Plasma polymerization of unsaturated alcohols for deposition of hydrophilic thin film

Kei 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. Structural interpretation of the polymer molecule revealed presence of oxygen atoms in abundance as the forms of hydroxyl, carbonyl, and etheric oxygen groups. Applications of the polymer were attempted to improve characters of sensing materials in analytical chemistry and to control dissolution rate of a powder pharmaceutical in an aqueous medium.

INTRODUCTION

Plasma polymerization for preparing hydrophilic thin film on solid substrates has been encountered with difficulty when oxygen containing organic compounds were used as the starting monomers (ref. 1–3). It was supposed that fragmentation of the monomers or oligomers efficiently proceeded within the discharge region probably with elimination of OH, CO, and other oxygen-containing primitive materials. Therefore, plasma polymers derived from oxygen-containing monomers yielded much less hydrophilic films than anticipated. 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 of the oxygen-containing fragments (ref. 4). Propargyl alcohol could be polymerized within 2 watts in ordinary laboratory plasma reactor. The resultant polymer involved an 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 to solid substrates so that some applications based upon these properties were attempted.

PLASMA REACTOR

A schematic diagram of the whole reactor system is illustrated in Fig. 1 (ref.4). The reactor consisted of a metal base and a glass bell jar (H 30 cm, D 25 cm) in which a pair of parallel electrodes was installed horizontally. 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 vapor into the plasma reactor. The vapor was once collected in a drum-shaped upper electrode and diffused downward through a number of nozzles drilled at the lower side.
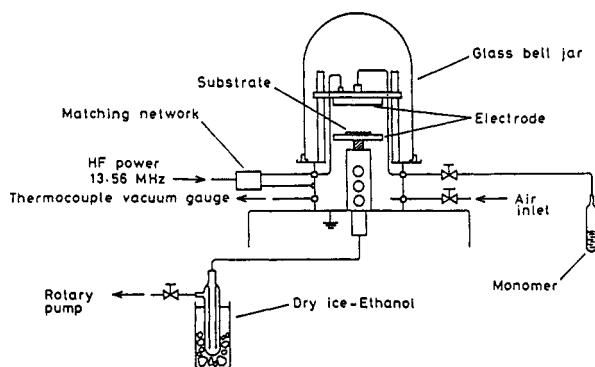

Fig. 1. Schematic diagram of plasma reactor

UNSATURATED ALCOHOL MONOMERS

Allyl alcohol (2-propen-1-ol, AA) would be a typical unsaturated alcohol, but propargyl alcohol (PA) was thought to be more promising for gentle polymerization because of having electronically active site at the tripple bond. 2-Methyl-3-butynol (MBO) was also considered as a monomer in anticipation of steric shielding of OH group by two methyl groups from the energetic electron during the plasma process. Operating parameters 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 having the tripple bond were several times as high as the monomers having the double bond.

TABLE 1. Operating parameters for plasma polymerization of unsaturated alcohol monomers

Parameter	Monomer		
	AA[a]	PA[b]	MBO[c]
Molecular structure	$H_2C=CH-CH_2OH$	$HC\equiv C-CH_2OH$	$HC\equiv C-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-OH$
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.

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.

FILM CHARACTERISTICS

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

A further attempt was made to intensify the hydrophilic property by using water-containing propargyl alcohol. It was of interest that the water-containing PA supplied vapor of practically the same composition as the liquid phase, provided that the liquid surface was exposed to a reduced pressure. The fact was evidenced by a preliminary test in which a cold trap was installed within the pipe line between the monomer reservoir and the plasma reactor and the condensed vapor was analyzed by gas chromatography. The composition of PA–H₂O system in liquid and vapor phase showed fine coincidence each other as illustrated in Fig. 2.
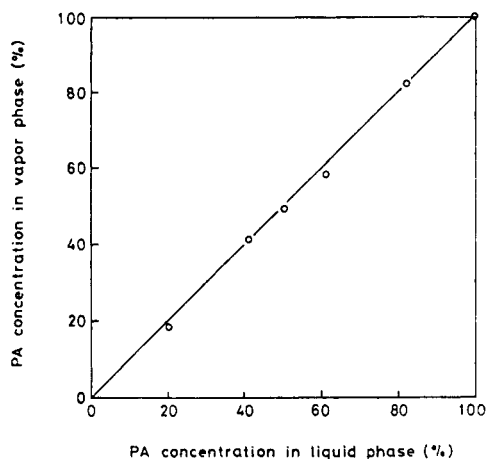

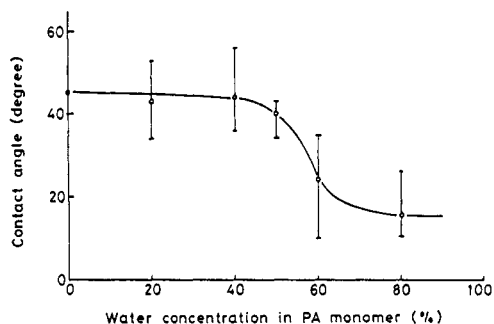
Fig. 2. Liquid–vapor composition diagram for PA–H₂O system

Fig. 3. Contact angle of water on PPPA films derived from water-containing monomers. Substrate, PMMA; drop volume, 10 μl; test, 15 min after coating.

Such a favorable phenomenon was probably due to a resemblance of vapor pressure between the two components and a lack of vapor-liquid equilibrium under the low pressure. Therefore, the polymerization could be carried out with the liquid monomer simply changing its water concentration. The contact angle significantly decreased when the water concentration exceeded 40% and we obtained less than 30° at water concentration of 60%. The data are illustrated in Fig. 3.

Fig. 4 shows IR spectra of the PA monomer and the resultant polymer. A noticeable disappearance of C≡C band and an appearance of intense C=O band in the latter spectrum was observed. The finger print region was also somewhat altered likely due to an appearance of C=C band. Details of the assignments are tabulated in Table 3. Polymers derived from the water-containing monomer showed practically the same IR spectra except somewhat intensified absorption bands of OH and C=O depending upon the water concentration.

TABLE 3. Assignment of IR absorption bands of PA and PPPA

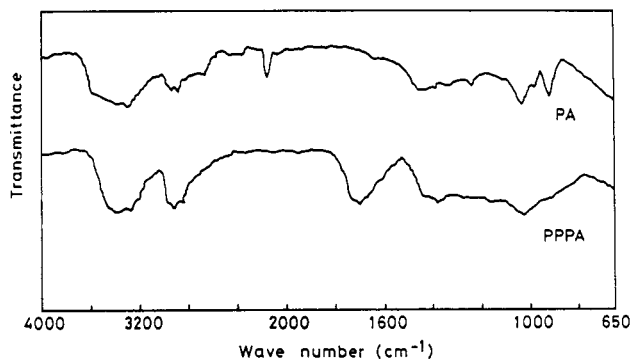| PA		PPPA	
Absorption band (cm^{-1})	Assignment	Absorption band (cm^{-1})	Assignment
3400	O-H stretch	3350	O-H stretch
3290	C-H stretch in alkyne	2900	C-H stretch
2930, 2880	C-H stretch	1700	C=O stretch
2140	-C≡CH stretch	1500~1300	O-H deformation
1500~1260	O-H deformation		CH$_2$ deformation
1230, 1030, 920	C-O stretch		C=C stretch
650	C-H deformation	1200~ 900	-CH=CH$_2$ deformation
			C-O stretch

Fig. 4. IR spectra of PA and PPPA.
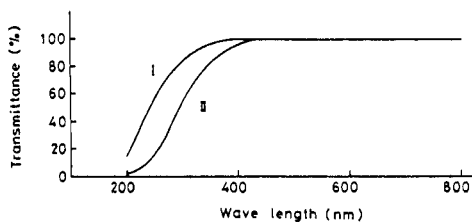
Fig. 5. Absorption spectra of PPPW. Film thickness: I, 1750 Å; II, 7550 Å.

Marked transparency was obtained with the polymer film either from the plain or water-containing monomer. Fig. 5 shows light transmission spectra of thin and thick polymer films derived from the 60% water-containing monomer (PPPW). Almost 100% transmittance was obtained throughout the visible region and the transmittance gradually decreased with shorter wave length at the UV region.

Solubility of the polymer materials to water and organic solvents largely differed depending upon their chemical interaction as illustrated in Fig. 6. About 40% of PPPA and 20% of PPPW was dissolved in water during a long time immersion, probably due to small molecular species coming out of the polymer matrices. Methanol and ethanol dissolved more than 90% of the polymers because of the similarity of the chemical property as the alcohols. Tetrahydrofuran, acetone, and chloroform showed moderate solubility, but nonpolar solvents such as benzene and hexane exhibited practically no solubility.

Vapor pressure osmometry was employed for measurement of number average molecular weight of the polymers. Methanol and ethanol were not usable as solvent for the measurement because of very low sensitivity. Methanol and tetrahydrofuran (1:4) mixture was therefore used for extraction of the polymer materials and the extracts were dried up to prepare samples for the vapor pressure osmometry. The solubility of the polymers to the solvent mixture and element composition of the polymer extract are listed in Table 4.
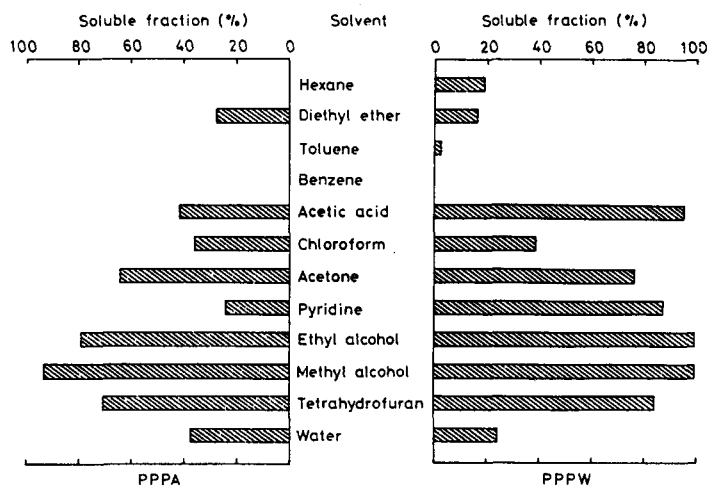
Soluble fraction (%)   Solvent   Soluble fraction (%)

Fig. 6. Solubility of PPPA and PPPW to different solvents

TABLE 4. Physical and chemical properties of PPPA and PPPW

	PPPA	PPPW
Intact polymer		
Element composition (%)		
H	7.30	7.44
C	66.13	59.08
O	26.57	33.48
Methanol-THF extract		
Fraction extracted (%)	63.0	99.9
Element composition (%)		
H	7.39	7.51
C	64.77	59.77
O	27.84	32.72
Average molecular weight	490	890
Molecular formula	$C_{26}H_{36}O_9$	$C_{44}H_{66}O_{18}$
Degree of unsaturation[a]	9	12

[a] Degree of unsaturation for $C_wH_xN_yO_z$: $R = w+1+(y-x)/2$

It should be noticed that 63% fraction of PPPA was extracted by the solvent mixture, while practically 100% of PPPW was by the same solvent. The number average molecular weight of PPPA and PPPW thus obtained was 490 and 890 respectively. Although the percentage fraction extracted from PPPA was considerably low, the element composition did not much differ from the intact polymer, so that the chemical structures of the intact polymer and its solvent extract were thought to be closely analogous. Molecular formulae and the resultant degree of unsaturation were calculated and are registered in the same table.

STRUCTURAL ELUCIDATION OF POLYMER MOLECULE

H-NMR (60 MHz) and C-NMR (20 MHz) spectrometries were applied to the polymer materials for elucidation of the chemical structures, but either technique was not successful to assign the signals to various chemical shifts in relation to the molecular structures. Wide variety of the chemical structures composed in the polymer molecules exhibited broad signals. However, high resolution H-NMR (300 MHz) spectrum of PPPA as shown in Fig. 7 made possible to give assignment as tabulated in Table 5. Intense signal of OH and C=O groups were observed while the presence of aldehyde and carboxyl groups were denied in the spectrum. Some signals assigned to aromatic ring were also noticeable. The spectrum of PPPW exhibited basically the same pattern as PPPA, but the signals assigned to the aromatic ring were eliminated.

TABLE 5. Assignment of H-NMR spectrum of PPPA

δ (ppm)	Assignment
1.10 ~ 1.90	CH₃-C-Y (Y : H, Ph, C=O)
1.20 ~ 1.30	R-CH₂-R'
1.65 ~ 1.75	CH₃-C=C-C=O
1.90 ~ 2.00	CH₃COR
1.95 ~ 2.05	CH₃-C=C-Y, CH₃COOY (Y : Conjugated system)
2.20 ~ 2.50	CH₃-Ph
2.60 ~ 2.90	R-CH₂-Ph
3.65 ~ 3.75	CH₃-O-Ph
4.10 ~ 4.20	R₂CH-OH
4.80 ~ 4.90	OH
6.90 ~ 7.50	Ph-H, Ph-CH=C-

TABLE 6. Quantitative analysis of functional groups in PPPA and PPPW

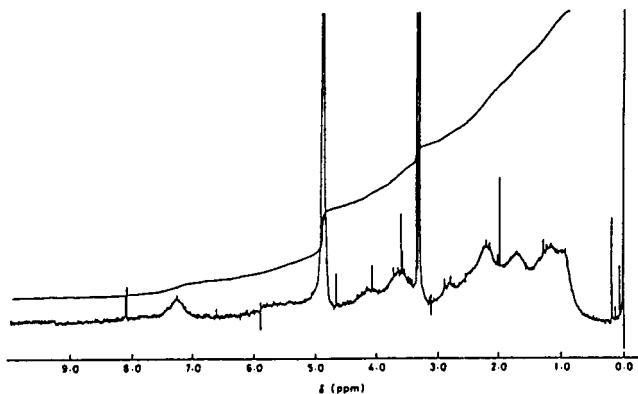| Function	PPPA	PPPW
Hydroxyl	4	7-8
Carbonyl	1	2
Olefinic unsaturation	2-3	1-2

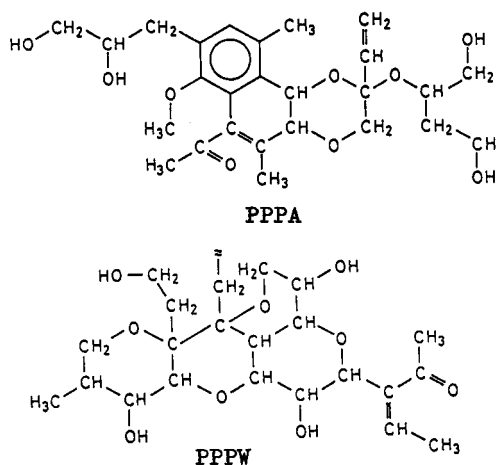Fig. 7.   H-NMR spectrum of PPPA : CD_3OD medium

Fig. 8.   Symbolic representation of chemical structures of PPPA and PPPW (1/2) at average molecular weight

Mass spectrometry of the polymers also made little contribution, but a fragment of m/z=44 was consistently obtained in the repeated analyses, so that an atom group of $-CH_2-CH_2-OH$ was supposed to remain in the polymer molecules.

Quantitative determination of OH, C=O, and C=C groups were carried out by means of H-NMR spectrometry, 2,4-dinitrophenylhydrazone formation, and Wijs' iodine addition respectively. Number of functional groups involved in each unit molecule having the average molecular weight are listed in Table 6. Integration of the foregoing information such as elemental analysis, molecular weight determination, NMR and mass spectromeries, and wet chemical analysis conducted to symbolic representation of chemical structures of the polymer molecules at the average molecular weight. Fig. 8 shows the unit molecule of PPPA and a half of the molecule of PPPW. Since the average molecular weight of PPPA was measured with the sample of 63% fraction extracted by the methanol-tetra-hydrofuran solvent (naturally the lower molecular species), the intact PPPA was supposed to be roughly twice as large as the molecular structure drawn in the figure.

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 sorking 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 fairly 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 well.

APPLICATIONS

Deposition of the PPPA film was first applied to a thin layer chromatographic plate to alter the chromatographic behavior of various organic compounds (ref. 5). The idea came out of the high transparency of the film and its amphipatic property due to the alkyl groups of various forms and 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 plates were mostly altered with the specific degree of the individual compound. It was evident, therefore, that the polymer film exhibited certain chemical inter-action with the organic compounds being tested. Table 7 and Table 8 show the results for azo dyes and amino acids respectively.

TABLE 7. 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. 9 Calibration curve of
glucose electrode

TABLE 8. R_f-values of amino acids on PA
plasma-coated silica gel plate

Compound	R_f-value (SD)†		Ratio of R_f-value; coated /uncoated
	Uncoated silica gel	PA plasma-coated silica gel	
Ethanol/water=63 : 37††			
Alanine	0.64 (0.05)	0.62 (0.05)	1.0
Phenylalanine	0.84 (0.03)	0.80 (0.02)	0.9
Serine	0.45 (0.06)	0.44 (0.04)	1.0
Tyrosine	0.78 (0.03)	0.76 (0.03)	1.0
Aspartic acid	0.78 (0.04)	0.74 (0.04)	0.9
Lysine·HCl	0.00 (0.00)	0.01 (0.01)	—
1-Butanol/acetic acid/ water=12 : 3 : 5††			
Alanine	0.20 (0.05)	0.20 (0.06)	1.0
Phenylalanine	0.59 (0.16)	0.54 (0.09)	0.9
Serine	0.10 (0.04)	0.12 (0.05)	1.2
Tyrosine	0.27 (0.12)	0.27 (0.10)	1.0
Aspartic acid	0.22 (0.03)	0.26 (0.05)	1.2
Lysine·HCl	0.09 (0.02)	0.12 (0.02)	1.3

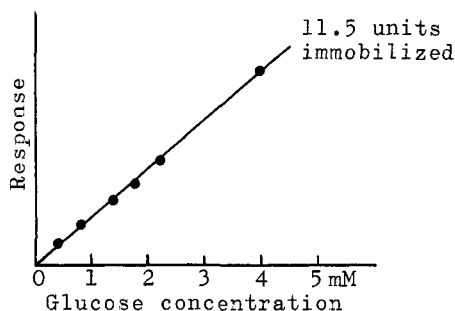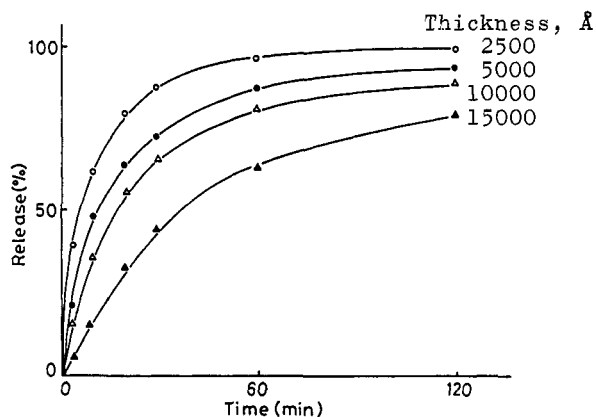† Standard deviation of 8 measurements; †† Developing solvent

Fig. 10. Release profiles of
antipyrine powder plasma-coated
for various film thickness

A porous membrane retaining certain enzyme protein could be enveloped by
deposition of the 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 small disk of cellulose
acetate membrane filter was impregnated with a solution of known quantity 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 attached to a
diaphragm of a dissolved oxygen sensor. Glucose in a sample solution permeated
through the PPPA film and reacted with the glucose oxidase consuming dissolved
oxygen. The electrode response to glucose concentrations lower than 4 mM
showed good linear relationship as illustrated in Fig. 9.

Microencapsulation of particulate matter by the 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 a certain extent,
while the film thickness was monitored on a glass slide placed beside the watch
glass. The microencapsulated antipyrine powder was subjected to the official
method of dissolution test (The Japanese Pharmacopeia). The concentration of
antipyrine in the aqueous medium was determined spectrophotometrically at a
wave length of 242 nm. Fig. 10 shows significant retardation of the dissolu-
tion rate with increasing polymer film thickness.

REFERENCES

1. H. Yasuda and C.E. Lamaze, _J. Appl. Polym. Sci._ __17__, 1519-1531 (1973).
2. J.R. Hollahan and A.T. Bell (eds), _Techniques and Applications of Plasma Chemistry_, p. 220, Wiley-Intersci., New York (1974).
3. H. Yasuda, _Plasma Polymerization_, p. 109, Academic Press, Orlando (1985).
4. K. Hozumi, K. Kitamura, T. Kitade, and K. Yoshimura, _Kobunshi Ronbunshu_, __42__, 881-890 (1985).
5. K. Yoshimura, K. Hozumi, K. Kitamura, T. Kitade, and Y. Okamoto, _Bunseki Kagaku_, __35__, 496-499 (1986).