

The Effect of Plasma-initiated Graft Copolymerization on Surface of PTMSP Membrane to Its Gas Permselectivity*

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Abstract

In this paper, some experiments of graft copolymerization using butyl acrylate(BA) or 1,1-dihydroperfluorobutyl acrylate(PFBA) onto surface of poly[1-trimethylsilyl(propyne)-1](PTMSP) dense membrane initiated by a glow discharge were described. The chemical composition and structure on surface of PTMSP membrane were changed as grafting copolymerization. It is found that the gas permeability of membrane grafted reduces and selectivity increase in contrast to those unmodified. The gas permselectivity of membrane grafted is related closely with the content of monomer in emulsion. The gas permeability of PTMSP membrane grafted by PFBA is better than that by BA, and those are due to higher gas solubility in membrane grafted by PFBA. There is not too much difference on gas diffusivity between membranes grafted by BA and PFBA.

Key word: Plasma-initiation, Poly[1-Trimethylsilyl(propyne)-1], Acrylate, Gas permselectivity

Introduction

The gas permeation rate of Poly[1-trimethylsilyl(propyne)-1] (PTMSP) is highest in all synthetic materials^[1,2], so it may be applied widely in the future. But its gas separation coefficient is poor, therefore, the material is modified with many method^[3], especially to the surface of the membrane^[4], so as to improve its gas separating coefficient. It is reported that character of separation of O/N of the membrane grafted copolymer on the surface of PTMSP initiated by UV^[5] is increased, and the loss of gas permeation coefficient is less.

* The Project was supported by National Nature Foundation of China

The report on method of modified surface by graft copolymer initiated by plasma is not much. The advantage of the method need not initiating and no other factor affecting the body of material. In this paper, graft copolymerization of BA and PFBA onto the surface of PTMSP dense membrane initiated by plasma is described, and the surface chemical compositions and structures of modified membrane is changed and gas selectivity is improved.

Experimental

Material

Poly[1-Trimethylsilyl(propyne)-1] (Shin-Etsu Chemical Co., Ltd)

Butyl acrylate (BA) (Beijing Chemical Plant)

1,1-Dihydroperfluorobutyl acrylate (PFBA) (prepared in own lab)

Sodium 1-Dodecanesulfonate (Beijing Chemical Plant)

Butyl acrylate (BA) was freed from inhibitor by distillation. The membrane was made by poured 1.0 wt% toluene solution of PTMSP to utensil glossy surface at room temperature. The Thickness of membrane is 100-120 μ m.

Characterization

A chemical composition of the surface of the sample was studied by ATR-FTIR(Bruker IFS 113v) and X-ray Photoelectron Spectroscopy(XPS) (Perkin Elemer Phi5300)The gas permeability J of the membrane was determined with a K-315-N gas permeability apparatus.(Rikaseiki Co., Japan)

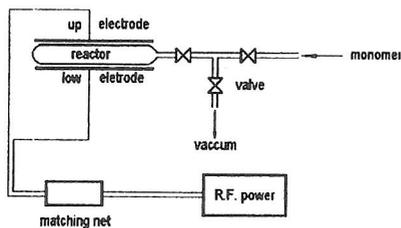


Figure 1. The scheme of instrument for initiated by plasma on surface of membrane.

Grafting Polymerization

A schematic diagram of the main part of the glow discharge reactor in this work is represented in Figure 1. The emulsion of monomer is made by mixing with 40ml distilled water, then adding Sodium 1-Dodecanesulfonate and stirring sufficiently. The PTMSP film was put into glow discharge reactor made-self. The pressure in the reactor is reduced to 40 Pa. followed by introduction of argon into the reactor. After that, plasma is generated at 100 w and last for 5 min.. After the plasma treatment, the emulsion of monomer was poured into the reactor and graft copolymerization were

performed for 4 h. at 75°C. The monomer homopolymer was Soxhlet extracted from the grafted films with acetone for 24h and then with water for 24h. Then the membrane were dried for 48h in vacuum oven. The condition of graft copolymerization on the surface of PTMSP membrane is showed in Table 1.

Results and Discussion

The results from XPS, ATR-FTIR spectra of membrane proved the graft copolymerization were successfully. The XPS, ATR-FTIR spectra of membrane original and after graft copolymerization were showed in Figure 2-7. The IR spectrum of PTMSP showed as Figure 5 is not contained carbonyl group, but that of membranes grafted BA or PFBA showed as Figure 6 and 7 are contained.

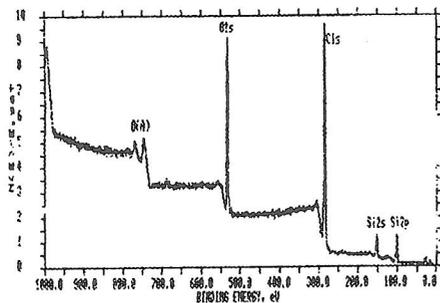


Figure 2. The XPS spectrum of PTMSP membrane.

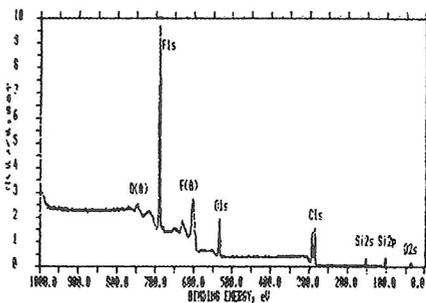


Figure 3. The XPS spectrum of PTMSP membrane grafted with PFBA.

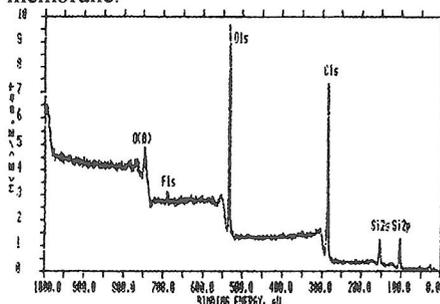


Figure 4. The XPS spectrum of PTMSP membrane grafted with BA.

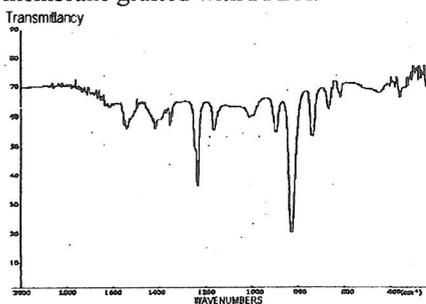


Figure 5. The IR spectrum of PTMSP.

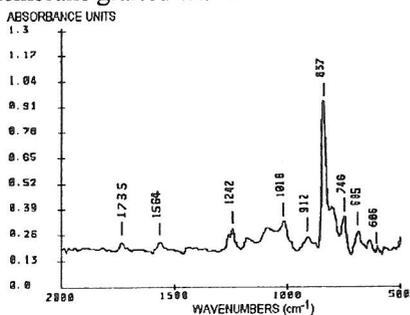


Figure 6. The IR spectrum of PTMSP membrane grafted with BA.

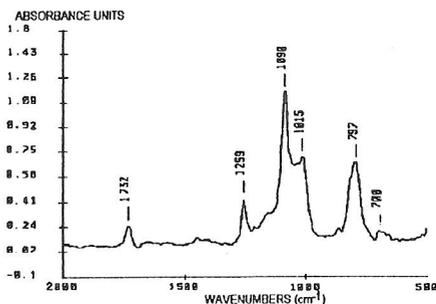


Figure 7. The IR spectrum of PTMSP membrane grafted with PFBA.

Table 1. The condition of graft copolymerization on the surface of PTMSP membrane.

| sample No. | monomer | Vm(lm)* | Vw(ml)** |
|------------|---------|---------|----------|
| 1 | BA | 1 | 40 |
| 2 | BA | 3 | 40 |
| 3 | BA | 10 | 40 |
| 4 | PFBA | 3 | 40 |
| 5 | PFBA | 5 | 40 |

* volume of monomer. ** volume of water.

The concentration of element on the surface of membrane grafted was changed apparently. The XPS spectrum of PTMSP showed as Figure 2 does not contain a F_{1s} peak, and a little amount of oxygen may be due to pollution. The atomic concentration on the surface of membrane grafted before and after was listed in Table 2.

Table 2. Compositional analysis of elementary by XPS on membrane surface of PTMSP before and after plasma-initiated graft copolymerization.

| sample No. | O/C | F/C |
|------------|------|------|
| PTMSP | 0.24 | 0 |
| 2 | 0.41 | 0 |
| 5 | 0.24 | 0.66 |

After graft copolymerization, the content of C on surface of the membrane is decreased relatively, that of O on the surface of PTMSP membrane grafted BA is increase, that of F on the surface grafted PFBA is rich, where it is shown that F was introduced to the surface region of the PTMSP membrane. The XPS spectrum of surface of the grafted BA showed a high level of oxygen to be present as Figure 4 and that of the grafted PFBA showed a high level of fluorine to be present as Figure 3.

The permeation rate of O₂, N₂, H₂, and CO₂ were determined, and the gas permeation coefficient and gas separation coefficient were listed in Table 3. The gas diffuse and soluble coefficient were listed in Table 4.

Table 3. The permeation and separation coefficient of hydrogen, oxygen, nitrogen and carbon dioxide in membrane of PTMSP original and grafted on its surface at 30°C and 1atm.

| sample | P(H ₂) | P(O ₂) | P(N ₂) | P(CO ₂) | P(H ₂)/P(N ₂) | P(O ₂)/P(N ₂) |
|--------|--------------------|--------------------|--------------------|---------------------|---------------------------------------|---------------------------------------|
| PTMSP | 8110 | 7450 | 5300 | 9010 | 15.3 | 1.41 |
| 1 | 693 | 238 | 76.3 | 992 | 9.08 | 3.12 |
| 2 | 84.2 | 22.9 | 6.00 | 90.2 | 14.0 | 3.82 |
| 3 | 70.6 | 20.2 | 5.38 | 96.6 | 13.1 | 3.75 |
| 4 | 3440 | 1430 | 689 | 4790 | 4.99 | 2.08 |
| 5 | 370 | 159 | 53.5 | 606 | 6.94 | 2.98 |

* unit: 1 barrer = 10⁻¹⁰[cm³(STP)·cm/cm²·s·cmHg]

Table 4. The diffuse coefficient and soluble coefficient of oxygen, nitrogen, and carbon dioxide in membrane of PTMSP original and grafted on its surface at 30°C and 1atm.

| sample | D(O ₂)* | D(N ₂) | D(CO ₂) | S(O ₂)** | S(N ₂) | S(CO ₂) |
|--------|---------------------|--------------------|---------------------|----------------------|--------------------|---------------------|
| PTMSP | 39.7 | 37.5 | 25.3 | 188 | 142 | 356 |
| 1 | 5.15 | 2.89 | 2.32 | 46.2 | 26.4 | 428 |
| 2 | 2.70 | 1.46 | 0.902 | 8.45 | 4.11 | 100 |
| 3 | 1.30 | 0.556 | 0.558 | 15.6 | 9.68 | 173 |
| 4 | 16.7 | 9.08 | 7.30 | 85.8 | 75.8 | 656 |
| 5 | 3.89 | 2.90 | 2.71 | 40.8 | 18.4 | 223 |

* unit: 10⁻⁶[cm²/s] ** unit: 10⁻⁴[cm³(STP)/cm³·cmHg]

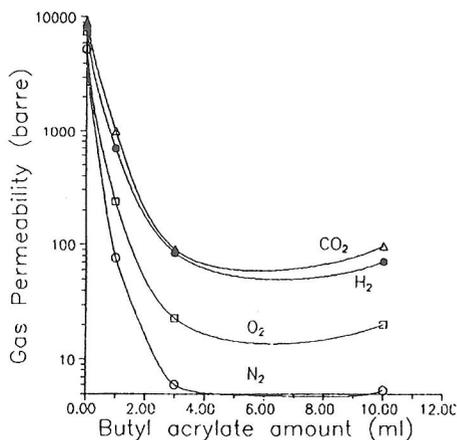


Figure 8. The influence of amount of butyl acrylate on permeability of H₂, O₂, N₂ and CO₂ in PTMSP membrane grafted BA.

The gas permeation coefficient of PTMSP membrane after grafted copolymerization BA is decreased in contrast to original. The More content of monomer in emulsion is, the more the decrease of the gas permeation coefficient is. The decrease of the gas permeation coefficient is apparent in low content of BA. As the content of BA in emulsion is 3ml, the gas permeation coefficient of PTMSP membrane after grafted copolymerization BA is stable, and the vary of value is not apparent to the content of BA is 5ml and 10ml. The change of gas separation coefficient is adverse to that of the gas permeation coefficient. The increase of separation coefficient is remarkable, however, the

vary is not apparent as the content of BA is 3ml in emulsion. The tendency of change is described as Figure 8.

Compared the gas diffuse coefficient and soluble coefficient of the PTMSP membrane with that of grafted BA, the gas permeation coefficient of membrane grafted is decreased apparently, its diffuse coefficient is decrease continuously, but soluble coefficient is decrease before the content of BA in emulsion is 3ml, then increased. It may be that the content of BA in emulsion is less 3ml, the character of membrane grafted is PTMSP, and that of BA in emulsion attained 3ml, the character of membrane is butyl acrylate. So as the content of monomer in emulsion is more 3ml, the grafted content on the surface is increased, the density of functional groups increase, it is advantage to gas molecular soluble into surface of membrane. According the XPS spectrum, the value of O/C grafted sample is more than that of original one. The decrease of gas diffuse coefficient is decided by the content of grafted on the surface. Furthermore, as the increase of functional group on the surface is advantage to

solubility of gas molecular on the surface, so gas soluble coefficient of membrane increase after decreasing .

According XPS spectra of membrane of original and grafted sample, PFBA is grafted onto the surface of PTMSP. The gas permeation coefficient of the membrane grafted is decreased and separation coefficient is increase. Compared with the membrane of grafted BA, the decrease of both gas permeation and separating coefficient of that grafted PFBA are little, and soluble coefficient is bigger, but diffuse coefficient is almost the same. So the difference between two kinds of membrane grafted is caused mainly by the difference of soluble coefficient.

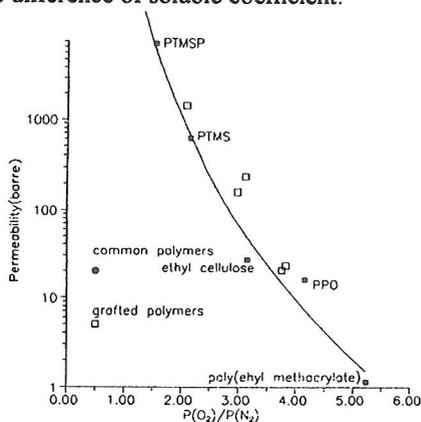


Figure 9. The composition of permeability between common polymer used as gas separation membrane and PTMSP grafted by acrylate on its surface.

The gas selective permeation of PTMSP membranes grafted BA and PFBA to common separating material are compared, and Figure 9 is the relation between gas permeation coefficient and separating coefficient. In low content of monomer, the gas permeation coefficient of the former is good, but in high content of monomer, the gas permeation coefficient of both is closed.

Conclusion

The gas permeation coefficient and gas selective coefficient of PTMSP can be improved by the graft copolymerization of BA and PFBA onto surface of PTMSP. the gas permeability of modified membrane reduces and permselectivity increase in contrast to those unmodified.

References and Notes

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