristic relaxation time in the order of 10^9 s or ∼30 years can be estimated for the enlarged free volume of $scCO_2$-treated PTMSP.

The pronounced stability of the enlarged free volume at room temperature may be explained by the extremely high T_g of PTMSP, above 300 °C. Since PTMSP is at room temperature far below its T_g, the polymer chain segments of the $scCO_2$-treated samples exhibit low mobility, and consequently, the excess free volume will relax extremely slowly. For polymers with a much lower T_g, such as polystyrene ($T_g \sim 100$ °C), on the other hand, the polymer chain segments are sufficiently mobile at room temperature to permit relaxation of the enlarged free volume.[26] It can be observed in Figure 3b that the intensities of the $scCO_2$-treated and untreated samples are fairly constant as a function of time.

To investigate the reproducibility of the $scCO_2$ treatment, a new sample starting from a fresh PTMSP solution was prepared and treated under equal conditions as before. Figure 4 shows all four *o*-Ps lifetimes of the two independently prepared and $scCO_2$-treated PTMSP samples (16 MPa, 70 °C). As can be seen in this figure, almost equal lifetimes were obtained. This almost perfect reproducibility demonstrates the robustness of the $scCO_2$ treatment and of the entire preparation method.

3.3. Temperature Stability of PTMSP Free Volume Enlarged by $scCO_2$. The long-term stability at room temperature of the free volume change achieved by subjecting PTMSP to $scCO_2$ was demonstrated in Figure 3. In real (membrane) applications, however, the materials are likely to be operated at higher temperatures, which could induce a decrease of the enlarged free volume if the operation temperature is close to or above the T_g. Therefore, stability measurements were carried out at higher temperatures on two selected $scCO_2$-treated samples and on the untreated reference sample. PALS measurements were performed during thermal treatment of the samples at a series of gradually increasing temperatures in the interval 30−170 °C. The samples were kept isothermally for 240 min (four spectra) at each temperature in this range with increments of 20 °C. After heating up to 170 °C, the temperature cycle was completed by cooling down the samples and isothermally keeping them at the same temperatures as during the heating sequence.

Since the T_g of PTMSP (>300 °C) is well above its degradation temperature (onset around 155 °C),[10] crossing the T_g during heating was impossible. Figure 5a shows the changes of the *o*-Ps lifetimes τ_3 and τ_4 of an untreated PTMSP sample as a function of temperature. It can be seen that after finishing the temperature cycle both lifetimes remain unaffected, indicating that no change of the free volume cavity sizes has occurred. In general, a clear expansion of the free volume due to an increase of a polymer's chain mobility could be anticipated upon heating a sample close to its T_g.[24] However, since the temperature profile is far from PTMSP's T_g, only a slight increase in τ_4 was observed, while τ_3 remained almost constant throughout the entire temperature range (Figure 5a). Since the onset temperature of PTMSP degradation is crossed during the temperature profile, chemical changes can be expected. A clear decrease of *o*-Ps intensity I_4 during the cooling sequence of the PALS measurement was indeed noticed, indicating chemical changes of the polymer (Figure 6a).

In contrast to the untreated reference sample, the enlarged free volume of the two selected $scCO_2$-treated samples was observed to partially relax when the temperature cycle was completed (Figure 5b,c). While a partial relaxation (12−16%) of τ_4 was observed for both samples, τ_3 dropped to the initial values of the untreated reference sample (Figure 5a).

Andersson et al. reported a complete relaxation of the free volume of poly(ethylene naphthalate) (PEN) treated for 6 h at 8 and 20 MPa CO_2 pressure and 100 °C and subsequently subjected to an identical temperature cycle.[24] In contrast to

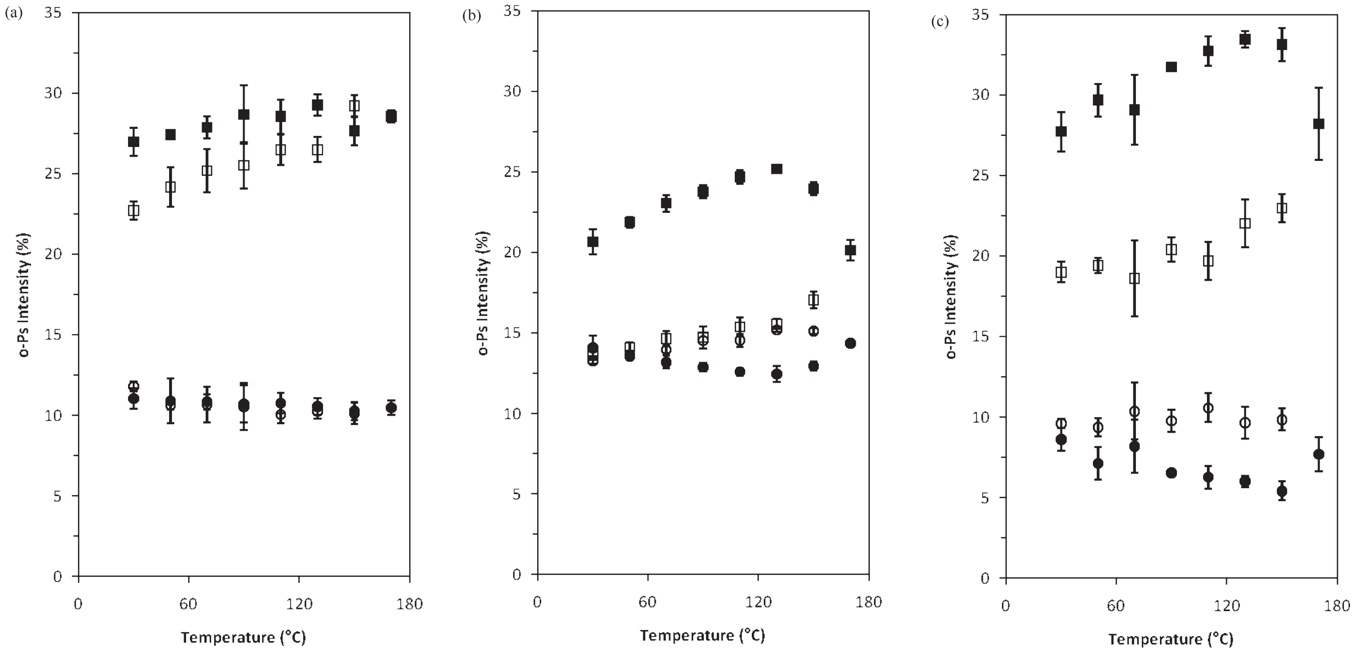


Figure 6. Changes of *o*-Ps intensities I_3 (●, ○) and I_4 (■, □) during a heating (filled symbols) and cooling (open symbols) sequence: (a) untreated PTMSP, (b) PTMSP $scCO_2$-treated at 20 MPa and 110 °C, and (c) PTMSP $scCO_2$-treated at 24 MPa and 150 °C.

our study, the T_g of PEN (120 °C) was crossed during the temperature cycle.

Subjecting the PTMSP samples to a CO_2 treatment at high pressures and temperatures clearly affects the chemical structure of the material as well. In Figure 6b, I_4 starts far below the initial intensity of the untreated PTMSP sample (Figure 6a). During heating a maximum is observed at 130 °C, after which the degradation initiates and the intensity decreases. In the cooling curve a further decrease of intensity is noticed, especially at temperatures >100 °C. For a sample treated at an even higher pressure and temperature (24 MPa and 150 °C), I_4 starts at the same level as the untreated sample, followed by a maximum at 130 °C and a drastic decrease upon cooling (Figure 6c). The curve of the intensity of the sample treated at 110 °C and 20 MPa is slightly shifted compared to the one treated at 150 °C and 24 MPa. The reasons for this shift are unclear at this moment.

Since degradation of PTMSP starts at 155 °C, applying the $scCO_2$-treated PTMSP films above this temperature is not recommended. On the other hand, Figure 5b,c show that the enhanced free volume partially withstands such harsh temperature conditions, demonstrating a proper stability. Typically, these polymer films could be used as membranes and applied in membrane processes between 25 and 100 °C, far below PTMSP's degradation temperature and T_g.

4. CONCLUSION

PTMSP films treated with $scCO_2$ at different pressures and temperatures resulted in *o*-Ps lifetime increments up to 74% for τ_3 and 48% for τ_4, as revealed by PALS. It was demonstrated that the free volume enlargement of the $scCO_2$-treated PTMSP films had a relaxation time of ~30 years and that the films can be produced with good reproducibility. At high temperatures (110−150 °C), *o*-Ps intensities and GPC data revealed chemical changes in the polymer sample due to thermal degradation of the PTMSP film. However, also at lower temperatures (40−70 °C), significant lifetime increases up to 47% for τ_3 and 23% for τ_4 could be achieved.

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