Polymer Bulletin 58, 995–1003 (2007)
DOI 10.1007/s00289-006-0720-2

Polymer Bulletin

Effect of Fumed Silica Nanoparticles on the Gas Permeation Properties of Substituted Polyacetylene Membranes

Toshiki Kono[1], Yanming Hu[1], Toshio Masuda[1] (✉), Katsuchisa Tanaka[2], Rodney D. Priestley[3], and Benny D. Freeman[4]

[1]Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University,
Katsura Campus, Kyoto 615-8510, Japan
[2]Department of Materials Chemistry, Graduate School of Engineering, Kyoto University,
Katsura Campus, Kyoto 615-8510, Japan
[3]Department of Chemical and Biological Engineering, Northwestern University,
Illinois 60208-3120, USA
[4]Center for Energy and Environmental Resources, University of Texas at Austin,
10100 Burnet Road, Building 133, Austin, Texas 78758, USA
E-mail: masuda@adv.polym.kyoto-u.ac.jp; Fax: +81 75 383 2590

Received: 18 October 2006 / Revised version: 5 December 2006 / Accepted: 12 December 2006

Summary

The gas permeability of three substituted polyacetylenes, poly(1-chloro-2-phenylacetylene) (PClPA), poly[1-phenyl-2-(4-trimethylsilyl)phenylacetylene] (PTMSDPA), and poly[1-(trimethylsilyl)-1-propyne] (PTMSP), increased systematically with increasing content of nonporous fumed silica (FS) nanoparticles. For instance, the oxygen permeability coefficient ($P\mathrm{O}_2$) of PClPA containing 30 wt% FS was 86 barrers, which was 10 times higher than that of the unfilled polymer ($P\mathrm{O}_2$ = 8.6 barrers). The extent of permeability increase with the addition of FS was smaller when the permeability of the original polymer was higher. The order of the permeability increase in FS-filled polymers was as follows: PClPA > PTMSDPA > PTMSP. The addition of FS resulted in the decrease of O_2/N_2 permselectivity of these polymers. The H_2/CH_4 permselectivity largely decreased with increasing FS content in PClPA, while it hardly changed with FS loading in PTMSP. The gas solubility of PClPA was practically independent of FS content, and the increase in gas permeability in filled PClPA resulted from an increase in diffusivity with the addition of FS.

Introduction

Organic-inorganic hybrids and nanocomposites are a relatively new class of polymeric materials with improved properties compared to their neat materials. They have attracted much attention as a new class of membranes for gas separation [1–6]. Traditional nanocomposite membranes are typically composed of porous inorganic particles, such as zeolites, dispersed into a polymer matrix [3–5]. In theory, such materials should display both the strong molecular sieving properties of zeolites and the desired mechanical and processing properties of polymers. In practice, attaining this synergy is difficult; i.e., composite membranes often fail to exhibit their theoretical separation performance due to the formation of relatively nonselective defects at the interface between the zeolite particles and the polymer matrix.

Recently, it has been found that the addition of nonporous fumed silica (FS) nanoparticles into high free volume glassy polymers, such as poly(4-methyl-2-pentyne) (PMP) [7–10], poly(1-trimethylsilyl-1-propene) (PTMSP) [11], and poly[2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole-*co*-tetrafluoroethylene] [12], simultaneously increases both permeability and vapor/permanent-gas selectivity. These results appear unusual because the addition of nonporous fillers typically reduces polymer permeability and has little effect on permselectivity [13,14]. In contrast to zeolites in polymer composite membranes, FS nanoparticles are nonporous and do not permeate gas molecules. Rather, when dispersed in a rigid polymer at load levels between 10–50 wt%, the FS nanoparticles alter polymer chain packing, thereby, permeation properties without introducing gross defects or reducing the mechanical strength of the membrane [11].

PTMSP membranes exhibit the highest gas permeability among all existing polymer [15,16]; poly[1-phenyl-2-(4-trimethylsilyl)phenylacetylene] (PTMSDPA) membranes also exhibit considerably high gas permeability, whose oxygen permeability coefficient ($P\mathrm{O}_2$) is as large as 1100 barrers [17]. Poly(1-chloro-2-phenylacetylene) (PClPA) is a substituted polyacetylene which exhibits a relatively low gas permeability. Although its oxygen permeability is not large ($P\mathrm{O}_2$ = 5.1 barrers), its O_2/N_2 permselectivity is as high as 5.0 [18]. In light of the results obtained with PMP and PTMSP [7–11], it is of interest to investigate the effect of FS addition on the gas permeation properties of these polymers to various permanent gases.

In the present study, we report the gas permeability, solubility and diffusion coefficients of FS-containing membranes of three substituted polyacetylenes, namely PClPA, PTMSDPA, and PTMSP. Six gases (He, H_2, O_2, N_2, CO_2, and CH_4) were employed as permanent gases to study permeability. The effects of FS content on these transport parameters and on the permselectivity of these polymers have been examined. The results obtained are subsequently discussed and compared with previous related results.

Experimental

Materials

Poly(1-chloro-2-phenylacetylene) (PClPA; M_w = 0.8 × 10^6, M_w/M_n = 2.7) was prepared according to a procedure outlined in the literature [19, 20]. Poly[1-phenyl-2-(4-trimethylsilyl)phenylacetylene] (PTMSDPA; M_w = 4.7 × 10^6, M_w/M_n = 5.9) and poly[1-(trimethylsilyl)-1-propyne] (PTMSP; M_w = 1.0 × 10^6, M_w/M_n = 2.6) were donated by Nippon Oil & Fat Corperation. Fumed silica nanoparticles (Cab-O-Sil TS-530) (FS) were purchased from Cabot Corp. The TS-530 FS has a specific gravity of 2.2 g/cm^3 and a BET surface area of 230 m^2/g [21]. This surface area corresponds to an equivalent spherical primary particle diameter of 13 nm. The FS has been chemically treated with hexamethyldisilazane to replace hydrophilic hydroxy surface groups with hydrophobic trimethylsilyl surface groups.

Membrane preparation

Membranes of PClPA, PTMSDPA, and PTMSP were prepared by casting toluene solutions of these polymers (1.0–1.5 wt% polymer) onto a flat-bottomed Petri dish. The dish was then covered with a glass vessel to slow solvent evaporation (ca. 4–7 days). After membrane preparation, they were immersed in methanol for 24 h and dried to constant weight at room temperature. In a similar way, FS-filled polymer membranes were prepared by casting toluene solutions of the corresponding polymers and 10, 30, and 50 wt% FS nanoparticles (against weight of whole membrane). In the case of PClPA, FS-filled membranes were prepared with only 10 and 30 wt% FS nanoparticles. This is because the 50 wt% FS-filled PClPA membrane was too brittle to conduct experiments. On the other hand, FS contents of 10, 30, and 50 wt% were adopted in the PTMSDPA and PTMSP membranes because the increment of gas permeability was not very large in these polymers. A typical procedure of membrane fabrication is outlined below: PTMSP was dissolved in toluene to form a 1.5 wt% polymer solution which was close to the solubility limit for PTMSP in this solvent and yielded a considerably viscous solution. After preparation of the toluene solution of PTMSP, FS was added to the polymer solution. The dispersion was then mixed with a high-speed blender (18000 rpm) for 5 min, and then casted immediately onto a flat-bottomed Petri dish. The high solution viscosity helped inhibit gravity-driven sedimentation of FS particles during membrane formation. The FS-filled polymer membranes were dried as described above. The thicknesses of the FS-filled membranes were about 80–120 µm. The membranes were practically transparent and homogeneous, which should be due to both the small particle size of FS and the trimethylsilyl modification of the FS surface.

Measurements

The gas permeability coefficients (P) of the polymer membranes were measured with a Rikaseiki K-315-N gas permeability apparatus equipped with a MKS Baratron detector at 25°C. The downstream side of the membrane was evacuated to 0.3 Pa, while the upstream side was filled with a gas at about 1 atm (10^5 Pa). The increase in pressure of the downstream receiving vessel was measured during the experiment. The P values were calculated from the slopes of the time-pressure curves in the steady state regime where Fick's law is valid [22].

The gas diffusion coefficients (D) were determined by the time lag method using the following equation:

$$D = l^2/6\theta \qquad (\mathbf{1})$$

Here, l is membrane thickness and θ is time lag which is given by the intercept of the asymptotic line of the time-pressure curve to the time axis. The membrane thickness was controlled so that the time lag would be in the range 10–300 s, preferably 30–150 s. When the time lag was < 10 s, the error of measurement became relatively large. If the time lag was > 300 s, the error based on baseline drift became serious. The gas solubility coefficients (S) were calculated by using equation:

$$S = P/D \qquad (\mathbf{2})$$

Results and discussion

Effect of FS content on permeability

Table 1 presents the permeability coefficients of PClPA containing 0, 10, and 30 wt% FS to six pure gas, namely He, H_2, O_2, N_2, CO_2, and CH_4. The FS contents of 10 and 30 wt% in the membrane are based on the weight of whole membrane. It is obvious that the gas permeability of the PClPA membrane increased significantly as the content of nonporous, nanoscale FS increased. For instance, the oxygen permeability coefficient (PO_2) of PClPA containing 30 wt% FS was 86 barrers, which is 10 times higher than that of the unfilled polymer (PO_2 = 8.6 barrers). Similar trends were observed with the other gases examined. This result is in contrast to the behavior observed in traditional polymer composite membranes, which shows a decrease in gas permeability due to an increase in the tortuous path provided by the filler particles [13,14]. Incorporation of FS into the glassy but relatively dense PClPA polymer altered the polymer matrix to permit more rapid penetrant transport. This increase in permeability is presumably attributed to an increase in the free volume of the polymer membrane by the addition of FS [8], and as discussed later, increased diffusivity is related.

For the sake of comparison the gas permeability coefficients of two high free volume, in other words, superglassy polymers PTMSDPA and PTMSP were also examined with the addition of various amounts of FS (see Tables 2 and 3). Similar to that of PClPA, the gas permeability of these two polymers was increased by the addition of FS. For example, the oxygen permeability of PTMSDPA containing 50 wt% FS (PO_2 = 8400 barrers) was 5.3 times higher than that of pristine PTMSDPA (PO_2 = 1600 barrers); the PO_2 value of PTMSP containing 50 wt% FS was 1.6 times higher than that of unfilled PTMSP. From tables 1–3, it is revealed that the extent of increase of gas permeability by the addition of FS is greatest in the less permeable PClPA, while the extent of increase with the addition of FS is smaller for the more permeable PTMSDPA and PTMSP.

Table 1. Gas permeability coefficients (*P*) of PClPA and filled PClPA

	P (barrer[a])						
FS (wt%)	He	H_2	O_2	N_2	CO_2	CH_4	PO_2/PN_2
0	33	49	8.6	1.8	48	2.8	4.8
10	67	110	18	4.0	94	5.6	4.5
30	220	350	86	28	380	53	3.1

[a] 1 barrer = 1 × 10^{-10} cm^3 (STP) cm cm^{-2} S^{-1} cm Hg^{-1}.

Table 2. Gas permeability coefficients (*P*) of PTMSDPA and filled PTMSDPA

	P (barrer[a])						
FS (wt%)	He	H_2	O_2	N_2	CO_2	CH_4	PO_2/PN_2
0	1400	3200	1600	800	6700	2400	2.0
10	1500	3400	1800	910	6800	2700	2.0
30	2800	5900	3000	1800	9600	4700	1.7
50	9700	18700	8400	5900	18200	13500	1.4

[a] 1 barrer = 1 × 10^{-10} cm^3 (STP) cm cm^{-2} S^{-1} cm Hg^{-1}.

Table 3. Gas permeability coefficients (*P*) of PTMSP and filled PTMSP

	P (barrer[a])						
FS (wt%)	He	H_2	O_2	N_2	CO_2	CH_4	PO_2/PN_2
0	11000	26000	15000	12000	47000	30000	1.3
10	12000	27000	15000	12000	47000	30000	1.3
30	14000	34000	17000	14000	48000	30000	1.2
50	24000	51000	24000	21000	50000	43000	1.1

[a] 1 barrer = 1 × 10^{-10} cm^3 (STP) cm cm^{-2} S^{-1} cm Hg^{-1}.

FS addition to PClPA, PTMSDPA, and PTMSP increased permeability to different degrees depending on the penetrant. Figure 1 plots the ratios of gas permeability coefficients of polymer membranes containing 30 or 50 wt% FS and membranes of pure polymers as a function of critical volume, V_C, which characterizes penetrant size. The increase in permeability due to FS addition to PClPA became progressively larger as the penetrant size increased. For example, the CH_4 (V_C = 99.2 cm^3/mol) permeability increased 18 times with the addition of 30 wt% FS, whereas the He (V_C = 57.4 cm^3/mol) permeability was only 6.7 times higher than that of the unfilled polymer. This behavior is similar to that observed with PMP [8], and is presumably explained by the idea that the accessible free volume increased in the PClPA/FS nanocomposites. In contrst, PTMSDPA showed almost the same permeability enhancements despite the penetrant size, while PTMSP exhibited slightly smaller permeability enhancements with increasing penetrant size. The CO_2 gas showed a different behavior from those of other gases with respect to the dependence on V_C, whose reason is not clear at the moment.

According to these results, the permeability enhancement in the FS-filled polymers was in the following sequence: PClPA > PTMSDPA > PTMSP. This indicates that the permeability enhancement decreases with increasing permeability of the pristine polymers.

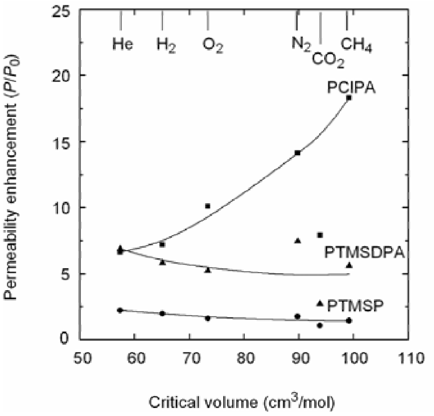

Figure 1. Gas permeability enhancement of PClPA (30 wt% FS), PTMSDPA (50 wt% FS), and PTMSP (50 wt% FS) against pure polymers as a function of penetrant size (*P* and P_0 denote the gas permeabilities of filled and pure polymer membranes, respectively).

Effect of FS content on permselectivity

Since the permeability enhancement ratios in FS-filled and original PClPA, PTMSDPA, and PTMSP membranes depended on the gas molecule, permselectivity would change with the addition of FS. Figures 2 and 3 illustrate the effects of FS content on the O_2/N_2 and H_2/CH_4 permselectivities, respectively. As seen in Figure 2, the O_2/N_2 permselectivity decreases with increasing FS content in these polymers. This tendency is strongest in the less permeable PClPA, while it is much weaker in PTMSDPA and PTMSP. This finding is consistent with the well-known permeability/permselectivity tradeoff relationship [23]. The results of H_2/CH_4 permselectivity (Figure 3) is quite different; that is, the H_2/CH_4 permselectivity sharply decreased with increasing FS content in PClPA, whereas it slightly increased with FS loading in PTMSP and PTMSDPA.

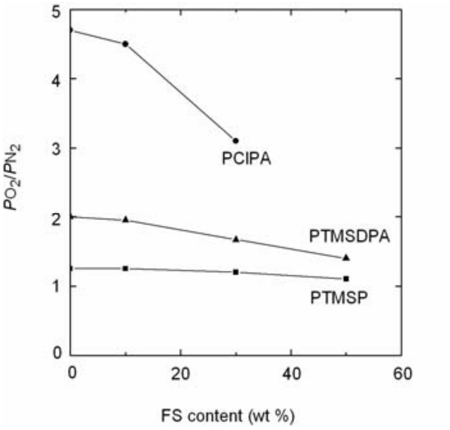

Figure 2. PO_2/PN_2 of PClPA, PTMSDPA, and PTMSP as a function of FS content.

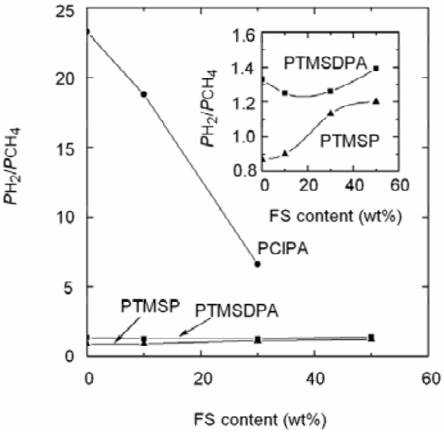

Figure 3. PH_2/PCH_4 of PClPA, PTMSDPA, and PTMSP as a function of FS content. The inset shows an expansion of the ordinate of the Figure.

Effect of FS content on solubility and diffusivity

The gas permeability coefficients (*P*) of PClPA and FS-filled PClPA were inspected in more detail by determining the gas diffusion coefficients (*D*) and gas solubility coefficients (*S*). The calculation method was explained in the experimental section. Figure 4 depicts the solubility coefficients (*S*) of PClPA containing 0, 10, and 30 wt% FS as a function of the critical temperature (T_C) of the gases. The *S* increases with increasing T_C for all gases in PClPA, which is the expected result. Interestingly, the *S* of PClPA to various gases is independent of FS content. Figure 5 illustrates the diffusion coefficients (*D*) of PClPA and FS-filled PClPA as a function of the critical volume of gases (V_C) which reflects the penetrant size of gases. The *D* decreases as V_C increases, which is also a usually observed phenomenon. It is noteworthy that the *D* of every gas increases with increasing FS content. The *D* of relatively large penetrants increased more than that of smaller penetrants, as the FS content increased from 0 to 30 wt%. For example, as the FS content increased from 0 to 30 wt%, the *D* of CH_4 increased by 20 times, while the *D* of H_2 increased by 8 times. This indicates that the diffusivity selectivity between the gases with different sizes becomes small in

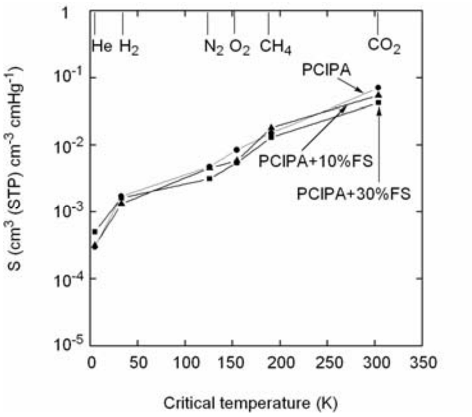

Figure 4. Solubility coefficients (*S*) of various gases in PClPA containing 0, 10, and 30 wt% FS.

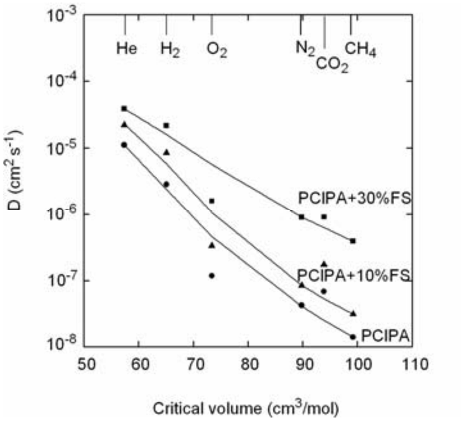

Figure 5. Diffusion coefficients (*D*) of various gases in PClPA containing 0, 10, and 30 wt% FS.

PClPA as the FS content increases, which is responsible for the decrease of permselectivity. These results also show that, in the context of solution-diffusion transport, the enhancement in gas permeability of PClPA with increasing FS content mainly originates from the increase in diffusion coefficients.

Conclusions

The addition of FS nanoparticles to three substituted polyacetylenes, PAClPA, PTMSDPA, and PTMSP, led to an increase in their gas permeabilities, unlike the case for traditional filled polymer composites. The permeability enhancement decreased as the original polymer was more gas-permeable. The permeability enhancement of the three polymers decreased in the following sequence: PClPA > PTMSDPA > PTMSP. In contrast to filled PTMSP, when PClPA was filled, the permeability coefficients of large gases increased more than those of small penetrants. The O_2/N_2 permselectivity decreased with increasing FS content, in accord with the well-known permeability/permselectivity tradeoff relationship. While the H_2/CH_4 permselectivity decreased with increasing FS content in PClPA, it slightly increased with FS loading in PTMSP. The penetrant solubility coefficients were independent of FS addition into PClPA, whereas the diffusion coefficients clearly increased with increasing FS content. This finding implies that the increase in permeability of PClPA/FS nanocomposites is caused by increased diffusion coefficients.

Acknowledgements. This research was partly supported by a Grant-in-Aid for Scientific Research (B), (No. 17350056) in 2005-06 from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

1. Compton J, Thompson D, Kranbuehl D, Ohl S, Gain O, David L, Espuche E (2006) Polymer 47: 5303
2. Espuche E, David L, Rochas C, Afeld JL, Compton JM, Thompson DW, Thompson DS, Kranbuehl DE (2005) Polymer 46: 6657
3. Mahajan R, Zimmerman CM, Koros WJ (1999) Polymer membranes for gas and vapor separation: Chemistry and Materials Science. Freeman BD, Pinnau I (ed) American Chemical Society, Washington (p 28)
4. Suer MG, Bac N, Yilmaz L (1994) J Membr Sci 91: 77
5. Duval JM (1993) J Membr Sci 80: 189
6. Jia M, Peinemann KV, Behling RD (1991) J Membr Sci 57: 289
7. Andrady AL, Merkel TC, Toy LG (2004) Macromolecules 37: 4329
8. Merkel TC, Freeman BD, Spontak RJ, He Z, Pinnau I, Meakin P, Hill A J (2003) Chem Mater 15: 109
9. Merkel TC, Freeman BD, Spontak RJ, He Z, Pinnau I, Meakin P, Hill A J (2002) Science 296: 529
10. He Z, Pinnau I, Morisato A (2002) Desalination 146: 11
11. Merkel TC, He Z, Pinnau I, Freeman BD, Meakin P, Hill A J (2003) Macromolecules 36: 6844
12. Merkel TC, He Z, Pinnau I, Freeman BD, Meakin P, Hill A J (2003) Macromolecules 36: 8406
13. Barrer RM (1968) Diffusion in polymers. Grank J, Park GS (ed) Academic Press, London (p 165)
14. van Amerongen GJ (1964) Rubber Chem Technol 37: 1065

15. Masuda T, Isobe E, Higashimura T (1983) J Am Chem Soc 105: 7473
16. Masuda T, Isobe E, Higashimura T (1985) Macromolecules 18: 841
17. Tsuchihara K, Masuda T, Higashimura T (1991) J Am Chem Soc 113: 8548
18. Masuda T, Iguchi Y, Tang BZ, Higashimura T (1988) polymer 29: 2041
19. Masuda T, Kuwane W, Higashimura T (1982) J Polym Sci: Polym Chem Ed 20: 1043
20. Taniguchi Y, Sakaguchi T, Shiotsuki M, Sanda F, Masuda T (2006) Macromolecules 39: 243
21. CAB-O-SIL TS-530 Treated Fumed Silica: Technical data (1991) Cabot Corporation
22. Masuda T, Iguchi Y, Tang BZ, Higashimura T (1988) Polymer 29: 2041
23. Robeson LM (1991) J Membr Sci 62: 165