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Polytrimethylsylylpropyne Gas Separation Membranes Modified by Radiochemical Grafting of Divinylbenzene

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ABSTRACT

A radiochemical method was employed to obtain poly(1-trimethylsilyl-1-propyne) (PTMSP)–divinylbenzene (DVB) grafted films. DVB monomer vapors were absorbed by the PTMSP, and the grafting reaction was thereafter accomplished by ^{60}Co γ-irradiation in a nitrogen atmosphere. The films so obtained were tested for nitrogen–oxygen separation. The performances of the membranes were studied as functions of time and percent of grafting. The DVB-grafted membranes show an increased selectivity factor and stability with time. The experimental data and some SEM observations confirm the presence of large voids in the PTMSP matrix. These voids are responsible for permeability changes during operation and disappear after the grafting procedure.

INTRODUCTION

Poly(1-trimethylsilyl-1-propyne) (PTMSP) is reported to be the most permeable among the polymers suitable for gas separation membranes (1–5).

The high permeability of PTMSP has been attributed to its large free volume, which can reach 27% or more (5, 7, 8) due to the polymeric

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chain structure and substituents aggregation (9). Nevertheless, PTMSP membranes show at least two drawbacks: 1) low selectivities (3, 6) and 2) permeabilities decreasing with aging (7, 8). The large free volume decrease during aging for different reasons is responsible for the worsening of membrane characteristics (3, 7, 10).

Many techniques have been suggested to improve the behavior and the performance of membranes made of PTMSP. Flux decay has been retarded by incorporating chemical additives (11–14) and using UV irradiation (15, 16). Copolymerization and surface treatments have also been used to this purpose (17–19), and good results have been obtained, although the mechanisms are not yet clear.

The effect of grafting on polymers properties (20) has been studied in our Institute since 1964. The results encouraged us to use this technique to prepare membranes having "tailored" characteristics (21). This technique allows the introduction of stable chemical and physical modifications in the polymer so that, by grafting the proper monomer onto PTMSP, it should be possible to obtain membranes having better and more constant properties.

Here we report the results of our research.

EXPERIMENTAL

Materials

The following materials were employed to synthesize 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
- Divinylbenzene (DVB) monomer from Fluka, washed, dried, vacuum distilled, and kept at 253 K

Films Preparation

PTMSP was obtained in our laboratory following the procedure suggested by Masuda (1, 22). The intrinsic viscosity of the samples was 4.7 dL/g.

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 film was then washed with methanol and vacuum dried to constant weight at room temperature. The films so obtained had a thickness ranging between 25 and 60 μm. They were directly used for gas permeation runs or for radiochemical graftings.

Grafted Membranes Preparation

PTMSP films so prepared were grafted with DVB monomer by means of γ-irradiation. In our case the grafting proceeds in a heterogeneous system. Radiochemical techniques would suggest that the film be irradiated in the presence of the liquid monomer (23), but this method could not be employed due to the solubility of PTMSP in the monomer used. Moreover, DVB polymerization involves crosslinking reactions which would make it very difficult to separate grafted PTMSP from DVB homopolymer. It is nevertheless reported (24) that PTMSP has unique characteristics as a polymeric gas absorbent. We exploited this property to obtain PTMSP films saturated with the monomer vapors, ready to undergo irradiation and graft copolymerization. This was achieved by means of the device described in Fig. 1.

A loosely wrapped piece of PTMSP film was placed in a holder made from steel netting and placed just over a small amount of the purified monomer. The device was then plunged into liquid nitrogen and connected through a valve to vacuum until 10 Pa residual pressure was reached. The

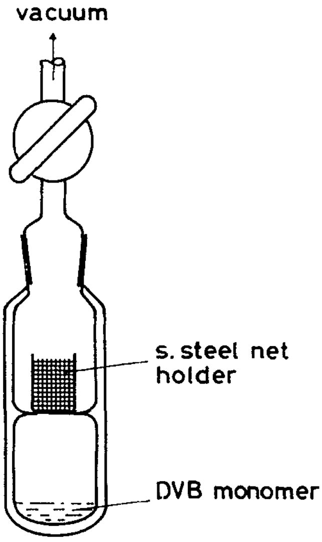

FIG. 1 Device used to obtain PTMSP films saturated with monomer vapors.

valve was then closed and the system temperature raised to 293 K by a thermostated water jacket. In such conditions the polymer film absorbs the monomer vapors, and the absorbed quantity depends on the time the specimen was left in the device. The films so treated were then subjected to γ-irradiation in a Vickrad "Gammacell" having a 300 C ^{60}Co activity. The (constant) dose rate was 447 Gy/h. During irradiation the samples were always kept in nitrogen. After irradiation, the films were soaked in boiling methanol. The amount of grafting was measured as the weight increase and referred to the ungrafted film weight.

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

where W_0 = ungrafted film weight
W = grafted film weight

Gas Permeation Measurements

Some authors (3) suggest the "Barathron" technique for measuring gas flow across the membrane, but we prefer to use a method closer to true operative conditions. For this reason we assembled the apparatus schematized in Fig. 2.

Gases were supplied by the cylinders (b, c), and their flux was measured and controlled by means of electronic regulators (F_1). The membrane under test was housed in the "plate-and-frame" module g described in Fig. 3. The membrane area was 0.001 m^2, and two membranes could be

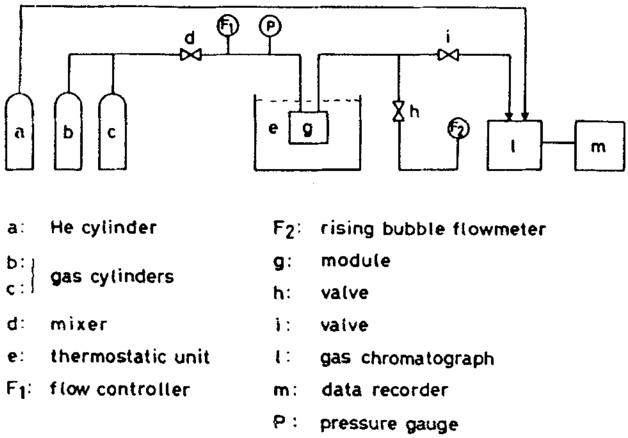

FIG. 2 Apparatus used for permeability measurements.

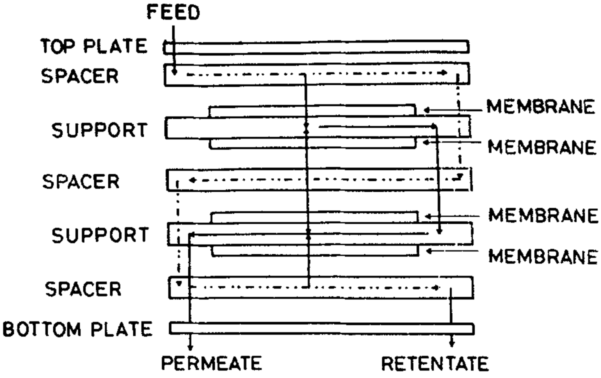

FIG. 3 Permeation cells. Device used for testing membranes.

separately characterized. The module temperature was controlled by the thermostatic unit (e).

Permeate flux collected from e was measured by means of a rising bubble flowmeter (F_2) and forwarded to the injection port of a Varian gaschromatograph (l) equipped with a molecular sieves column and TC detector. The carrier gas was helium. This apparatus could work up to 1 MPa. Most experiments were carried out at this pressure and at 303 K. Permeability (barrer) and selectivity factor α were measured, with α defined as the ratio between the concentrations 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 for stiffening the samples) and broken in order to reveal the inner structural details. The samples were gold-coated before SEM observation.

RESULTS AND DISCUSSION

PTMSP Ungrafted Membranes

The plot of Fig. 4 reports the permeability *P* (barrer) to air measured during 200 hours and the corresponding selectivity factor α.

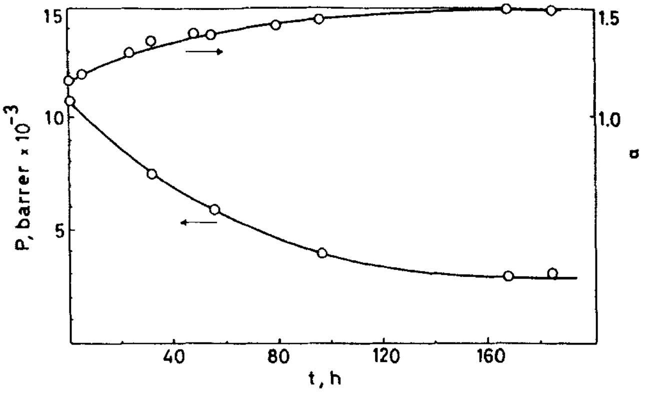

FIG. 4 Permeability P and selectivity α vs time for ungrafted membranes.

The trend of Fig. 4 is in agreement with the characteristics of PTMSP as widely described (7–9) and can be more easily summarized by plotting the ratio P/P_0, where P_0 is the initial membrane permeability (Fig. 5).

It clearly appears that the permeability of such a membrane decreases to less than 20% of the initial value after 200 hours. As mentioned before, this behavior has been attributed to the presence of voids inside the film; the dimensions of these voids can range from interchain spaces up to large pores. As will be further demonstrated by SEM, our films look like a multilayered structure. This suggested to us that, during the test under

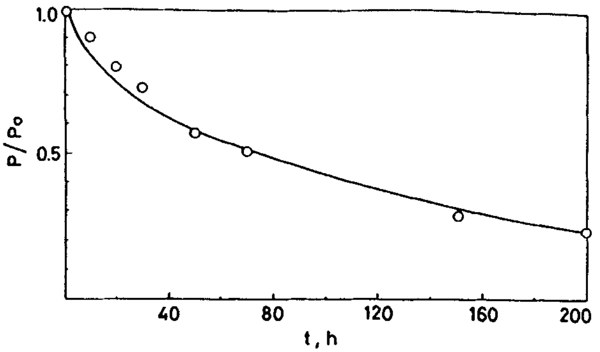

FIG. 5 Permeability percentage decrease with time. Solid line: calculated trend.

pressure, the "layers" could approach each other, thus making a large contribution to the decrease in permeability. Another cause of the decrease in gas flux is, of course, the already mentioned molecular motions (10).

The overall permeability could therefore be considered as the sum of two distinct phenomena that we will name "mechanical" and "chemicophysical." A mathematical approach is attempted here in order to achieve a better interpretation of the experimental trend. The proposed equation for permeability reduction is

$$P/P_0 = A\exp(-kpt) + (1 - A)\exp(-Kt) \tag{2}$$

where A = membrane fraction pressure sensitive = 0.24
t = time, hours
k = constant = 0.07
K = constant = 0.0062
p = pressure, MPa

The first part of this equation takes into account the permeability change due to reduction of "large" voids inside the membrane due to mechanical effects, and the second part is related to molecular motions (arrangement of substituents). The value of A has been deduced by averaging the porosity values found in the literature, while an approximate value of K has been obtained by measuring the permeability decrease at low pressure by means of the "Barathron" technique. The value of k is the best fitting with the experimental data trend.

The solid line in Fig. 5 has been obtained solving Eq. (2), while the points are experimental values. A similar equation will be used to interpret the features of DVB grafted membranes.

It clearly appears from the plots of Fig. 4 that permeability decreases as selectivity increases. This behavior has been studied (25), and some mathematical equations have been proposed. We tried a similar approach with our experimental data, and the following equation was found to fit them.

$$\alpha = (\alpha_{\max}^{-1})\exp(-cP) + 1 \tag{3}$$

where $\alpha_{\max}$ is the highest value found in the literature for PTMSP
c = constant = 0.14 in our case
P = air permeability of the membrane (barrer)

The experimental data are reported in Fig. 6, superimposed on the calculated trend. The dependence of α on permeability is typical and in agreement with that found elsewhere (25).

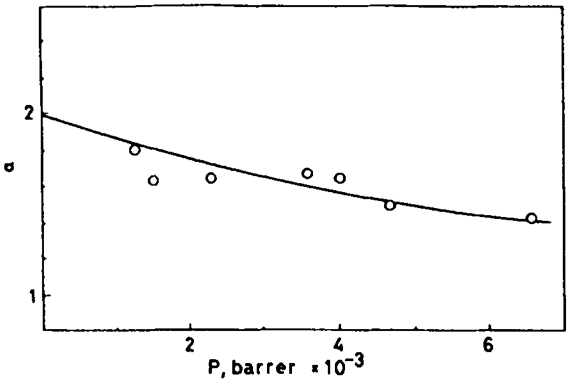

FIG. 6 Dependence of α on permeability P; the solid line was obtained by Eq. (3).

DVB Grafted Membranes

DVB has been chosen because it also crosslinks during polymerization, thus causing stiffening of the PTMSP network. At the same time, it should be able to stop conformational changes and to fill up the "microvoids" as well (8).

The PTMSP films were grafted with the technique described above. Different amounts of grafting were obtained based on the experimental conditions used. The kinetics of monomer vapors absorption were studied, and the experimental results are reported in Fig. 7.

Figure 7 shows that a maximum value of absorbed monomer is reached after 3 hours. Grafting can be controlled either by using the absorption

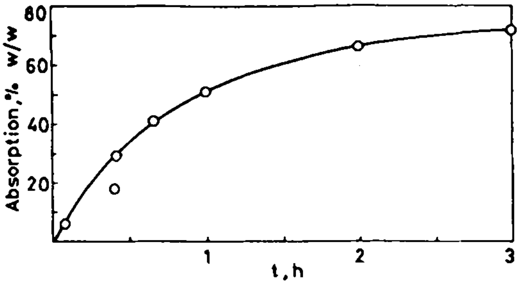

FIG. 7 Influence of the exposed time t on DVB vapors absorption.

of different amounts of monomer or by using different irradiation doses. Due to the trend shown in Fig. 7, it was decided to keep the absorbed monomer constant at the value obtained after 3 hours (72% w/w) and to vary the irradiation dose. The grafting reaction was carried out under these conditions, and the results are shown in Fig. 8.

The experimental data show a trend typical of such radiochemical grafting reactions (26), and which can be approximately represented by

$$G\% = M[1 - \exp(-kD)] \tag{4}$$

where $G\%$ = grafting % (w/w)
M = % of absorbed monomer
D = irradiation dose (Gy)
k = constant = 5.95×10^{-5}

The grafted membranes were tested with air at 1 MPa. The air was fed over their surface at a flow rate about 100 times the permeating flow in order to avoid substantial feed composition change during the test. The experimental results are reported in Fig. 9, where permeability and separation factor changes are plotted as functions of time.

The following observations can be drawn from the plotted results.

1. The grafting is highly effective on both permeability and selectivity factors.
2. The selectivity factor α grows above the net value of PTMSP and shifts toward the value which should be typical of DVB homopolymer. To our knowledge, no data about pure PDVB selectivity are available in the literature. Nevertheless, by plotting α vs grafting (Fig. 10), it

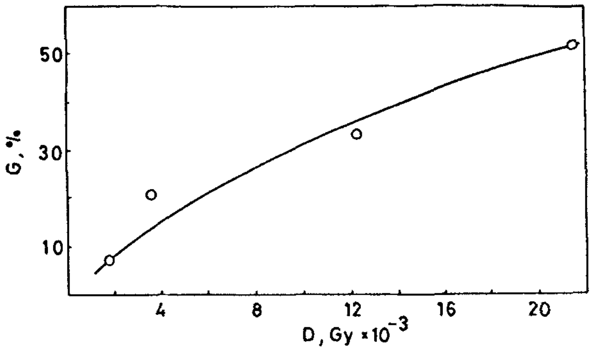

FIG. 8 Influence of radiation dose D on DVB grafting G.

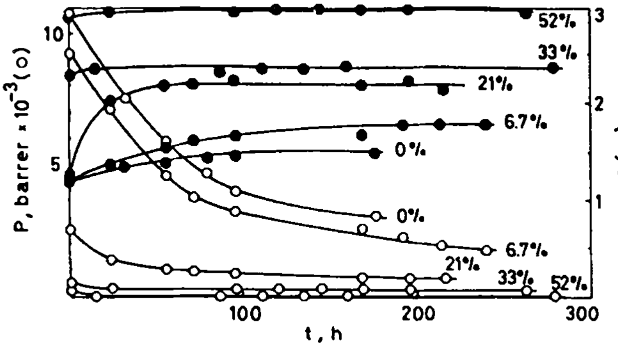

FIG. 9 Permeabilities P and selectivity factors α vs time for differently grafted membranes.

was possible to extrapolate α to approximately 5 (very similar to the value for polystyrene).

Values of P/P_0 are reported in Fig. 11.

One can infer from the plots in Figs. 9 and 11 that the permeability of PTMSP is strongly reduced by grafting; on the other hand, a more constant behavior with time is achieved. Membranes seem somehow to increase their stability with grafting. The effect of "mechanical" compaction is much less sensitive when the amount of grafted DVB exceeds 30%. A proper compromise between selectivity, permeability, and stability can be obtained by controlling the degree of grafting.

A mathematical approach has been tried in order to better interpret the phenomenon and to predict the effect of grafting on membrane perfor-

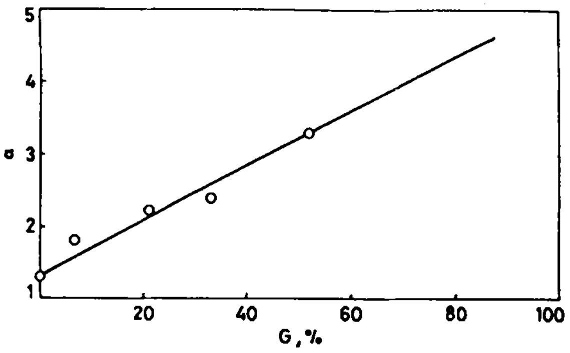

FIG. 10 Influence of grafting G on selectivity factor α.

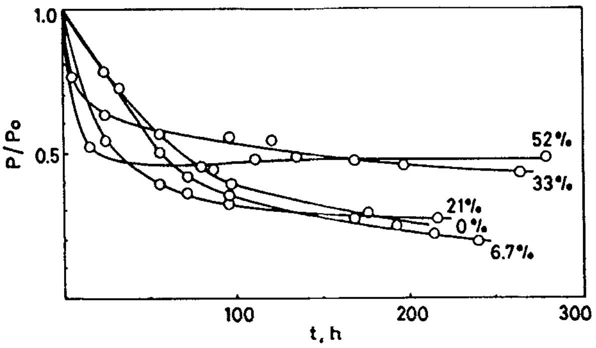

FIG. 11 P/P_0 vs time for differently grafted membranes.

mance. The following equation was used to describe the permeability change:

$$P/P_0 = A\exp(-kpt) + (1 - A)\exp(-Kt) \qquad (5)$$

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

The change of A with grafting can be related to PTMSP swelling occurring during monomer absorption. The grafting reaction follows and "freezes" the PDVB molecules into the PTMSP matrix. This results in an increased compressible volume and a faster permeability reduction when the membrane is subjected to pressure.

The change of k is due to different mechanical characteristics of the grafted PDVB.

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

Grafting (%)	A	k	K
0	0.24	0.07	0.0062
6.7	0.26	0.09	0.0058
21	0.30	0.20	0.0040
33	0.36	0.30	0.0016
52	0.50	0.51	0.00012

K should represent, as mentioned before, the tendency of "pendant groups" to rearrange themselves with time. It seems reasonable that the grafting of such a stiff molecule as PDVB could greatly hinder molecular motions and conformational rearrangements. This leads to a more constant permeability once the "mechanical" factors are no longer active.

By introducing the proper values of such parameters, it is possible to obtain calculated trends of P/P_0 vs time which reasonably fit with the experimental data. As an example, the fitting of the calculations with the measured values for two differently grafted membranes are reported in Fig. 12.

Electron Microscopy

The photographs of Fig. 13 shows sections of (a) ungrafted membrane and (b) 33% DVB grafted membrane. The photographs show that the ungrafted membrane has a layered structure which allows the presence of large voids between the layers. This structure is in agreement with the behavior of the membranes and is, in our opinion, responsible for the "mechanical" contribution to permeability decrease with time.

The grafted section shows a better homogeneity, in agreement with the lower measured permeability.

From a practical point of view, the 33% grafted membrane should represent a good compromise between the high PDVB selectivity and the high permeability of the PTMSP matrix. This is confirmed by previously reported results.

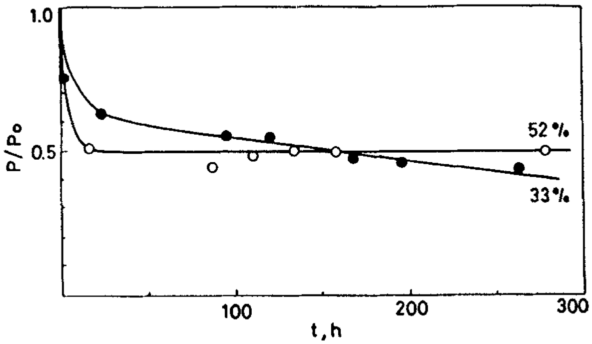

FIG. 12 Comparison of experimental with calculated P/P_0 values as a function of time for two grafting percentages. The solid line is the calculated trend.

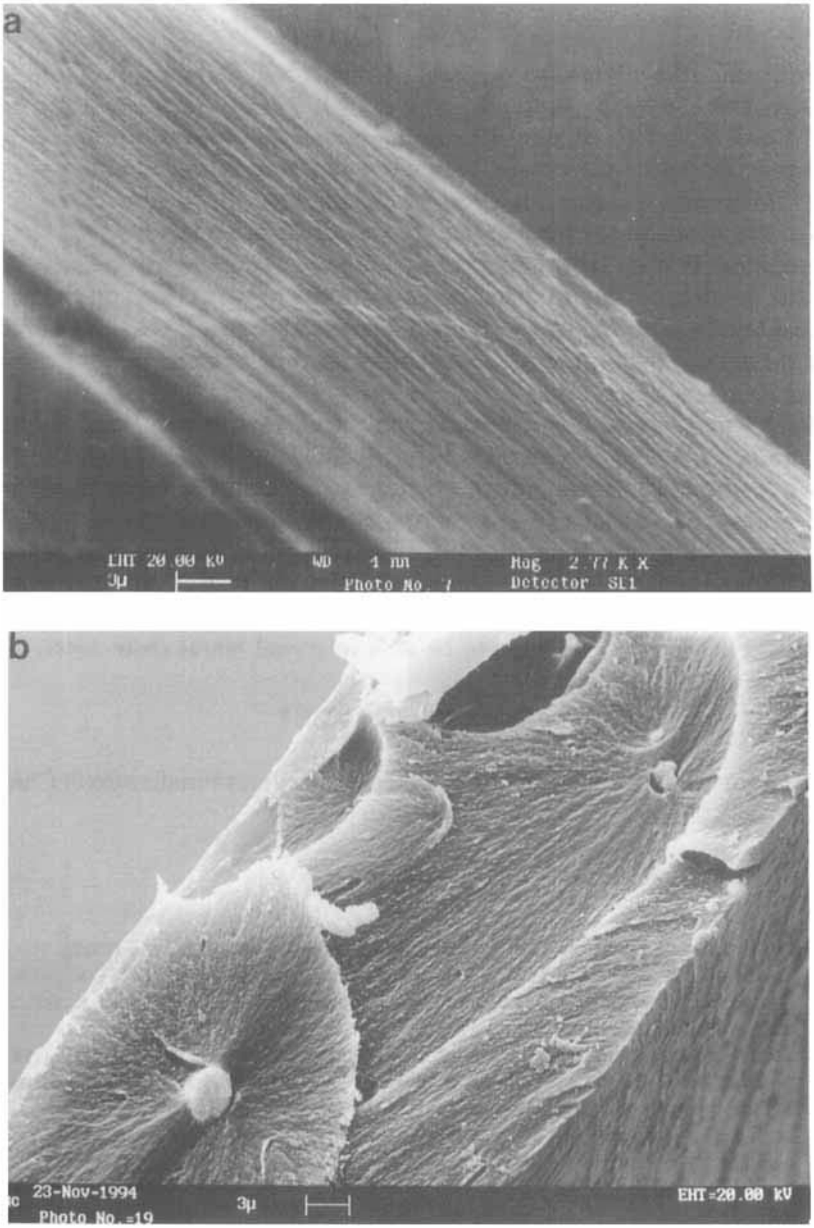

FIG. 13 Sections of PTMSP membranes. (a) Ungrafted: magnification 2700×. (b) 33% DVB grafted: magnification 2200×.

CONCLUSIONS

Although PTMSP has outstanding permeability characteristics, and for this reason has been proposed for practical applications (28), it has the drawback of inconstant performances. Many authors have attributed this behavior to molecular motions caused by physicochemical conditions arising during membrane use or even during storage.

On the basis of our measurements and SEM observations, we are of the opinion that, at least under our experimental conditions, a large part of this behavior is due to discontinuities in the polymer structure. These discontinuities are similar to cracks, and it is likely that mechanical forces should act on them more (or faster) than do the chemicophysical conditions.

Both "mechanical" and "chemicophysical" factors can be controlled by grafting a stable polymer inside the PTMSP network. The grafting of DVB is successful in stopping or slowing the molecular motions and filling the large voids, so that a good compromise can be reached among selectivity, permeability, and time reliability. The selectivity factor increases with grafting and tends to reach a value typical for the grafted polymer alone. This fact has encouraged us to try further grafting experiments with different monomers; we hope to be able to report about them soon.

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REFERENCES

1. Y. Ichiraku, S. A. Stern, and T. Nakagawa, *J. Membr. Sci.*, *34*, 5–18 (1987).
2. T. Masuda, E. Isobe, and T. Higashimura, *J. Am. Chem. Soc.*, *105*, 7473–7474 (1983).
3. K. Takada, H. Matsuya, T. Masuda, and T. Higashimura, *J. Appl. Polym. Sci.*, *30*, 1605–1616 (1985).
4. T. Masuda, Y. Iguchi, B. Z. Tang, and T. Higashimura, *Polymer*, *29*, 2041–2049 (1988).
5. N. A. Platé, A. K. Bokarev, N. E. Kaliuzhnyi, E. G. Livitnova, V. S. Khotiminskii, V. V. Volkov, and Yu. P. Yampol'skii, *J. Membr. Sci.*, *60*, 13–14 (1991).
6. H. Odani and T. Masuda, in N. Tshima (Ed.), *Polymers for Gas Separation*, VCH, New York, 1992, pp. 107–144.
7. Yu. P. Yampol'skii, S. M. Shishatskii, V. P. Shantrovich, E. M. Antipov, N. N. Kuzmin, S. V. Rykov, V. L. Khodyaeva, and N. A. Platé, *J. Appl. Polym. Sci.*, *48*, 1935–1944 (1993).
8. S. R. Auvil, R. Srinivasa, and P. Burban, *J. Membr. Sci.*, *86*, 67–86 (1994).
9. T. Nakagawa, in Y. Osada and T. Nakagawa (Eds.), *Membrane Science and Technology*, Dekker, New York, 1992, pp. 239–287.

10. A. Tanaka, K. Nitta, R. Maekawa, T. Masuda, and T. Higashimura, *Polym. J.*, *11*, 1173–1180 (1992).
11. T. Nakagawa, T. Saito, S. Asakawa, and Y. Saito, *Gas Sep. Purif.*, *2*, 3–8 (1988).
12. M. Langsam and L. Robeson, *Polym. Eng. Sci.*, *29*, 44–54 (1989).
13. H. Nishide, H. Kwaklami, Y. Sasame, K. Ishiwata, and E. Tsuchida, *J. Polym. Sci., Polym. Chem. Ed.*, *30*, 77–82 (1992).
14. A. Asakawa, Y. Saito, K. Waragai, and T. Nakagawa, *Gas Sep. Purif.*, *3*, 117–122 (1989).
15. K. K. Hsu. S. Nataraj, R. M. Thorogood, and P. S. Puri, *J. Membr. Sci.*, *79*, 1–10 (1993).
16. G. Chen, H. J. Griesser, and A. H. Mau, *Ibid.*, *82*, 99–115 (1993).
17. T. Nakagawa, S. Nagashima, and A. Higuchi, *Desalination*, *90*, 183–192 (1992).
18. Z. Guodong, T. Nakagawa, A. Higuchi, and K. Nagai, *Chin. J. Polym. Sci.*, *10*, 203–209 (1992).
19. M. Langsam, M. Anand, and E. J. Karwachi, *Gas Sep. Purif.*, *2*, 162 (1988).
20. C. Uliana, P. Traverso, and F. Vigo, *Eur. Polym. Sci.*, *30*, 453–456 (1994).
21. C. Uliana, F. Vigo, and P. Traverso, *Sep. Sci. Technol.*, *29*, 1621–1637 (1994).
22. T. Masuda, E. Isobe, T. Hamano, and T. Higashimura, *Macromolecules*, *19*, 2448–2450 (1986).
23. H. A. J. Battaerd and G. W. Tregear, in *Graft Copolymers*, Interscience, New York, 1967, pp. 54–60.
24. L. M. Robeson and M. Langsam, *Sep. Sci. Technol.*, *27*, 1245–1258 (1992).
25. L. M. Robeson, *J. Membr. Sci.*, *62*, 165–185 (1991).
26. S. Munari, G. Tealdo, and C. Rossi, *Chim. Ind.*, *45*, 1494–1501 (1963).
27. L. Jia and J. Xu, *Polym. J.*, *5*, 417–425 (1991).
28. G. R. Rigby and H. C. Watson, *J. Membr. Sci.*, *87*, 159–169 (1994).

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