ISPC-8 Tokyo, 1987
Paper number S3-01

PLASMA POLYMERIZATION OF UNSATURATED ALCOHOLS FOR DEPOSITION OF HYDROPHILIC THIN FILM

K. Hozumi
Kyoto Pharmaceutical University
Yamashina, Kyoto 607, Japan

ABSTRACT

Plasma polymerization of propargyl alcohol (2-propyn-1-ol) produced highly hydrophilic polymer film on solid substrates. The hydrophilic property was further enhanced by using the same monomer containing 60% water. The polymer film deposited on a solid substrate preserved good adherence, transparency, and wettability after immersion in water for one month. A few applications of the method have been attempted.

INTRODUCTION

plasma polymerization for preparing hydrophilic thin film on solid substrate has been encountered with difficulty when oxygen containing organic compounds were used as the starting monomers (1-3). It was supposed that fragmentations of the monomers or oligomers significantly proceeded within the discharge region likely with eliminations of OH, CO, and other oxygen containing primitive materials. Therefore, plasma polymers derived from oxygen-containing monomers yielded much less hydrophilic films than we expected. We have recently attempted the polymerization of a few unsaturated alcohol monomers by supplying considerably low wattage of high frequency power and found that monomers having alkyne group underwent efficient polymerization without splitting off the oxygen-containing fragments (4). Propargyl alcohol could be polymerized within 2 watts in ordinary laboratory plasma reactor. The resulting polymer involved high abundance of oxygen, but the oxygen content was further increased when the plasma polymerization was carried out using water-containing monomer. The IR spectra of the polymers showed the presence of OH, C=O, and C=C groups with a noticeable disappearance of the C≡C group in the starting monomer. The polymer film derived from either plain or water-containing monomer showed good transparency, wettability, and adherence on solid substrates so that some applications based upon these properties were attempted.

PLASMA REACTOR

A laboratory scale reactor employed consisted of a metal base and a glass bell jar (H 30 cm, D 25 cm) in which a pair of parallel electrode was installed horizontally (4). The monomer alcohols in liquid phase were stored in a small glass reservoir which was connected to a pipe line so as to introduce the monomer vapors into the plasma reactor. The vapors were once collected in a drum-shaped upper electrode and diffused downward through a number of holes drilled at the lower side. A schematic diagram of the whole reactor system is illustrated in Fig. 1.

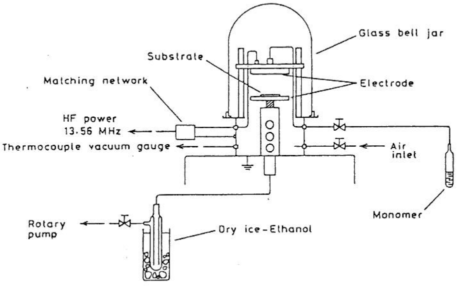

Fig. 1. Schematic diagram of plasma reactor

UNSATURATED ALCOHOL MONOMERS

Allyl alcohol (2-propen-1-ol) would be a typical unsaturated alcohol, but propargyl alcohol would have been more promising for gentle plasma polymerization because of having electronically active site at the tripple bond. 2-Methyl-3-butynol was also considered in anticipation of steric shielding of OH group by two methyl groups from the energetic electron during the plasma process. Operating condition used for the polymerization of these monomers are tabulated in Table 1. The minimum requirement for sustaining the glow discharge of allyl alcohol was 10 watts, while the others required only about 2 watts. Inversely, the deposition rates of the monomers havnig the tripple bond were several times as high as the monomers having double bond.

Table 1. Operating condition for polymerization of unsaturated alcohols

	Monomer		
	AA[a]	PA[b]	MBO[c]
Molecular structure	$H_2C=CH-CH_2OH$	$HC\equiv C-CH_2OH$	$HC\equiv C-\overset{CH_3}{\underset{CH_3}{C}}-OH$
Boiling point (°C)	96-97	114-115	104-105
HF power (W)	10.0	1.5	2.0
Pressure (mmHg)	0.05	0.15	0.20
Flow rate (mg min^{-1})	2.1	24.0	31.1
Deposition rate (Å min^{-1})	50	450	370

[a] Allyl alcohol (2-propen-1-ol). [b] Propargyl alcohol (2-propyn-1-ol). [c] 2-Methyl-3-butyn-2-ol.

FILM CHARACTERISTICS

Table 2. Film character of plasma-polymers derived from unsaturated alcohols

Character of polymer film		Monomer		
		AA	PA	MBO
Contact angle of water (degree)[a]		70	45	66
Element composition (%)				
Monomer	H	10.41	7.19	9.59
	C	62.04	64.27	71.39
	O	27.55	28.54	19.02
Polymer	H	9.83	7.30	9.52
	C	69.39	66.13	76.98
	O	20.66	26.57	13.50

[a] Substrate, PMMA; drop volume, 10 μl; test, 15 min after deposition.

The polymer films derived from the three monomers exhibited different contact angles and oxygen contents as listed in Table 2. The plasma polymerized propargyl alcohol (PPPA) showed the lowest contact angle with the highest abundance of oxygen, while the polymer from methyl butynol was not hydrophilic because of two methyl groups in the chemical construction.

A further attempt was made to intensify the hydrophilic property by using water-containing propargyl alcohol. It had been known that the water content in liquid phase was practically the same as in vapor phase under the reduced pressure, so that the polymerization was carried out with the monomer changing its water content. The contact angle significantly decreased when the water content exceeded 40% and we obtained less than 30° at water content of 60%. The data are illustrated in Fig. 2.

Fig. 3 shows IR spectra of the monomer and the resultant polymer. A noticeable disappearance of C≡C band and an appearance of intense C=O band in the latter spectrum were observed. The finger print region was also somewhat altered likely due to an appearance of C=C band.

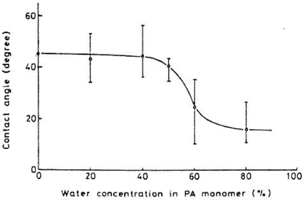

Fig. 2. Contact angle of water on PPPA films derived from water-containing monomers. Substrate, PMMA; drop volume, 10 μl; test, 15 min after coating.

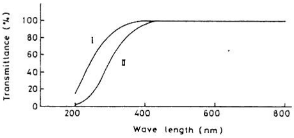

Fig. 4. Absorption spectra of PPPA. Film thickness: I, 1750 Å; II, 7550 Å. Monomer, PA: H_2O=1:1.

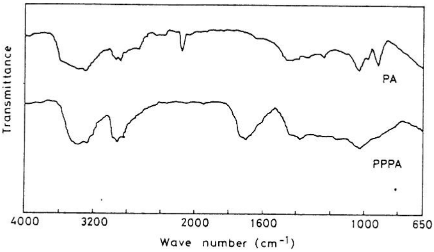

Fig. 3. IR spectra of PA and PPPA.

Marked transparency was obtained with the polymer film either from the plain or water-containing monomer. Fig. 4 shows light transmission spectra of thin and thick polymer films derived from the 50% water-containing monomer. Almost 100% transmittance was held throughout the visible region and the transmittance gradually decreased with shorter wave length at the UV region.

Solubility of the polymer material to water and organic solvents largely differed depending upon the chemical interaction. About 20% of the polymer was dissolved in water during a long time immersion, probably due to small molecular species coming out of the polymer matrix. Methanol and ethanol dissolved 90% of the polymer because of the similarlity of the chemical property as the alcohols. Tetrahydrofuran, acetone, and chloroform showed moderate solubilities, but nonpolar solvents such as benzene and hexane exhibited practically no solubility.

Vapor pressure osmometry was employed for measurement of the number average molecular weight using a tetrahydrofuran solution of the polymer. The polymer derived from the plain monomer gave Mw=490, while the other from the water-containing monomer resulted in Mw=890, although there were some polymer fraction left insoluble in the organic solvent due to much higher molecular weight.

STRUCTURAL ELUCIDATION OF POLYMER MOLECULE

H- and C-NMR spectrometries were applied to the polymer materials for elucidation of the chemical structures, but either technique was not so helpful to depict the molecular structures. Wide variety of the chemical structures composed in the polymer molecules exhibited broad signals. Only a high resolution H-NMR made possible to give assignments as tabulated in Table 3. Intense

Table 3. Assignment of H-NMR spectrum of plasma polymer derived from 50% water-containing PA

δ (ppm)	Assignment
0.90 ~ 1.00	CH_3-R
1.20 ~ 1.30	R-CH_2-R′
1.10 ~ 1.90	CH_3-C-Y (Y : C=O, H)
1.95 ~ 2.05	CH_3-COR
1.95 ~ 2.10	CH_3-C=C-Y, CH_3COOY (Y : Conjugated system)
4.80 ~ 4.95	OH

signals of OH and C=O groups were observed while the presence of aldehyde and carboxyl groups were denied in the spectrum.

Mass spectrometry also made no contribution, but a fragment of m/z=44 was consistantly observed in repeated analyses, so that $-CH_2-CH_2-OH$ was supposed to remain in the polymer molecules.

Quantitative determinations of OH, C=O, and C=C groups were carried out by means of H-NMR spectrometry, hydrazone formation, and iodine addition respectively. Number of functional groups involved in an unit molecule having the average molecular weight are listed in Table 4. Integration of the foregoing informations such as elemental analysis, molecular weight determination, NMR and mass spectrometries, and wet chemical analysis conducted to imaginary chemical structures of the polymer molecules at the average molecular weights. Fig. 5 shows a half of the unit molecule drived from the water-containing monomer.

Table 4. Quantitative analysis of functional groups in PA plasma polymers

Function	Polymer from	
	plain monomer	$PA-H_2O$ mixture
Hydroxyl	4	7-8
Carbonyl	1	2
Olefinic unsaturation	2-3	1-2

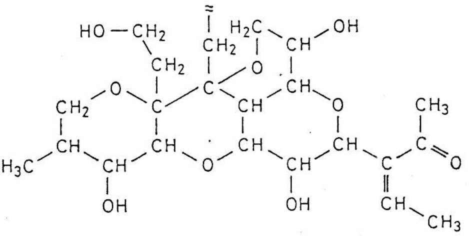

Fig. 5. Imaginary chemical structure depicted as a half of unit molecule of water-containing PA plasma polymer

DURABILITY IN AQUEOUS MEDIUM

A polymethyl methacrylate plate coated by the PPPA film was soaked in water for increasing period of days and its surface morphology before and after the soaking was investigated by an optical microscope. Flat and uniform surface was preserved until 5 days, but some short wrinkles appeared after 10 days while no more change was observed until one month. It was supposed, therefore, that the polymer film stiffly adhered to the plastic plate for fairely long time in aqueous medium and any possible defects such as crack and pinhole were not seen in the optical microscopy. The transparency and the wettability of the polymer film were also preserved as well.

APPLICATIONS

The PPPA film was first applied to a thin layer chromatographic plate to alter the chromatographic behavior of various organic compounds (5). This application was suggested by high transparency of the film and its chemical nature due to the polar functional groups such as OH and C=O. The migration rates (Rf value) of azo dyes, amino acids, and steroids on the plasma-treated thin layer plate mostly increased with the specific degree of the individual compound. It was evident, therefore, that the polymer film exhibited certain chemical interaction with the organic compounds being tested. Table 5 shows an example for azo dyes.

Table 5. R_f-values of azo dyes on propargyl alcohol (PA) plasma-coated silica gel plate using benzene as developing solvent

	R_f-value (SD)†		Ratio of R_f-value; coated /uncoated
	Uncoated silica gel	PA plasma-coated silica gel	
Azobenzene	0.75 (0.02)	0.78 (0.02)	1.0
Sudan III	0.41 (0.07)	0.59 (0.05)	1.4
p-Hydroxyazobenzene	0.14 (0.01)	0.21 (0.03)	1.5

† Standard deviation of 12 measurements

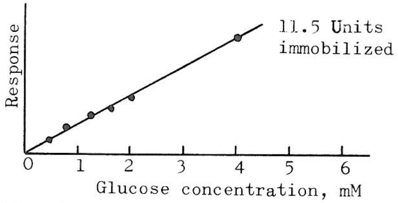

Fig. 6. Calibration curve for glucose electrode using PPPA-coated glucose oxidase membrane

A porous membrane retaining certain enzyme protein could be enveloped by deposition of PPPA film onto the both sides to form an immobilized enzyme membrane. Extremely low wattage needed for the polymerization was also contributory to preserve the enzyme activity. A cellulose acetate membrane filter was immersed in a solution of glucose oxidase, dried, and then exposed to the PA plasma for 5 min at either side. The immobilized glucose oxidase membrane thus made was cut in a small disk to fit on a diaphragm membrane of a dissolved oxygen sensor. The electrode response to glucose concentrations lower than 4 mM showed good linear relationship as illustrated in Fig. 6.

Microencapsulation of particulate matter by PPPA thin film is now strongly under way to control release rate of powder pharmaceuticals in aqueous dissolution medium. Antipyrine powder having an average diameter of 200 μm was chosen as a model pharmaceutical and was spread on a watch glass to form thin layer. Deposition of the polymer film onto the powder was continued for 20 min and the process was interrupted for manual agitation. The same process was repeated several times until the film thickness grew up to 5000 Å. The microencapsulated antipyrine powder was subjected to the official method of dissolution test. The concentration of antipyrine in the aqueous medium was determined spectrophotometrically at a wave length of 242 nm. The result showed significant retardation of the dissolution rate compared with the intact antipyrine.

REFERENCES

(1) H. Yasuda and C.E. Lamaze, J. Appl. Polym. Sci., 17, 1519(1973)
(2) J.R. Hollahan and A.T. Bell (eds), "Techniques and Applications of Plasma Chemistry", p220, Wiley-Interscience, New York (1974)
(3) H. Yasuda, "Plasma Polymerization", p109, Academic Press, Orlando, Florida (1985)
(4) K. Hozumi, K. Kitamura, T. Kitade, and K. Yoshimura, Kobunshi Ronbunshu, 42, 881 (1985)
(5) K. Yoshimura, K. Hozumi, K. Kitamura, T. Kitade, and Y. Okamoto, Bunseki Kagaku, 35, 476 (1986).