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Gas Separation Membranes Prepared by Styrene-Grafted Polytrimethylsilylpropyne

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ABSTRACT

Poly(1-trimethylsilyl-1-propyne) (PTMSP)–styrene (St) grafted films were obtained by a radiochemical method. St monomer vapors were absorbed by the PTMSP, and the grafting reaction was thereafter accomplished by Co^{60} gamma irradiation in a nitrogen atmosphere. The films so grafted were tested for nitrogen–oxygen separation. The performances of the membranes were studied as functions of time and percent of grafting. The PTMSP–St grafted membranes showed an increased selectivity factor and better stability in comparison with pure PTMSP. The experimental data and some SEM observations confirmed that the grafting procedure changes the PTMSP matrix structure, filling the voids responsible for the PTMSP permeability change with time.

INTRODUCTION

It is well known that the outstanding characteristics of poly(1-trimethylsilyl-1-propyne) (PTMSP), such as high permeability, decrease due to physical aging, which has been related to several structural reasons (1–4).

In a previous paper (5) we reported the effects of radiochemical grafting on the performances of PTMSP gas separation membranes, and we found

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that grafted polydivinylbenzene (PDVB) could be used to stabilize both permeability and selectivity (separation factors) of the PTMSP films.

Such effects have been ascribed to the filling of structural voids by the grafted polymer and to the presence of crosslinked PDVB. In particular, it was pointed out that the separation factor (α) of the membranes can be increased above the value usually reported for pure PTMSP (6, 7) by increasing the amount of grafted PDVB. It was hypotized that the limiting value of α could be that of the grafted polymer PDVB, although no reports on the selectivity of this polymer have been found in the literature.

As a consequence, it would be interesting to check the effect of grafting different polymers, such as polystyrene (PSt), whose separation factor against oxygen–nitrogen mixtures is reported to be higher than that of PTMSP (8). Another reason for choosing styrene is related to the chemical structure of this momomer which is similar to DVB but is much less subject to crosslinking reactions.

Therefore, the use of St can be useful for checking the contribution of void filling on PTMSP characteristics in the absence of crosslinking reactions. The radiochemical grafting procedure was again used for the reasons outlined in the previous paper (5) The results of our research are reported here.

EXPERIMENTAL

Materials

The following materials were used to synthesize the polymer PTMSP, to make films, and to perform the grafting.

1-Trimethylsilyl-1-propyne (TMSP) from Fluka, purified by distillation over calcium hydride and stored under an argon atmosphere
Toluene from Fluka, refluxed over lithium aluminum hydride
Methanol from Fluka, high purity grade
Tantalum chloride from Aldrich
Styrene monomer from Fluka, washed, dried, vacuum distilled, and stored at 253 K
Chromatographic purity-grade gases (air, He, Ar, N_2) from CARBOGAS

Films Preparation

As in the previous work, PTMSP was synthesized following the procedure suggested by Masuda (9, 10). The membrane films were obtained from dilute solutions (2% in toluene). The solvent was allowed to evaporate under controlled conditions for 1 week; the polymer films were then washed with methanol and vacuum dried to constant weight at room temperature. The thickness of the films obtained ranged between 40 and 60 μm. They were used for the radiochemical graftings.

Grafted Membranes Preparation

PTMSP films were grafted with St monomer by means of gamma irradiation following the same procedure described for DVB grafting (5). Also in this case, it was impossible to irradiate the film in the presence of the liquid monomer due to the solubility of PTMSP in styrene. Moreover, it would be very difficult to separate grafted PTMSP from St homopolymer. Once again we exploited the characteristics of PTSMP as a polymeric gas absorbent (11) and saturated the films with monomer vapors before submitting them to irradiation and graft copolymerization. This was achieved by using the device and the procedure already described (5).

The films treated in this way were then placed under gamma-rays irradiation in a Vickrad "Gammacell" having a 300 C ^{60}Co activity. The (constant) dose rate was 402 Gy/h. During irradiation the samples were kept under a nitrogen atmosphere.

After irradiation the films were washed with boiling methanol, then dried to a constant weight under vacuum. The amount of grafting was measured as the weight increase referred to the initial film weight.

$$G\% = (W - W_0)100/W_0 \tag{1}$$

where W_0 = ungrafted film weight
W = grafted film weight

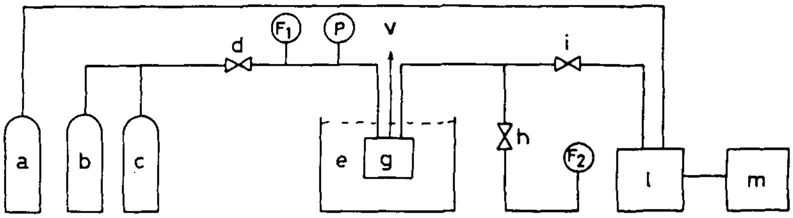
Gas Permeation Measurements

The same method described in a previous paper (5) was used in order to test the membranes operating performances in conditions very close to real ones. The apparatus is schematized in Fig. 1.

Gases were supplied by cylinders, and their flux was measured and controlled by means of electronic regulators. The membrane under test was housed in a "plate-and-frame" module. The tested membrane area was 0.001 m^2, and two membranes could be separately characterized. The temperature was controlled by a thermostatic unit.

Permeate flux was measured by means of a rising bubble flowmeter and forwarded to the injection port of a Varian gas-chromatograph equipped with a molecular sieves column and TC detector; the carrier gas was helium.

This apparatus works up to 1 MPa, and the measurements were carried out mainly at this pressure and at 303 K. Permeability (barrer) and selectiv-



a : He cylinder
b : } gas cylinders
c :
d : mixer
e : thermostatic unit
F_1: flow controller
v : vent
F_2: rising bubble flowmeter
g : module
h : valve
i : valve
l : gas chromatograph
m : data recorder
P : pressure gauge

FIG. 1 Apparatus used for permeability measurements.

ity factor α were measured, with α defined as the ratio between the concentration of the faster permeating gas in the permeate and in the feed.

Electron Microscopy

PTMSP films and the prepared membranes were observed by SEM. A Leica Cambridge Stereoscan 440 apparatus was used. The samples were frozen with liquid helium (liquid nitrogen has proven to be ineffective in stiffening the samples) and broken in order to reveal the inner structural details. The samples were gold-coated before SEM observation.

RESULTS AND DISCUSSION

PSt Grafted Membranes

The PTMSP films were grafted with the technique above described. Different amounts of grafting were obtained, according to the experimental conditions used. The kinetics of monomer vapors absorption were studied, and the experimental results are reported in Fig. 2 where the experimental points are superimposed on a curve calculated by the equation

$$A\% = kt^a \tag{2}$$

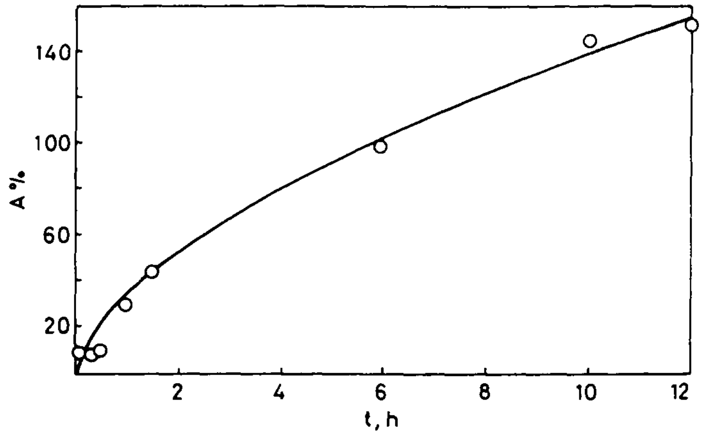


FIG. 2 Effect of the exposition time (hours) on the amount of absorbed styrene ($A\%$).

where $A\%$ = weight increase due to the absorbed monomer
$k = 30$
$a = 0.66$

It is evident from Fig. 2 that the amount of absorbed St quickly reaches large values; a 151% weight increase was measured after 12 hours of exposure.

As in the case of DVB, grafting can be controlled either by the absorption of different amounts of monomer or by using different irradiation doses. Due to the trend shown in Fig 2, and to the radiochemical conversion factor of St (12), it was decided to graft PTMSP films having different amounts of absorbed St while keeping the irradiation dose (7230 Gy)/ constant. The grafting reaction was carried out under these experimental conditions and the results are shown in Fig. 3.

Equation (3) gives a good fit of the experimental results:

$$G\% = K(A\%)^{0.5} \tag{3}$$

where the value of K is 3 as shown in Fig. 3. In Fig. 3 the percentage of grafting for different amounts of absorbed monomer as calculated from Eq. (3) (solid line) are reported.

The data show a trend typical of such radiochemical grafting reactions (12) and confirm that radiochemical graftings can be easily obtained when St is used. The grafted membranes were tested with air at 1 MPa. Air was fed over the membrane surface at a flow rate about 100 times higher than

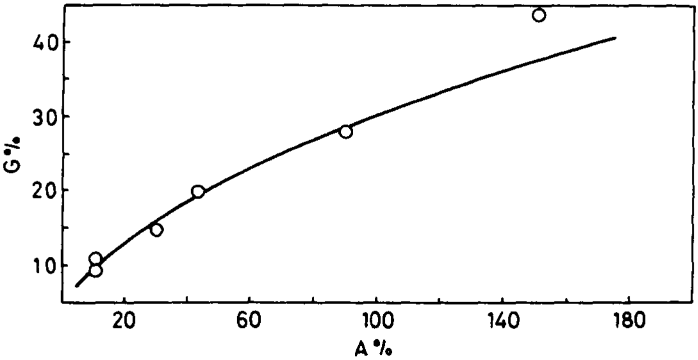


FIG. 3 Grafting percent (*G*%) vs the absorbed amount of St vapors (*A*%) at constant irradiation dose (7230 Gy).

the permeating flow in order to avoid a substantial feed composition change during the test. The experimental results are reported in Figs. 4 and 5 where permeability and separation factor changes are plotted as functions of time.

The following observations can be drawn from the plotted results.

Grafting is highly effective on both permeability and selectivity factors. The selectivity factor α grows above the value of pure PTMSP and moves toward the value which would be typical of St homopolymer.

By plotting α vs the grafted fraction $G\%/(1 + G\%)$ (Fig. 6), it is possible to extrapolate a value close to 4, in good agreement with the averaged value obtained from the data found in the literature (8, 13). Experiments were run for 200 hours, and this time was chosen in order to minimize the aging effect.

To better understand and summarize the effect of grafting on PTMSP characteristics, values of P/P_0 (P_0 is the initial membrane permeability) are also reported in Fig. 7.

From the plots in Fig. 6 one can infer that the permeability of PTMSP is strongly reduced by grafting; on the other hand, a more constant behavior with time is achieved when grafted specimens are used (see Fig. 7). Membranes increase their stability with grafting.

The effect of densification during gas separation tests is much less evident as the amount of grafted St reaches 44%. Moreover, it must be pointed out that such an effect is lower than that observed for the system PDVB/PTMSP (5). This is to be expected because very little crosslinking

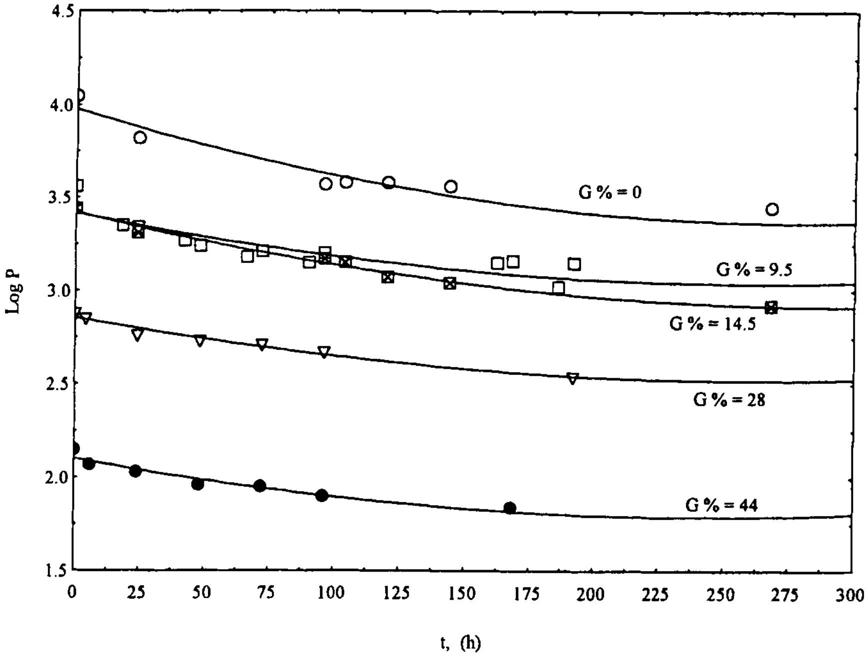


FIG. 4 Permeability (*P* barrer) vs time for differently grafted membranes.

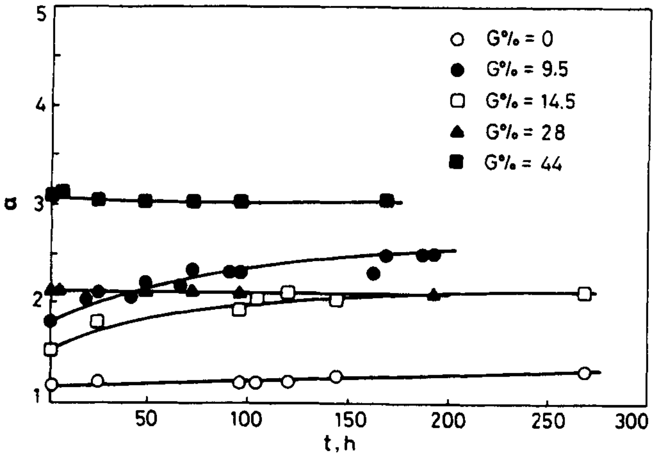


FIG. 5 Selectivity ALFA vs time for differently grafted membranes.

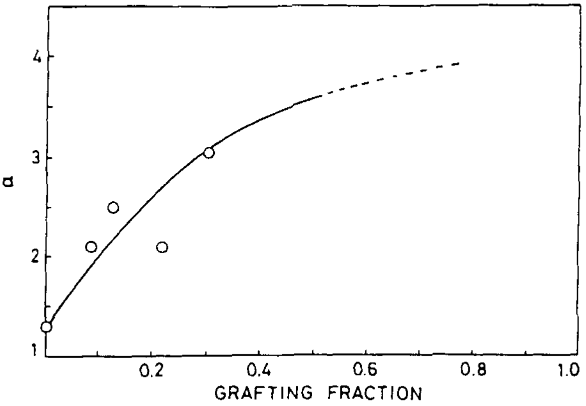


FIG. 6 Influence of grafting onto separation factor α. (values measured at t = 200 hours).

takes place with St. The grafted St probably influences PTMSP permeability by filling its structural voids, while PDVB provides more rigid structures. Different mechanisms, such as polystyrene phase organization, can be envisaged. Nevertheless, a good compromise among permeability, selectivity, and stability can be foreseen by controlling the degree of grafting for the PSt/PTMSP system.

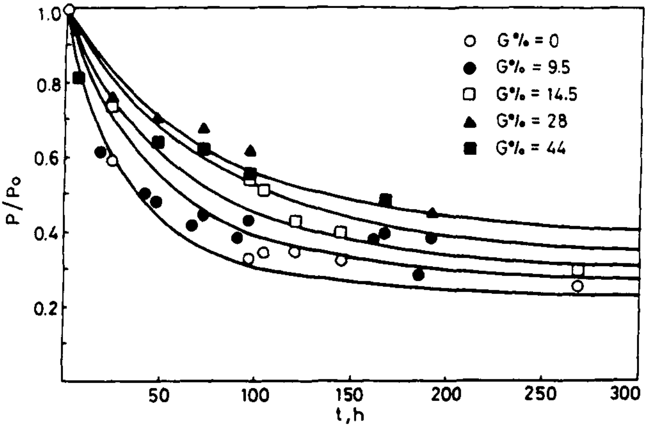


FIG. 7 P/P_0 vs time for differently grafted membranes.

The mathematical approach previously suggested (5) has been used in order to predict the effect of styrene grafting on membrane performance. The following equation was used to describe the permeability change:

$$P/P_0 = Ae^{(-kpt)} + (1 - A)e^{(-Kt)} \tag{4}$$

where A = membrane fraction pressure sensitive; in the case of ungrafted PTMSP, it is close to the "free volume" value (4)
t = time, hours
k = constant
K = constant
p = pressure = 1 MPa in our experimental runs

The values of A, k, and K, which must take into account the influence of different membrane compositions due to different amounts of grafted St, are reported in Table 1.

The value of A is considered to be dependent on the "mechanical" suitability of the membranes to be compacted by the applied pressure; i.e., it represents the part of the polymeric film that collapses easily when pressure is applied to it. As mentioned before, this value is equal to the void percentage in the case of ungrafted PTMSP.

The PTMSP films used in this case are slightly different from those used for DVB grafting and more permeable to air. For this reason the best fitting A value is 0.28 instead of 0.24 (as reported in Ref. 5). This means that the permeability decrease of the ungrafted film should be slightly faster, and this is confirmed by the experimental measurements.

Also in this case, the change of A with grafting can be related to PTMSP swelling phenomena occurring during monomer absorption. When the grafting reaction takes place, the PTMSP matrix is in some way "frozen" in the swollen condition, and this also results in a different trend in the permeability decrease when the membrane is subjected to pressure.

TABLE 1
Influence of Grafting on the Values of A, k, and K

Grafting %	A	k	K
0	0.28	0.0006	0.03
9.5	0.32	0.00045	0.021
14.5	0.35	0.0004	0.018
28	0.38	0.0003	0.014
44	0.42	0.0002	0.0136

The change of k has been related to different mechanical characteristics of the grafted polymer. K should represent the tendency of "pendant groups" to rearrange themselves with time. It seems reasonable that the grafting of a stiff molecule such as PDVB, which is a well-known crosslinking agent, would hinder the molecular motions and conformational rearrangements more.

In the present work, grafted PSt cannot have the same influence on the properties of the resulting membrane, so its main role is *supposed* to be void filling. Therefore, it should be less active in hindering the motion of pendant groups; this leads to a slower achievement of steady permeability value. Styrene-grafted PTMSP behaves like a more plastic structure.

By introducing the proper values of such parameters into Eq. (4), it is possible to obtain calculated trends of P/P_0 vs time which fit the experimental data reasonably well can be directly checked in Fig. 7 where the solid lines have been calculated and the points are the experimental values. Also, the behavior of separation factor α can be related to the permeability by mathematical equations (14). In our case the membrane permeability is strictly related to the amount of grafting. By trying a mathematical approach, the following equation has been found to give the best fit for our experimental data:

$$\alpha = 1 + (\alpha_0 - 1)(1 - G) + kG(\alpha_{\mathrm{St}} - 1)e^{(-G)} \tag{5}$$

as shown in Fig. 6 where the calculated trend (line) together with experimental values of α are reported. The calculated trend enables us to predict a 4.09 value for pure PSt.

Electron Microscopy

The photographs shown in Fig. 8 are related to the sections of (a) ungrafted membrane and (b) 44% PSt grafted membrane.

As in a previous paper (5), it can be seen that the ungrafted membrane shows a layered structure, allowing the presence of large voids between the layers. This is in accordance with the performances of the membranes and is still responsible for the "mechanical" contribution to permeability decrease with time. Such a structure is, in our opinion, a consequence of the film's preparation method rather than to the sample fracturing procedure. In the second case, we should also observe it in the grafted samples.

The grafted section shows a more compact structure; layers can no longer be observed although some diffused inhomogeneities could still contribute to the performances changing with the test time. The different types of flaws (holes instead of cracks) and the distribution of such defects could be responsible for the low permeability measurements.

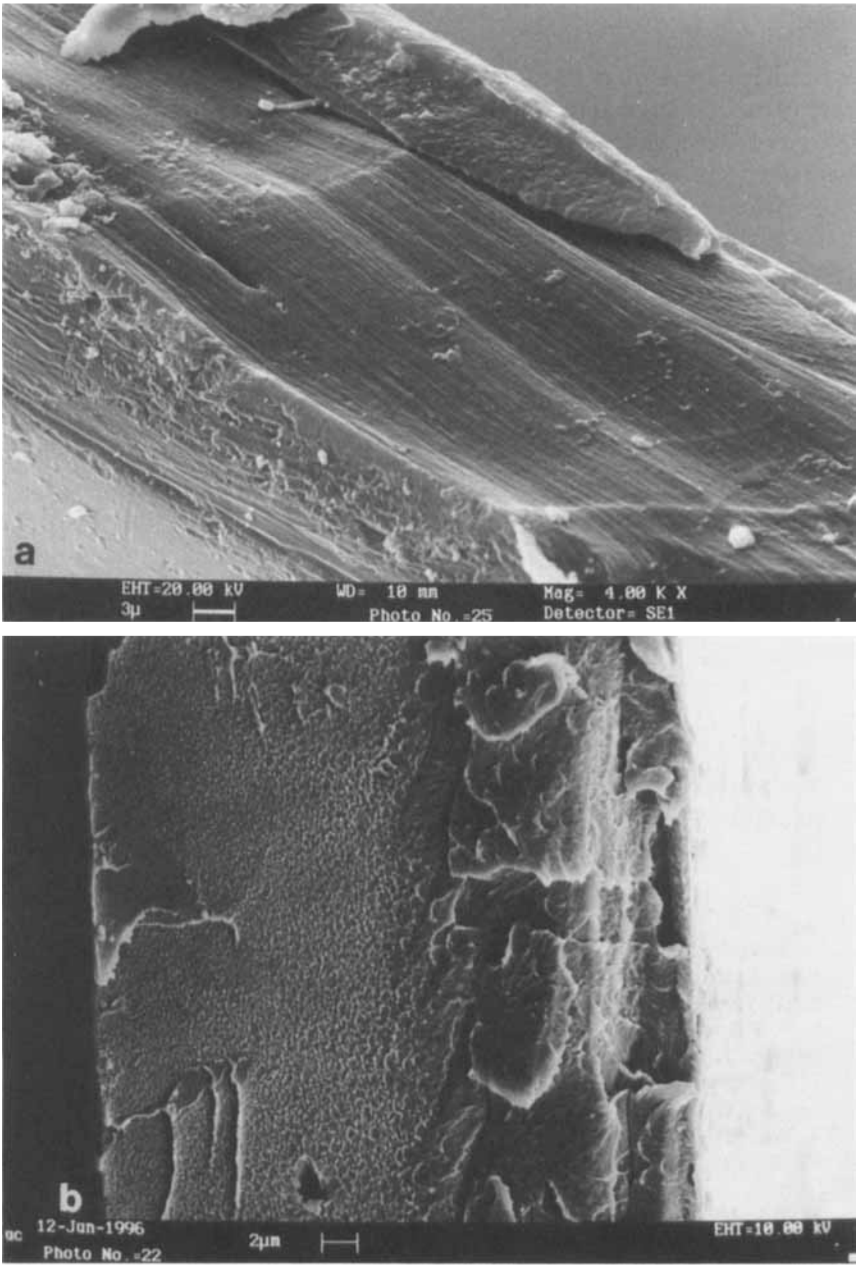


FIG. 8 Sections of PTMSP membranes. (a) Ungrafted, magnification 2500×. (b) 44% St grafted, magnification 2000×.

CONCLUSIONS

Though PTMSP has outstanding permeability characteristics, and for this reason has recently been proposed for practical applications (15), it still has the drawback of inconsistent performances. In our case this is due to the presence of large discontinuities in the structure of the films we prepared. The data we have obtained confirm that grafting is successful in filling them. Therefore, the aging effect is less dramatic and the selectivity is increased by moderate grafting. Comparison with data obtained by grafting DVB demonstrates that St, as expected, is less effective in stiffening PTMSP films. The absence of crosslinking reactions could explain the different behavior. For this reason, St-grafted membranes reach constant performance more slowly than do DVB-grafted ones. The same mathematical approach can be applied, but the equation needs quite different coefficients.

Our suppositions are based on experimental results obtained by membrane performance data. Density measurements should be useful to support them. Unfortunately, we are not yet able to measure significant density changes. Work is in progress, and further grafting experiments with different monomers are planned. We hope to report on them in the near future.

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