Preparation and Gas Permeation of Immobilized Fullerene Membranes

AKON HIGUCHI,[1] TOSHIHIRO AGATSUMA,[1] SHIGEYUKI UEMIYA,[1] TOSHINORI KOJIMA,[1] KEISHIN MIZOGUCHI,[2] INGO PINNAU,[3] KAZUKIYO NAGAI,[4] BENNY D. FREEMAN[4]

[1] Department of Industrial Chemistry, Seikei University, Kichijoji Kitamachi 3, Musashino, Tokyo 180-8633, Japan

[2] Department of Polymer Physics, National Institute of Materials and Chemical Research, Higashi, Tsukuba, Ibaraki 305, Japan

[3] Membrane Technology and Research, Inc., Willow Road, Suite 103, Menlo Park, California 94025-1516

[4] Department of Chemical Engineering, North Carolina State University, Raleigh, North Carolina 27695-7905

ABSTRACT: Fullerene-dispersed membranes were homogeneously prepared under the conditions in which a 10 wt % polystyrene solution containing 1 wt % fullerene was dried under a reduced pressure of 50 cmHg at room temperature. The fullerene membranes prepared with 1,2-dichlorobenzene were found to have the darkest color, and showed no evidence of fullerene crystals in their photomicrographs. UV-visible and infrared absorption spectra of the fullerene membranes showed fullerene bands, which indicated that the fullerene was homogeneously dispersed in the membranes. The permeability coefficients of pure nitrogen, oxygen, carbon dioxide, ethane, and ethylene were found to increase significantly in the fullerene membranes compared to those in the polystyrene membranes, although the ideal separation factors for oxygen/nitrogen and ethylene/ethane in the fullerene membranes (i.e., 4.3 and 1.7, respectively) were slightly less than the separation factors in the polystyrene membranes. The permeability increase originated from the increase in diffusion coefficients in the fullerene membranes. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 529–537, 2000

Key words: membrane; fullerene; gas permeation; diffusion

INTRODUCTION

Buckminsterfullerene, C_{60}, and its derivatives show great potential for effective antiviral and other therapeutic agents, and have outstanding electronic, conducting, and magnetic properties due to their unusual extended π-electron system.[1–5]

Several research studies[6–9] have also been carried out to develop some possibilities for technological applications of fullerene such as photoconductive and electroconductive fullerene films. Earlier works[7–12] concerning the deposition of pure fullerene using the LB technique[12] or a mixture of pure fullerene in a polymer matrix[7,8] have revealed great difficulty in the preparation of the fullerene films dispersed uniformly, because the fullerene readily crystallizes in the films. Hwang and Mauzerall[10] and Bensasson et al.[11] prepared ultrathin lipid films in which the small aggregates of fullerenes C_{60} and C_{70} were incorporated and conferred on them photoconducting properties.

Spin-casting (coating) and drop casting methods[7,8] were, therefore, used for the preparation of

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homogeneous films of fullerene/polymer blends to avoid the crystallization and aggregation of fullerenes in the films. Eom et al.[13] reported fabrication of free-standing C_{60} membranes using C_{60} deposition by thermal evaporation on silicon wafers. They reproducibly made free-standing C_{60} membranes with an area of 6.4 by 6.4 mm^2 and 2000 to 6000 angstrom thick.[13]

In this study, we succeeded in obtaining homogeneous fullerene (a mixture of C_{60} and C_{70})-dispersed polystyrene membranes having a diameter of more than 90 mm using the casting method under reduced pressure. The fullerene membranes were found to be free standing, because they were prepared to have 40–60 μm thickness for the measurement of gas permeation through them.

Pure crystalline fullerene is known to show a molecular rotor,[14] having a diameter of 7 angstroms at room temperature, and fullerene readily forms solid solvates with several host solvents such as n-pentane,[15] hexane,[14,16] n-decane,[17] and benzene.[14] These intrinsic characteristics of fullerene prompted us to prepare homogeneous fullerene-dispersed polymeric membranes (i.e., fullerene/polymer blend membranes), and to investigate gas permeation through the fullerene membranes where the fullerene is spinning as a molecular rotor and solvates with penetrant gases.

The aim of the present work was to find optimal conditions for the preparation of homogeneous fullerene-dispersed polystyrene membranes, and to investigate the effect of fullerene in the permeation of inorganic gases, ethane and ethylene, through the membranes.

EXPERIMENTAL

Materials

Polystyrene (Ave. MW = 280,000) purchased from Aldrich Co., Ltd., was used as received. Fullerite (approximately 90% C_{60} and 10% C_{70}, F-4023, Aldrich-Sigma Co., Ltd.) was used as received. Other chemicals purchased from Aldrich Chemicals Co., Ltd., were of reagent grade, and were used without further purification.

Preparation of Fullerene Membranes

Fullerite (fullerene) was dissolved in its good solvents of benzene, toluene, 1,2-dichlorobenzene, 1,2-dichloroethane, 1-methyl-2-pyrrolidone, and pyridine. After a 1 wt % fullerene solution was prepared, the polystyrene was dissolved in the fullerene solution to 10 wt %. The fullerene/polymer solution was agitated for 24 h, filtered through filter paper (No. 5, Toyo Roshi International, Inc.), and subsequently allowed to stand for at least 24 h.

The 10 wt % polystyrene solution containing 1 wt % fullerene was cast on flat Petri dishes having a diameter of 90 mm. The membranes were finally prepared by drying the solution under three conditions, which were at atmospheric pressure and room temperature (20–25°C) for a week (condition A), under a reduced pressure of 50 cmHg at room temperature (20–25°C) for 12 h (condition B), and under a pressure of 50 cmHg at an elevated temperature, i.e., 100 or 150°C, for 12 h (condition C). The fullerene films of 40–60-μm thickness were peeled off the flat Petri dishes and finally dried under vacuum at 120°C for 24 h. Four different fullerene membranes were prepared under each condition for observation of the crystalline blocks measured from photographs and photomicrographs. Fullerene membranes of approximately 10-μm thickness were also prepared by the same procedures described above, and were used for the UV-visible and IR measurements.

Characterization of Fullerene Membranes

The photomicrographs of the fullerene membranes were taken with an inverted microscope (Diaphoto TMD 300, Nikon Co.). Those shown in Figures 2 and 4 are typical examples from 20 measurements using four different membranes under each condition.

Infrared spectra of fullerene membranes were taken with a Perkin-Elmer 2000-type FTIR spectrometer with a DTGS detector under dry N_2 flow (2000 cc/min). UV-visible spectra of the fullerene membranes were measured with a JASCO V-550 instrument (JASCO Corporation). Spectra shown in Figures 5–8 were averages of four measurements using four different membranes under each condition. The standard deviation of the spectra was less than 8% of their absorbance, which was mainly due to the error in membrane thickness measurements. In any case, the spectral tendencies were exactly the same in the spectra of the membranes prepared under the same conditions.

Gas Permeation through Fullerene Membranes

The permeability and diffusion coefficients of gases through the membranes were determined by the vacuum-pressure method using a K-315N gas permeation instrument (Rikaseiki Co., Ltd.). The transport theory and calculation of the permeability and diffusion coefficients were performed according to the general method.[18–20] The permeability coefficient (P) was calculated from the slope of the time–downstream pressure curves in the steady state. The diffusion coefficient (D) was determined using the time lag method[18]

$$D = L^2/6\theta \tag{1}$$

where θ is the time lag, and L is the thickness of the membrane. The solubility (S) was calculated by the permeability coefficient divided by the diffusion coefficient. The permeability and diffusion coefficients were obtained from the average of six measurements using two different membranes. Their standard deviations were found to be less than 9 and 21% of their values, respectively.

RESULTS AND DISCUSSION

Solvent Effects on Preparation of Fullerene Membranes

Six solvents, i.e., benzene, toluene, 1,2-dichlorobenzene, 1,2-dichloroethane, 1-methyl-2-pyrrolidone and pyridine, were selected as casting solvents for the preparation of fullerene-dispersed polystyrene membranes (fullerene membranes), because the six solvents are good solvents for both fullerene and polystyrene. The membranes were prepared by drying the 10 wt % polystyrene solution containing 1 wt % fullerene under the three conditions described in the Experimental section.

The fullerene membranes were prepared under condition A, and were investigated to determine whether the fullerene-dispersed polystyrene membranes were homogeneously prepared under this condition. Figure 1 shows photographs of the overall fullerene membranes and the fullerene solution prepared with the six solvents under condition A. The solid membranes were obtained using the solvents benzene, toluene, 1,2-dichloroethane, and pyridine, while the fullerene solution was still in a liquid state using the solvents 1-methyl-2-pyrrolidone and 1,2-dichlorobenzene
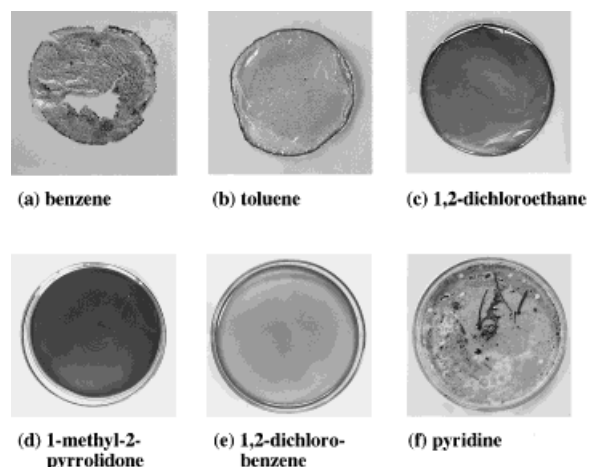

(a) benzene   (b) toluene   (c) 1,2-dichloroethane

(d) 1-methyl-2-pyrrolidone   (e) 1,2-dichlorobenzene   (f) pyridine

Figure 1 Photographs of fullerene membranes and fullerene solution prepared with the solvents benzene (a), toluene (b), 1,2-dichloroethane (c), 1-methyl-2-pyrrolidone (d), 1,2-dichlorobenzene (e), and pyridine (f) under condition A.

due to their high boiling points a week after casting the membranes (i.e., 202°C for 1-methyl-2-pyrrolidone and 180–183°C for 1,2-dichlorobenzene). Dispersed small crystals of fullerene were visually observed on the fullerene membranes prepared with benzene, toluene, and pyridine as their solvents. Needle-like crystals of fullerene of more than 10 mm were observed on the fullerene membranes prepared with pyridine. It is found that the fullerene membranes prepared with 1,2-dichloroethane are the best homogeneous fullerene-dispersed membranes on a macroscopic level when the membranes are prepared under condition A.

The photomicrographs of the fullerene membranes were taken by an inverted microscope, and examination was done to determine whether the fullerene was homogeneously dispersed in the fullerene membranes prepared with 1,2-dichloroethane on a microscopic level.

Figure 2 shows photomicrographs of the fullerene membranes prepared with benzene, toluene, and 1,2-dichloroethane as the solvents under condition A. Crystalline blocks of fullerene of 5–10-μm length were widely observed in the photomicrographs of the fullerene membranes prepared with 1,2-dichloroethane as the solvent. On a microscopic level, the fullerene membranes prepared with 1,2-dichloroethane under condition A were also found not to be homogeneously dispersed fullerene membranes.

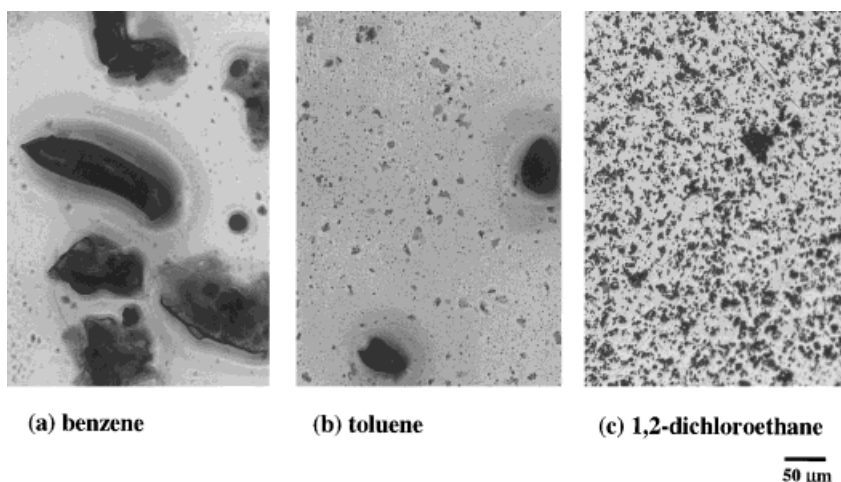For comparison of the membranes prepared with benzene, toluene, and 1,2-dichloroethane as

Figure 2 Photomicrographs of fullerene membranes prepared with the solvents benzene (a), toluene (b), and 1,2-dichloroethane (c) under condition A.

the solvents, the photomicrographs of the fullerene membranes prepared with benzene and toluene were also examined. Crystalline blocks of fullerene of approximately a 200×50-μm length were observed in the fullerene membranes prepared with benzene as the solvent and were much bigger crystals compared with those found in the fullerene membranes prepared with 1,2-dichloroethane in Figure 2. This is consistent with the results observed in Figure 1. In the fullerene membranes prepared with toluene, smaller crystalline blocks of fullerene of approximately a 0.5–10-μm length were frequently observed, and bigger crystalline blocks of approximately a 50×50-μm length were less frequently observed in Figure 2.

Under condition A, fullerene was the most homogeneously dispersed in the fullerene membranes prepared with 1,2-dichloroethane. This is caused by the low boiling point of 1,2-dichloroethane (i.e., 83.7°C). Because 1,2-dichloroethane in the fullerene solution evaporates faster than other solvents in the fullerene solution under condition A, the phase separation from sol to gel occurs faster in the fullerene solution of 1,2-dichloroethane, and there would not be enough time to generate bigger fullerene crystals in the solution.

A method of reducing the phase separation time to avoid the crystalline growth of fullerene was, therefore, used in the following experiments. Under condition B, the polystyrene solution containing fullerene was cast on flat Petri dishes and subsequently dried under a reduced pressure of

50 cmHg at room temperature (i.e., condition B). Figure 3 shows photographs of the overall fullerene membranes prepared with six solvents under condition B. The solid membranes were prepared in any case under condition B. The darkness of the films depended on the solvents used in the casting solution, and was observed in the following order of the solvents: 1,2-dichlorobenzene = pyridine > 1-methyl-2-pyrrolidone > benzene = toluene > 1,2-dichloroethane. The darkest membranes were obtained with the fullerene membranes prepared with 1,2-dichlorobenzene and pyridine under condition B.
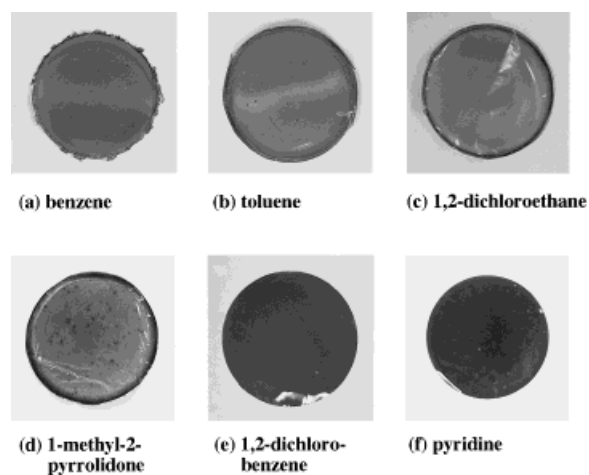

Figure 3 Photographs of fullerene membranes prepared with the solvents benzene (a), toluene (b), 1,2-dichloroethane (c), 1-methyl-2-pyrrolidone (d), 1,2-dichlorobenzene (e), and pyridine (f) under condition B.
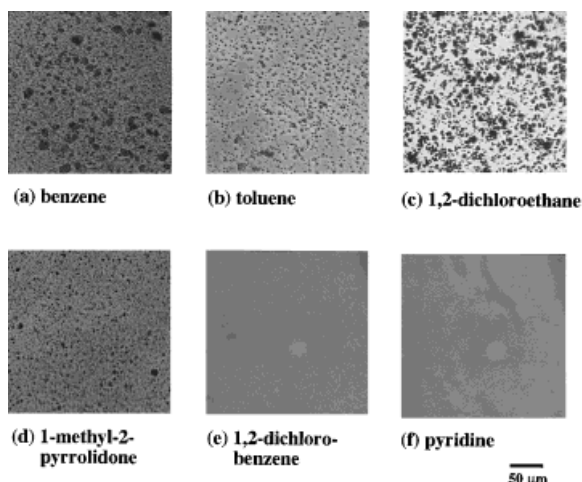
Figure 4 Photomicrographs of fullerene membranes prepared with the solvents benzene (a), toluene (b), 1,2-dichloroethane (c), 1-methyl-2-pyrrolidone (d), 1,2-dichlorobenzene (e), and pyridine (f) under condition B.

Micrographs of the fullerene membranes were taken to investigate the size of the fullerene crystals in the membranes and to determine whether the fullerene was homogeneously dispersed in the membranes on a microscopic level. Figure 4 shows photomicrographs of the fullerene membranes prepared with six solvents under condition B. Crystalline blocks of fullerene of approximately a 5–10-μm length were widely observed in the photomicrographs of the fullerene membranes prepared with 1,2-dichloroethane as the solvent. A similar size and dispersion of fullerene crystals were observed in the fullerene membranes prepared with 1,2-dichloroethane under both condition A and condition B. This is probably due to the low boiling point of 1,2-dichloroethane (i.e., 83.7°C), which causes evaporation of 1,2-dichloroethane in the fullerene membranes even at atmospheric pressure (i.e., condition A).

Smaller crystalline blocks of fullerene compared with those in the fullerene membranes prepared with 1,2-dichloroethane were observed in the photomicrographs of the fullerene membranes prepared with benzene, toluene, and 1-methyl-2-pyrrolidone. It is found that better membranes that have more homogeneously dispersed fullerene are obtained by reducing the phase separation time in the fullerene membranes under condition B. The fullerene membranes with 1,2-dichlorobenzene and pyridine as the solvent under condition B showed no evidence of fullerene crystals in the photomicrographs, and were found to be the best membranes in which

fullerene was the most homogeneously dispersed in this study. This indicates that the size of the fullerene crystals is less than 0.5 μm from the limited resolution of the photomicrograph, if the fullerene crystals exist in the membranes. Consistent results are obtained from Figures 3 and 4, in which the color of the fullerene membranes is darker when the size of fullerene crystals is smaller in the membranes.

The fullerene membranes were also prepared with 1,2-dichlorobenzene as the solvent at elevated temperatures of 100 and 150°C under condition C. No difference in the appearance at macroscopic and microscopic levels was found in this study (data not shown).

UV-Visible Spectra of Fullerene Membranes

UV-visible absorption spectra of the fullerene membranes were investigated, and the absorption spectra of fullerene in the membranes were compared to those in the solution where the fullerene is homogeneously dispersed. Figures 5 and 6 show the absorption spectra of polystyrene, fullerene in benzene solution, and the fullerene membranes prepared with benzene, toluene, 1,2-dichlorobenzene, 1,2-dichloroethane, 1-methyl-2-pyrrolidone, and pyridine as the solvent under condition B. The fullerene membranes used for the absorption spectra were selected membranes having a membrane thickness of 10 ± 2 μm, and the spectra of the fullerene membranes in Figures
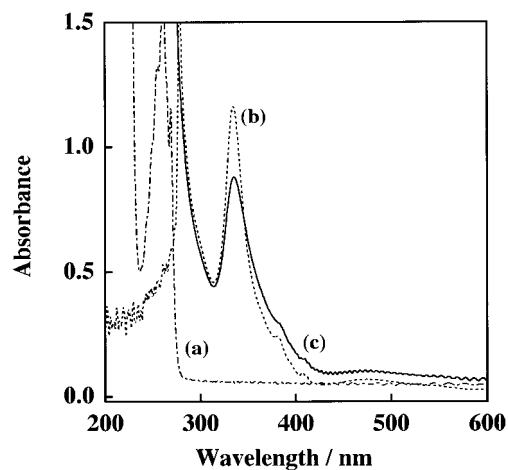

Figure 5 UV-visible spectra of polystyrene (a), 5 wt % fullerene in benzene solution measured by 1 cm path length (b), and the fullerene membrane prepared with the solvent 1,2-dichlorobenzene (c) under condition B.
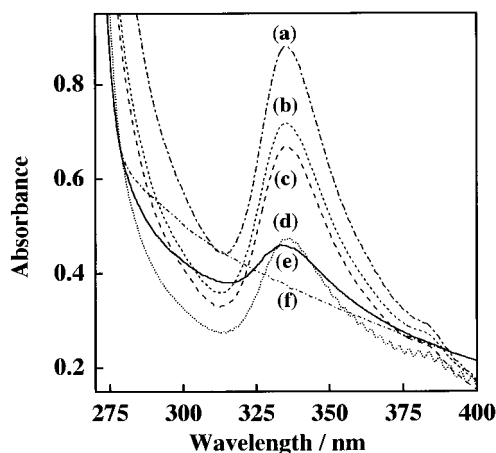
Figure 6 UV-visible spectra of the fullerene membranes prepared with the solvents 1,2-dichlorobenzene (a), toluene (b), benzene (c), 1,2-dichloroethane (d), pyridine (e), and 1-methyl-2-pyrrolidone (f) under condition B.

5 and 6 were normalized to those of a 10-μm thickness from the Lambert-Beer equation.

No significant absorption peak was observed in the spectra of polystyrene at a wavelength of > 290 nm, as found in Figure 5. The maximum peak in the spectra around 335 nm therefore solely originates from the fullerene in the fullerene membranes. The spectra of the fullerene membranes are similar to those of Langmuir-Blodgett films containing a mixture of fullerene and arachidic acid[12] and the spectra reported in other literature.[13,21,22] The spectra of the fullerene membranes prepared with 1,2-dichlorobenzene, toluene, benzene, pyridine, and 1,2-dichloroethane around 335 nm are exactly the same as those of the fullerene solution, although the peak around 335 nm is not observed for the fullerene membranes prepared with 1-methyl-2-pyrrolidone. These results indicate that the fullerene in the membranes prepared with 1-methyl-2-pyrrolidone is not homogeneously dispersed in the membranes based on the UV-visible spectroscopic measurements.

The absorbance at 335 nm, which reflects the concentration of fullerene dispersed homogeneously, was observed to increase in the following order of the solvents used for the preparation of the fullerene membranes, 1-methyl-2-pyrrolidone < pyridine = dichloroethane < benzene < toluene ≪ 1,2-dichlorobenzene from Figure 6. The highest absorbance at λ = 335 nm is observed in the fullerene membranes prepared with 1,2-dichlorobenzene. This suggests that fullerene is much

more homogeneously dispersed in the membranes prepared with 1,2-dichlorobenzene compared to the membranes prepared with the other solvents in this study.

IR Spectra of Fullerene Membranes

Infrared spectra of the fullerene membranes were investigated to compare the absorbance of fullerene in the fullerene membranes prepared with six different solvents.

Figure 7 shows infrared spectra of a polystyrene membrane, fullerene, and a fullerene membrane prepared with 1,2-dichlorobenzene under condition B. The fullerene exhibits four main absorption bands at 1429, 1183, 575, and 525 cm^{-1}. The fullerene membrane in Figure 7 shows almost the same spectrum as that of the polystyrene membrane due to the strong absorption bands of polystyrene compared to those of fullerene at wavenumber > 600 cm^{-1}, because the fullerene is present at only 10 wt % in the fullerene membranes in this study.

Because the absorption band of polystyrene at 540 cm^{-1} is relatively weak in the spectra of polystyrene, and the absorption bands of fullerene at 575 and 525 cm^{-1} are relatively strong in the spectra of fullerene, infrared spectra from 600 cm^{-1} to 500 cm^{-1} of the polystyrene membrane and fullerene membranes prepared with the six solvents were investigated in detail. Figure 8 shows the infrared spectra of fullerene, the polystyrene membrane, and fullerene mem-
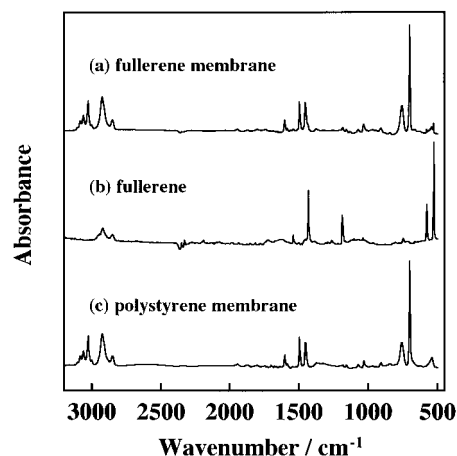

Figure 7 Infrared spectra of fullerene membrane prepared with the solvent 1,2-dichlorobenzene under condition B (a), solid fullerene in KBr pellet (b), and polystyrene membrane (c) at 0.5 cm^{-1} resolution.
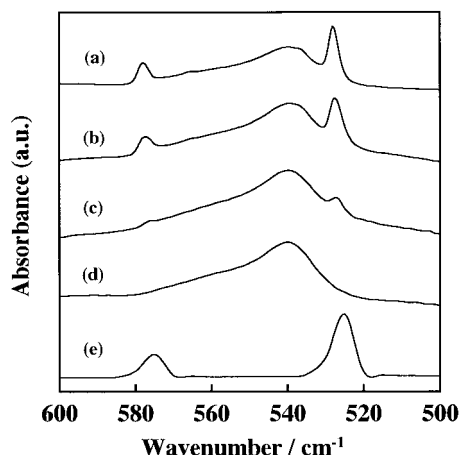
Figure 8 Infrared spectra of the fullerene membranes prepared with the solvents 1,2-dichlorobenzene (a), benzene (b), and 1-methyl-2-pyrrolidone (c) under condition B, polystyrene membrane (d), and fullerene (e) at 0.5 cm^{-1} resolution.

branes prepared with 1-methyl-2-pyrrolidone, benzene, and 1,2-dichlorobenzene under condition B. The absorbance at 525 cm^{-1} compared to the absorbance at 540 cm^{-1}, which reflects the concentration ratio of fullerene to polystyrene, was observed to increase in the following order, 1-methyl-2-pyrrolidone < benzene < 1,2-dichlorobenzene in Figure 8.

The following function, α, is introduced to find the fullerene concentration in the fullerene membranes quantitatively,

$$\alpha = [A(525) - A(600)]/[A(540) - A(600)] \quad (2)$$

where A(600) is the absorbance at 600 cm^{-1} that is selected as the baseline of the polystyrene and fullerene peaks, A(525) is the absorbance of the peak top around 525 cm^{-1} that is assigned to the fullerene peak, and A(540) is the absorbance at 540 cm^{-1} that is assigned to the polystyrene peak. α indicates the concentration ratio of fullerene to polystyrene, and is an index of how homogeneously the fullerene is dissolved in the fullerene membranes.

The dependence of α on Hildebrand solubility parameters of the solvents that were used for the preparation of the fullerene membranes under condition B was investigated, and is shown in Figure 9. The fullerene membrane prepared with 1,2-dichlorobenzene shows the highest value of α in this study, which shows that the membrane contains the most homogeneously dispersed

fullerene based on the infrared spectra in this study. α was observed to increase in the following order of the solvents used for the preparation of the fullerene membranes, 1-methyl-2-pyrrolidone < pyridine = 1,2-dichloroethane < benzene = toluene < 1,2-dichlorobenzene in Figure 9. This order is similar to the order of absorbance strength of the solvents found in the UV-visible spectra at 335 nm in Figure 6.

In summary, fullerene is the most homogeneously dispersed in the membrane prepared with 1,2-dichlorobenzene under condition B based on the investigations of UV-visible spectra (i.e., Fig. 6) and infrared spectra (i.e., Fig. 9), not only from the microscopic observations in Figure 4 in this study.

Gas Permeation in Fullerene Membranes

The gas permeation properties of the fullerene membranes and polystyrene membranes were investigated for pure nitrogen, oxygen, carbon dioxide, ethane, and ethylene. The fullerene membranes used for the gas permeation experiments were the membranes prepared with 1,2-dichlorobenzene under condition B.

Table I shows permeability coefficients, diffusion coefficients, and solubilities of the gases in the fullerene membranes and polystyrene membranes. The permeability coefficients of the gases used in this study were found to significantly increase in the fullerene membranes compared to
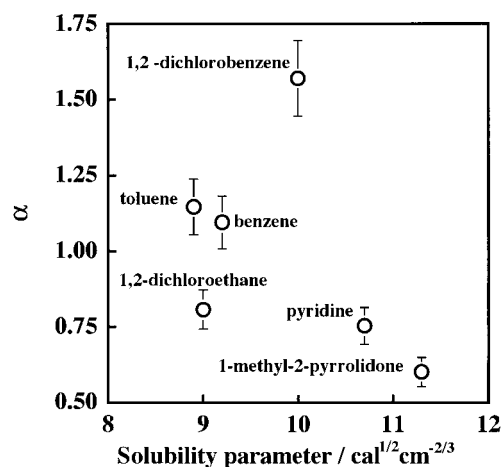

Figure 9 Dependence of α on Hildebrand solubility parameters of solvents used for the preparation of the fullerene membranes under condition B. Data are expressed as the means ± SD of four measurements using four different membranes under each condition.

Table I   Permeation Parameters for Various Gases in Fullerene Membranes and Polystyrene Membranes at 308 K

Membranes	P $(10^{-10}$ cm^3 (STP) $\cdot$ cm/cm$^2 \cdot$ s $\cdot$ cmHg)					D $(10^{-8}$ cm^2/s)					S (cm^3 (STP)/cm$^3 \cdot$ cmHg)				
	N_2	O_2	CO_2	C_2H_4	C_2H_6	N_2	O_2	CO_2	C_2H_4	C_2H_6	N_2	O_2	CO_2	C_2H_4	C_2H_6
Polystyrene	0.38	2.0	9.3	0.58	0.28	6.5	16.0	6.6	0.34	0.14	0.06	0.12	1.4	1.7	2.0
Fullerene	0.56	2.4	9.6	0.82	0.49	8.0	18.0	6.8	0.44	0.25	0.07	0.13	1.4	1.9	2.0

those in the polystyrene membranes (e.g., 47% increase for nitrogen, 75% increase for ethane, and 41% increase for ethylene). The increase in permeability of the gases originates from the increase in diffusion of the gases in the fullerene membranes compared to the diffusion coefficients in the polystyrene membranes, although the solubilities of the gases are almost equal in the fullerene membranes and polystyrene membranes (see Table I). The permeability increase in the fullerene membranes is explained by the enhanced free volume of the membranes with fullerene. The enhanced free volume is generally effective for the increase in the diffusion coefficient but not for the increase in solubility.[23]

A significant increase in the solubilities of ethane and ethylene in the fullerene membranes is not observed in the fullerene membranes having a polystyrene matrix, although it is reported that the fullerene readily forms solid solvates with alkanes and alkenes.[14–17]

Ideal separation factors for oxygen/nitrogen and ethylene/ethane in the fullerene membranes are calculated to be 4.3 and 1.7 from Table I, respectively, which are not improved values compared with those in the polystyrene membranes (5.3 and 2.1, respectively), although increased permeability of gases is observed in the fullerene membranes.

CONCLUSIONS

Fullerene-dispersed membranes can be homogeneously prepared under conditions in which a 10 wt % polystyrene solution containing 1 wt % fullerene is dried under a reduced pressure of 50 cmHg at room temperature. The fullerene membrane prepared with 1,2-dichlorobenzene is found to have the most homogeneously dispersed fullerene based on microscopic observation and the UV-visible and infrared spectra of fullerene.

The permeability coefficients of pure nitrogen, oxygen, carbon dioxide, ethane, and ethylene were found to increase significantly in the fullerene membranes compared to those in the polystyrene membranes (e.g., 47% increase for nitrogen, 75% increase for ethane, and 41% increase for ethylene), although the ideal separation factors for oxygen/nitrogen and ethylene/ethane in the fullerene membranes (i.e., 4.3 and 1.7, respectively) were slightly less than the separation factors in the polystyrene membranes. The permeability increase originates from the increase in diffusion coefficients in the fullerene membranes, which is due to the enhanced free volume of the membranes with fullerene.

The fullerene membranes prepared in this study will be effective for the applications of photoconductive[6–9,24,25] or electroconductive[26,27] membranes and other applications,[28,29] rather than for the application of gas separation membranes investigated in this study, because the homogeneously dispersed fullerene membranes can be easily prepared using the present conditions and methods.

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