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Plasma-polymerization of F-propene/acetylene and F-propene/ethylene mixtures and their gas permeability

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SUMMARY

Plasma-polymerized thin films from the mixture of F-propene and acetylene (C_2H_2) or ethylene (C_2H_4) were investigated by elemental analysis, infrared spectroscopy, and ESCA. The chemical composition for the plasma-polymers depended on these gaseous mixture composition. The F/C elemental ratio for the plasma-polymers decreased with increasing the C_2H_2 or C_2H_4 concentration, and at the same time the H/C ratio increased. The plasma-polymers were composed of $\underline{C}F_3$, $\underline{C}F_2$, $\underline{C}F\text{-}CF_n$, $\underline{C}F$, and $\underline{C}\text{-}CF_n$ units. The addition of C_2H_2 or C_2H_4 depressed the formation of the plasma-polymers with highly-fluorinated carbon units such as CF_3, CF_2 groups, and encouraged that of polymers with less-fluorinated carbon units. Furthermore, such changes of the plasma-polymers in the chemical composition by adding C_2H_2 or C_2H_4 were favourable to improve gas separation abilities. The ratio of oxygen and nitrogen permeation coefficient increased from 1.7 to 3.5 by adding C_2H_2 of 50 mol% and also increased to 2.9 by adding C_2H_4 of 37.5 mol%. Less-fluorinated carbon units seem to play an important role in the separation from the oxygen/nitrogen mixture.

INTRODUCTION

Plasma-polymerization is an unique thin-film process, which proceeds in stepwise reactions by repetition of the fragmantation of monomers and the recombination of activated fragments (YASUDA, 1985). When the mixture of two different monomers is used as the starting material polymers formed will contain the two monomer's elements, and their chemical composition and physical properties strongly depend on the composition of the mixture.

The permeation through nonporous films involves two essential process: (i) adsorption and solution of gases at the film surfaces and (ii) diffusion of the dissolved gases toward the other surface side by concentration differences (KREVELEN, 1976). Therefore, the effective separation from gas mixtures with mambranes requires large differences either in the solubility (S) or in the diffusion coefficient (D) between the two component-molecules of the gas mixture. S and D values are resultants of interactions between dissolved gas molecules and polymer chains, and may be closely related to the cohesive energy density of the polymeric films. Crosslinkage also influences the permeability.

In this study F-propene having affinity to oxygen molecules is used as a primary monomer, and acetylene or ethylene as second monomers to increase the cohesive energy density and also to induce intense crosslinking reactions. Plasma-polymerization in these mixture systems are investigated, and the permeability of their plasma-films are examined as a function of the C_2H_2 and C_2H_4 concentration.

EXPERIMENTAL

The apparatus used for plasma-polymerization in this study was a bell-jar-type reaction chamber (400 mm diameter, 470 mm high), which was the same as reported elsewhere (INAGAKI, 1983). Glow discharge between a pair of aluminum electrodes (150 mm square) was driven by capacitive coupling of a 20 kHz ultrasonic frequency (a constant uf current of 50 mA), and magnetic enhancement was employed. The experimental procedures for the plasma-polymerization were the same as have been reported previously (INAGAKI, in press). F-propene (HFP) (97 - 99 % purity) (from PCR Research Chemicals, Inc.), acetylene and ethylene (99 %) (from Matheson) were used as monomers without further purification.

The C, H, and N contents for the plasma-polymers were determined with a Yanagimoto analyzer MT-2. The F content was determined by colorimetric analysis (alizarine complex method). The O content was different between the sample weight and the sum of the C, H, N, and F contents determined.

Infrared spectra for the plasma-polymers were recorded with a Nihon Bunko fourier-transform spectrometer FT/IR-3. ESCA spectra for the plasma-polymers deposited on silicon wafers (approximately 100 nm thick) were recorded with a Shimadzu electronspectrometer ESCA 750 employing Mg K_α exciting radiation at 8 kV and 30 mA. An Au core level at 84.0 eV was temporarily used for calibration of the energy scale. The complex C_{1s} spectra were resolved with a Shimadzu data system ESCAPAC 760. Three parameters, the position and height of the peak, and the full width at half-maximum (FWHM), were varried to correspond roughly to the observed spectra. The FWHM value for all the resolved curves was within 2 eV.

The contact angles of water, glycerol, formamide, diiodomethane, and tricresyl phosphate on the plasma-polymers deposited on a glass slide were measured by a drop-on-plate method using an Erma contact anglemeter G-I with a goniometer. The contact angle data were analyzed to estimate a dispersive contribution, γ_s^d, and a polar contribution, γ_s^p, according to Kaelble's method (KAELBLE, 1971).

The permeation rate of gases through the plasma polymer-films deposited on porous membrane filters (MF Milipore VSWP, pore size 25 nm) was measured at 20 °C in ranges of pressure differences (7.8 - 19.6 x 10^4 Pa (0.8 - 2.0 kg/cm^2)) between the upstream and the down stream sides according to ASTM D143V. Oxygen and nitrogen (99.99 %) purified with a line filter (Fuji Kinzoku Kohsaku Co. Ltd., FUFL 915) and a dry column (Nikka Seiko Co Ltd., DC-A4), were used as the feed gases. The thickness of the plasma-films was estimated by interferrometry. From data of the permeation rate and the plasma-films thickness the permeation coeffifients (P_{O2} and P_{N2}) were calculated.

RESULTS AND DISCUSSION

Light-yellow polymer films were obtained from the HFP/C_2H_2 and HFP/C_2H_4 mixture. They contained large amounts of C, F, and H with small amounts of O and N. The elemental composition of the plasma-polymers strongly depended on the starting composition of the HFP/C_2H_2 and

FP/C_2H_4 mixtures: The F/C molar ratio for the plasma-polymers, as shown in Figure 1 and 2, decreased with increasing the C_2H_2 or C_2H_4 concentration, while, the H/C molar ratio increased. Being accompanied with these changes in the elemental composition the surface energy for the plasma-polymers increased linearly from 20 to 38 dyn/cm with increasing the C_2H_2 or C_2H_4 concentration. These results suggest that C_2H_2 and C_2H_4 molecules may be copolymerized with HFP molecules to yield plasma-polymers, as it were copolymers of HFP and C_2H_2 or C_2H_4.

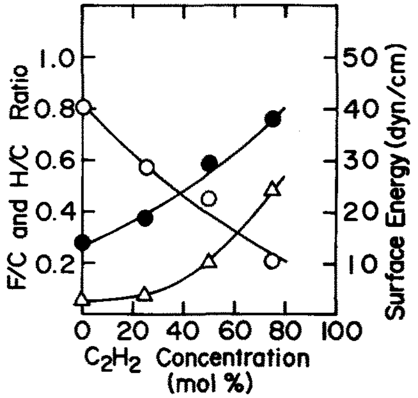

Fig. 1 Elemental Ratio and Surface Energy for Plasma-polymers from HFP/C_2H_2 Mixture; ○, F/C; △, H/C; ●, Surface Energy.

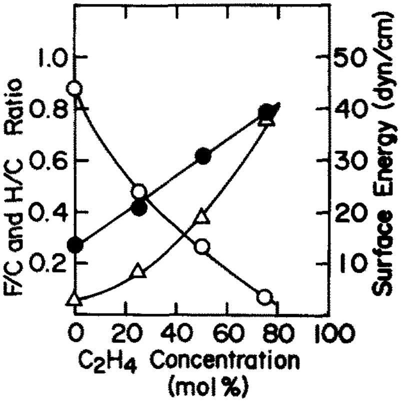

Fig. 2 Elemental Ratio and Surface Energy for Plasma-polymers from HFP/C_2H_4 Mixture; Remarks are the same as those in Fig. 1.

The plasma-polymers from HFP showed strong infrared absorptions at 3450 (OH), 1725 (C=O, -CF=CF_2), 1230, 990, and 745 cm^{-1} (C-F). The plasma-polymers, when C_2H_2 or C_2H_4 molecules were added to HFP, showed characteristic absorptions due to C-H groups on their infrared spectra. New absorptions appeared at 2960 (CH_3), 1830 (-CH=CH_2), 1650 (C=C), 1460 (CH_3), 1440 (CH_2), and 1380 cm^{-1} (CH_3); and the absorptions due to C-F groups still remained. The intensity of the absorptions related to C-H groups augmented with increasing the C_2H_2 or C_2H_4 concentration, while, that of the absorptions related to C-F groups diminished. Such changes in the chemical composition of the plasma-polymers by the addition of C_2H_2 or C_2H_4 molecules could be quantitatively examined by ESCA.

Figure 3 and 4 show ESCA(C_{1s}) spectra for the plasma-polymers as a function of the C_2H_2 or C_2H_4 concentration. The plasma-polymers from HFP showed a complex C_{1s} spectra which could be resolved into five features. These are $\underline{C}F_3$, $\underline{C}F_2$, $\underline{C}FCF_n$, $\underline{C}F$, and $\underline{C}$-CF_n groups of which the peak positioned at 294.4, 292.4, 289.9, 287.9, and 285.5 eV, respectively (CLARK, 1975). The plasma-polymers from the HFP/C_2H_2 or HFP/C_2H_4 mixture showed also complex C_{1s} spectra which were different from the former. The C_{1s} spectra changed the shape with increaasing the C_2H_2 or C_2H_4 concentration, and a main peak shifted to low-binding-energy regions. These C_{1s} spectra also could be resolved into five features ($\underline{C}F_3$, $\underline{C}F_2$, $\underline{C}F\text{-}CF_n$, $\underline{C}F$, and $\underline{C}\text{-}CF_n$ groups). The relative concentration of the five C_{1s} features was plotted against the C_2H_2 or C_2H_4 concentration (Figure 3 and 4). These figures show decreases of highly-fluorinated carbon units such as CF_3 and CF_2 groups and increases of less-fluorinated carbon units such as C-CF_n groups with increasing the C_2H_2 and C_2H_4 concentration. A remarkable increase of the less-fluorinated carbon units occurs at C_2H_2 and C_2H_4 concentrations of more than 50 and 35 mol%, respectively.

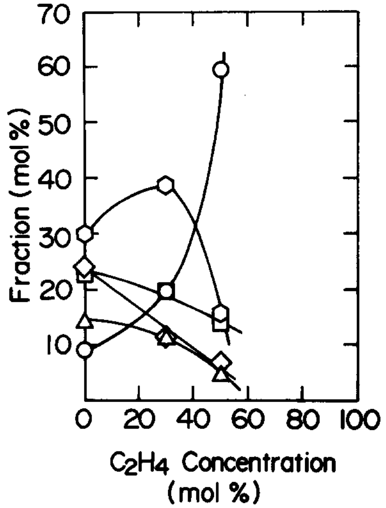

Fig. 3 C_{1s} Components for Plasma-polymers from HFP /C_2H_2 Mixture; △, CF_3; ◇, CF_2; □, CF-CF_n; ⬡, CF; ○, C-CF_n.

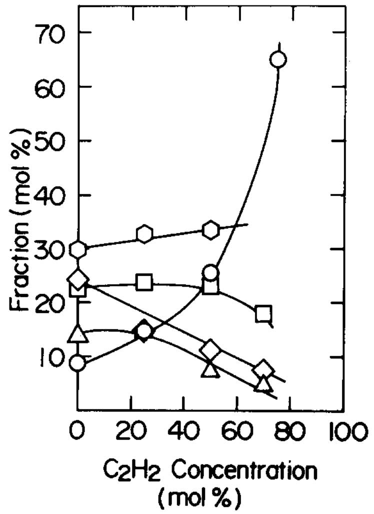

Fig. 4 C_{1s} Components for Plasma-polymers from HFP /C_2H_4 Mixture; Remarks are the same as those in Fig. 3.

The plasma-polymers formed from the HFP/C_2H_2 and HFP/ C_2H_4 mixtures and deposited on Milipore filters were provided for the permeation experiments. Preliminary experiments showed that the plasma-films of more than 300 nm thick were required to cover porous Milipore membranes surfaces, and that oxygen and nitrogen permeability coefficients had no dependency on the feed pressure within 7.8 - 19.6 x 10^4 Pa. Therefore, the plasma-films of 370 - 680 nm thick were served for permeation experiments, and the average of seven measurements at different feed pressures was taken as a permeability coefficient. Table 1 shows the oxygen and nitrogen permeability coefficients (P_{O2} and P_{N2}) and their ratio (P_{O2}/P_{N2}) as a function of the HFP/C_2H_2 and HFP/C_2H_4 mixture composition, indicating dependences of the P_{O2} and P_{N2} values and of the P_{O2}/ P_{N2} ratio on the staring composition of these gaseous mixtures. For the plasma-films from the

Table 1 Permeability Coefficient of Plasma-Polymers

Monomer		Film Thickness	P_{O2}	P_{N2}	P_{O2}/P_{N2}
HPF/C_2H_2	1/0	500 nm	0.25	0.15	1.7
	3/1	620	2.03	0.74	2.7
	1/1	560	1.42	0.41	3.5
	1/3	540	0.06	0.05	1.1
HFP/C_2H_4	1/0	500	0.25	0.15	1.7
	7/1	370	0.39	0.21	1.9
	3/1	520	0.95	0.45	2.1
	5/3	520	0.38	0.13	2.9
	1/1	430	0.71	0.28	2.5

Permeability Coefficient is in x 10^9 $cm^3(STP)cm/cm^2$ -sec-cmHg.

HFP/C_2H_2 mixture there is a tendency that the P_{O2} and P_{N2} values decreased with increasing the C_2H_2. The P_{O2}/P_{N2} ratio for the plasma-films from the HFP/C_2H_2 mixture decreased with increasing the C_2H_2 concentration, reached the maximum of 3.5 at a C_2H_2 concentration of 50 mol%, and then decreased. Similarly, the P_{O2}/P_{N2} ratio for the plasma-polymers from the HFP/C_2H_4 mixture showed a maximum of 2.9 at a C_2H_4 concentration of 37.5 mol%. In some cases, gas transport process through polymer films is explained by the solution-diffusion mechanism, and the permeability coefficients, P_{O2} and P_{N2}, are product of solubility and diffusion of each gas molecule, which are strongly influenced by the chemical structure of the polymer chains. Figure 5 shows the P_{O2}/P_{N2} ratio for the plasma-polymers is plotted against the $\underline{C}$-CF_n concentration determined by ESCA. The ratio, as shown in Figure 5, increased with increasing the $\underline{C}$-CF_n concentration, reached the maximum at approximately 30 mol%, and then decreased independently of the kind of monomer mixtures. From this result it could be assumed that the less-fluorinated carbon units play an important role in separation from oxygen/nitrogen mixtures.

Conclusively, this study provides a worth aspect on the preparation of effective gas-separation membranes.

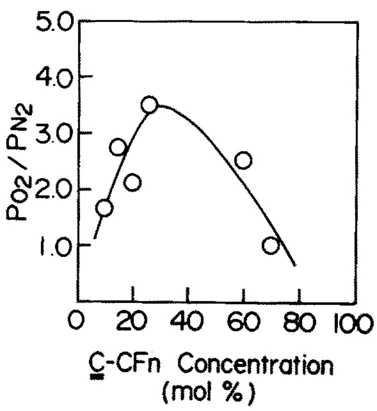

Fig. 5 Permeability Coefficient Ratio for Plasma-polymers.

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