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Novel High Free Volume Polymer, Addition Polytrimethylsilylnorbornene: Diffusion or Solubility Controlled Permeation

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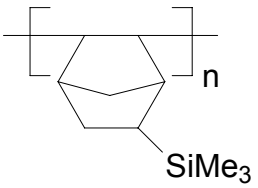
1.Introduction

Recently the group of high free volume, highly permeable glassy polymers (mainly polyacetylenes and perfluorinated polymers) was replenished with a novel polymer with entirely different structure – addition poly(trimethylsilyl norbornene) (PTMSN):



This polymer is characterized by relatively high gas permeability, ($P(O_2)$=800 Barrer, $P(CO_2)$=4350 Barrer). It is interesting that for the series of gaseous alkanes C_1-C_4 permeability increases when the size of the penetrant increases and reaches the value $P(C_4H_{10})$=17500 Barrer (at 1 atm). It is also noteworthy that this polymer keeps high permselectivity in separation of the mixture butane/methane ($\alpha(C_4/C_1)$=22) which is close to the ideal separation factors for this gas pair [1]. This is quite unusual because permselectivity in mixed gas separation often decreases due to plasticization phenomena

2. Results and discussion

In order to ascribe this unusual gas permeation behavior, we have studied vapor sorption thermodynamics in this polymer (using inverse gas chromatography (IGC) and the pressure decay (PD) method), measured the diffusion coefficients *D* (gas permeation and sorption experiments) and studied free volume (positron annihilation lifetime spectroscopy and IGC). It was shown that PTMSN is characterized by unusually high solubility coefficients, larger than those in poly(trimethylsilyl propyne)) (PTMSP) which so far has been considered as “the champion” in gas

solubility. The data of the IGC and PD methods are in good agreement. On the other hand, the diffusion coefficients in PTMSN found using the two methods were shown to be

smaller than those in PTMSP: this explains higher permeability of the latter as compared with PTMSN.
Estimation of the size of free volume elements in PTMSN using several methods resulted in values in the range 700-1200 $Å^3$ which is somewhat smaller than that reported for PTMSP. In addition, the slope of the dependence $\log D = ad^2 + b$, where d is the cross-section of the diffusant molecules, was shown to be intermediate between those in PTMSP and conventional glassy polymer.

3. Conclusion

Bearing in mind all these results a conclusion can be made that permeability and permselectivity of PTMSN are determined by solubility controlled permeation. Its high free volume can be envisaged as overlapping of the opened and closed porosity.

References

[1] E.Finkelshtein, K.Makovetskii, M.Gringolts, Yu.Rogan, T.Golenko, L.Starannikova, Yu.Yampolskii, V.Shantarovich, T.Suzuki, Macromolecules, 39 (2006) 7022-7029.