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Preparation of plasma-polymerized membranes from fluoroalkyl acrylates and methacrylates and gas permeability through the membranes

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Summary

Plasma-polymerized membranes were prepared from fluoroalkyl acrylates and methacrylates by two different directions of monomer injection and the permeation rates of O_2 and N_2 through the membranes were investigated. The chemical structure and composition of the plasma-polymerized membranes varied significantly by the direction of monomer injection. The optimum plasma conditions to yield maximum gas separation characteristics was obtained by the remote plasma excitation at the W/FM value of 20 J/mg, where W is the discharge power, F is the monomer flow rate and M is the molecular weight of the monomer.

Introduction

Fluorine-containing compounds generally possess unique properties of high thermal and chemical stability, high hydrophobicity and oleophobicity and high affinity for oxygen gas. Of these materials, poly(fluoroalkyl acrylate)s and poly(fluoroalkyl methacrylate)s have attracted much interest because of their potential applications as electron beam resists, optical fibers, and contact lens materials(1-5). It is difficult, however, to prepare pinhole-free thin films because of lack of solubility of the fluoro polymers. Plasma polymerization offers a means for the formation of pinhole-free thin films. According to this method, it is possible to prepare pinhole-free thin films from almost all the organic vapors. In this study, plasma polymerized membranes were prepared from fluoroalkyl acrylates and methacrylates by two different directions of monomer injection and the permeation rates of O_2 and N_2 gas through the membranes were investigated.

Experimental

A bell-jar type of reactor(Fig.1) was used for plasma-polymerization. Plasma was generated by an inductive coupled rf(13.56 MHz) power source. 2,2,2-Trifluoroethyl acrylate (TFEA), 2,2,2-trifluoroethyl methacrylate (TFEM), 2,2,3,3-tetrafluoropropyl acrylate (TFPA) and 2,2,3,3,4,4,5,5-octafluoropentyl acrylate (OFPA) obtained from Osaka Organic Chemical Ind. were used as the monomer without further purification, while argon was used as the carrier gas. Before the monomer was introduced into the reactor, it was degassed several times via freezing and thawing cycles in vacuum. After a reactor was exposed to Argon plasma for 10 min, the reactor was then evacuated to 0.01 Torr and the monomer gas adjusted to a fixed flow rate was injected into the reactor. The monomer was fed by two different methods. In the method a), the monomer was fed through the energy input zone (direct plasma excitation). In the method b), it was fed in the tail-flame portion of the reactor (remote plasma excitation). The plasma polymerization was carried out at a total pressure of 0.1-0.3 Torr and discharge power of 10-80 W for a certain period. A porous polypropylene film (cellgard 2400) was used as the substrate of plasma polymer. The polymer deposition rate was evaluated from a weight increase of the substrate.

The permeation rates of O_2 and N_2 gas were measured by the apparatus previously described(6). XPS spectra of plasma polymers deposited on Al foil were recorded on Schimadzu ESCA-750 spectrometer employing Mg K_α exciting radiation at 8 kV and 30 mA. Component analysis of the C_{1s} and O_{1s} core level spectra was accomplished on a Schimadzu-ESCA PAC 760 data system using Gaussian peaks at known component binding energies.

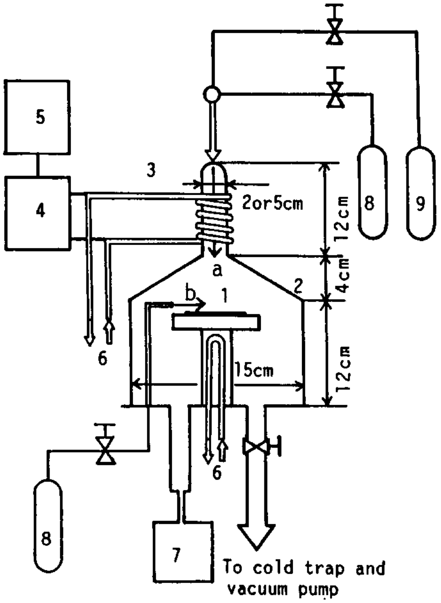

Fig. 1. A schematic diagram of the plasma polymerization system. 1,sample stage; 2,glass chamber; 3,RF coil; 4, matching unit; 5,RF generator(13.56MHz); 6, cooling water; 7, vacuum gauge; 8,monomer; 9,Ar gas

Results and Discussion

Plasma Polymerization of Fluoroalkyl acrylates and methacrylates

Fluoroalkyl acrylates and methacrylates, like methyl methacrylate(7), polymerized easily in plasma. Transparent light-yellow polymer membranes were obtained from TFEA, TFEM, TFPA and OFPA and these membranes were insoluble in all solvents tested.

The amount of polymer deposition was found to be linear with duration time of plasma polymerization. In the case of TFEA and TFEM, no significant difference in deposition rates due to the difference in the direction of monomer injection was observed. In the case of TFPA and OFPA, however, the remote plasma cxcitation showed a considerable higher polymer deposition rate than the direct plasma excitation. The optimum condition at which the deposition rate of the plasma polymer is maximized was determined by the plots of deposition rate vs. the

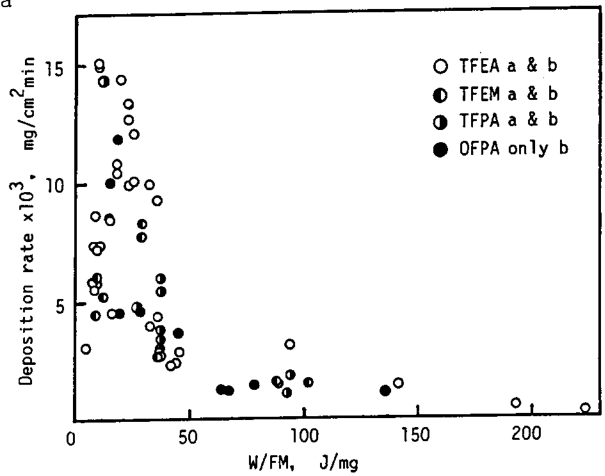

Fig. 2. Deposition rate of plasma-polymerized fluoroalkyl (meth)acrylates vs. W/FM.

composite parameter W/FM, where W is the discharge power, F is the monomer flow rate and M is the molecular weight of the monomer. This parameter means an apparent input rf energy per mass of the monomer. The applicability of this quantity to describe conditions of plasma polymerization has been demonstrated repeatedly(8,9). The variation in the deposition rate of plasma-polymerized fluoroalkyl acrylates and methacrylates with the composite parameter W/FM is shown in Fig. 2, which also shows that the deposition rate increases with increasing W/FM up to a W/FM value of 20 J/mg and then decreases sharply with increasing W/FM. Thus, the proper condition for membrane preparation lies in the intermediate region between the energy-deficient region and the monomer-deficient region.

Gas Permeation through the Membranes

Table 1 shows the permeation rates of O_2 and N_2 and the permeation rate ratios of O_2 to N_2 through plasma-polymerized membranes. The permeation rate and the permeation rate ratio were influenced by the plasma conditions for membrane preparation, where the composite parameter W/FM plays an important role in obtaining good separation characteristics.

Table 1. Gas permeation rates[1] of plasma-polymerized membranes.

Monomer	Plasma condition[2]				Deposition	Permeation rate[3]		R_{O_2}/R_{N_2}
	Method	Power [W]	Pressure [Torr]	W/FM [J/mg]	[10^2mg/cm^2]	R_{O_2}	R_{N_2}	
TFEA	a	20	0.1	34.0	12.2	13	7.7	1.7
	a	20	0.1	89.6	4.32	*	*	1.0
	a	20	0.2	10.6	22.4	44	19	2.3
	a	50	0.1	142	4.19	*	*	1.0
	a	50	0.2	33.0	30.4	7.3	3.3	2.2
	b	20	0.1	27.0	11.1	2.2	0.72	3.1
	b	50	0.2	24.4	16.7	1.9	0.70	2.7
	b	50	0.1	70.1	2.31	*	*	1.0
TFEM	a	20	0.1	37.8	4.18	*	*	1.0
	a	20	0.2	9.22	13.4	*	*	1.0
	a	50	0.1	88.3	2.44	*	*	1.0
	a	50	0.2	29.6	23.4	15	8.7	1.8
	b	20	0.1	25.6	6.60	2.0	0.68	2.9
	b	20	0.2	13.3	4.98	1.1	0.31	3.4
	b	50	0.1	82.9	1.15	1.2	0.62	1.9
	b	50	0.2	40.8	12.2	3.0	0.93	3.2
TFPA	a	20	0.1	38.0	11.6	9.0	7.3	1.2
	a	50	0.1	84.0	3.30	*	*	1.0
	b	20	0.1	28.4	7.29	0.99	0.32	3.1
	b	20	0.2	11.4	21.5	0.92	0.27	3.4
	b	50	0.2	32.2	28.8	1.0	0.43	2.3
OFPA	a	10	0.1	18.7	13.5	*	*	1.0
	a	20	0.1	40.0	8.90	*	*	1.0
	b	20	0.1	19.9	27.1	3.6	0.94	3.8
	b	20	0.2	22.1	63.3	2.2	0.88	2.5
	b	50	0.1	62.2	17.0	2.0	1.0	2.0
	b	50	0.2	18.9	65.3	2.6	0.76	3.4

[1] Permeation rate in $\times 10^{-6}[\mathrm{cm^3(STP)cm^{-2}s^{-1}cmHg^{-1}}]$.

[2] a;direct plasma excitation, b;remote plasma excitation, and plasma duration time= 15-30 min.

[3] (*);permeation rate greater than $10^{-4}\mathrm{cm^3(STP)cm^{-2}s^{-1}cmHg^{-1}}$.

Membranes obtained at around the optimum condition to yield maximum deposition rate exhibit high permeation rate ratios, while those at high W/FM values did not show separation characteristics. Yasuda et al. demonstrated on fluoro compounds that the optimum condition to yield maximum separation factor was in the intermediate region between the energy-deficient region and the monomer deficient region of plasma polymerization(10). In a previous report(6), we also reported that the optimum condition at which the deposition rate of the plasma polymer is maximized agreed with the optimum value to yield maximum separation factor of gases through the plasma-polymerized membrane from trimethylsilylpropyne. Thus, it is concluded that the optimum plasma condition to yield maximum separation characteristics lies around the W/FM value of 20 J/mg. Table 1 also shows that characteristic differences between direct and remote plasma excitation processes have been observed in the gas permeation behavior. The permeation rates of O_2 through the membranes obtained by the remote plasma excitation were in the order of 10^{-6} $cm^3(STP)cm^{-2}s^{-1}cmHg^{-1}$ and the permeation rate ratios of O_2 to N_2 were higher than those of the membranes obtained by the direct plasma excitation. In the case of the direct plasma excitation, the membranes seems to have pinholes judging from a large permeation rate and very low separation characteristics. These results suggest that the chemical structure and composition of the plasma-polymerized membranes from fluoroalkyl acrylates and methacrylates could vary drastically by the direction of monomer injection.

XPS Spectra of the Membranes

XPS spectra of plasma-polymerized TFEA and OFPA prepared by two different directions of monomer injection are shown in Figs. 3 and 4. The C_{1s} spectra of plasma-polymerized TFEA showed four components, which involves a main peak at 285.0 eV and three shoulder peaks at 287.1, 289.2 and 292.9 eV. These components can be assigned to $-\underline{C}H_2-\underline{C}H-$, $-\underline{C}H_2O-$, $-\underline{C}(O)O-$ and $-\underline{C}F_3$, respectively(11). The C_{1s} spectra of plasma-polymerized OFPA also showed four components corresponding to $-\underline{C}H_2-\underline{C}H-$ at 285.0 eV, $-\underline{C}H_2O-$, at 287.3 eV, $-\underline{C}(O)O-$ at 289.1 eV and $-\underline{C}F_2$ at 290.9 eV. The O_{1s} spectra of plasma-polymerized TFEA and OFPA involve two components assigned to the carbonyl group oxygen at 532.8 eV and the ester group oxygen at 534.3 eV(12). It can be seen from Figs. 3 and 4 that the direct plasma excitation of OFPA monomer remarkably reduced the components assigned to CF_2

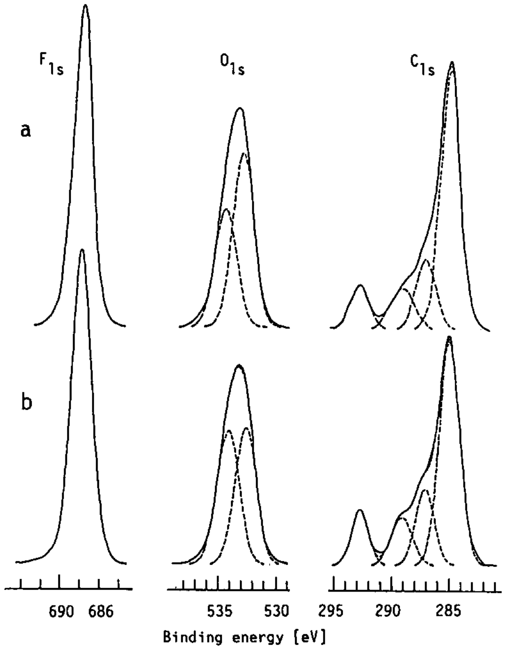

Fig. 3. XPS spectra of plasma-polymerized TFEA; a; direct plasma excitation, b; remote plasma excitation.

and the ester group oxygen.

Table 2 shows ratios of elements calculated from the XPS spectra of plasma-polymerized membranes from TFEA, TFEM and OFPA. It is to be noted that the F/C atomic ratio for the plasma-polymerized membrane prepared from OFPA by the direct plasma excitation decreased significantly compared with that of the membrane prepared by the remote plasma excitation, while the O/C ratios of the former membrane was larger than that of the latter and even than that of the OFPA monomer. It is evident, therefore, that the fluorine is significantly eliminated and the oxygen is incorporated into the membranes prepared by the direct plasma excitation. These results is presumably due to the decomposition of the monomer gas by the direct plasma excitation. The decomposition occurs most drastically in the case of OFPA which has a long side chain and occurs weakly in the case of TFEA and TFEM. The incorporation of oxygen may be due to a high concentrations of free radicals and/or unsaturated sites in the plasma polymer generated by the direct plasma excitation of OFPA, which may react with oxygen upon exposure of the membrane to air.

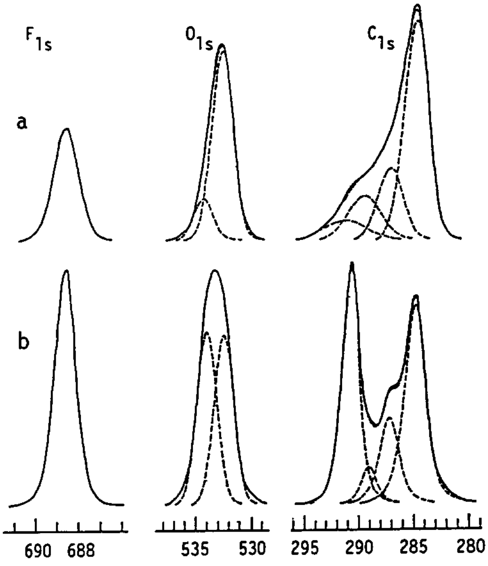

Fig. 4. XPS spectra of plasma-polymerized OFPA; a; direct plasma excitation,b;remote plasma excitation.

Thus, it is concluded that the chemical structure and composition of the plasma-polymerized membranes from fluoroalkyl acrylates and

Table 2. Ratios of elements calculated from the XPS spectra of plasma-polymerized membranes.[1]

Monomer	Plasma conditions[2]			O/C	F/C
	Method	rf power [W]	Pressure [Torr]		
TFEA	a	20	0.2	0.23(0.4)	0.42(0.6)
	b	20	0.2	0.25	0.44
TFEM	a	20	0.2	0.19(0.33)	0.33(0.5)
	b	20	0.2	0.20	0.31
OFPA	a	20	0.2	0.33(0.25)	0.12(1.0)
	a	50	0.2	0.36	0.09
	b	20	0.2	0.20	0.93

[1] Values in parentheses were calculated from the chemical formula of monomer.

[2] a:direct plasma excitation, b:remote plasma excitation.

methacrylates vary significantly by the direction of monomer injection and the optimum plasma conditions to yield maximum gas separation characteristics of the membranes can be obtained by the remote plasma excitation.

References

1. Kakuchi, M., Sugawara, S., Murase, K., and Matsuyama., J. Electrochem. Soc. 124, 1648(1977)
2. Jpn. Kokai Tokkyo Koho JP5429660 (1979)
3. Harada, K., J. Electrochem. Soc., 127, 491(1980)
4. Jpn. Kokai Tokkyo Koho JP5751705 (1982)
5. Ishiwari, K., Ohmori, A., and Koizumi, S., Nippon Kagaku Kaishi, 1985, 1924
6. Kita, H., Sakamoto, T., Tanaka, K., and Okamoto, K., Polym. Bull., 20, 349(1988)
7. Gangal, S. A., Hori, M., Morita, S., and Hattori, S., Thin Solid Films, 149, 341(1987)
8. Yasuda, H., "Plasma Polymerization" Academic Press Orlando, Chapter 9 (1985)
9. Boenig, H. V., "Fundamentals of Plasma Chemistry and Technology" Technomic Publishing Company, Inc., Chapter 15 (1988)
10. Nomura, H., Kramer, P. W., and Yasuda, H., Thin Solid Films, 118, 187(1984)
11. Clark, D. T., and Shuttleworth, D., J. Polym. Sci. Polym. Chem. Ed., 18, 27(1980)
12. Clark, D. T., and Thomas, H. R., J. Polym. Sci. Polym. Chem. Ed., 16, 791(1978)

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