

- p. 77 (1980).
- M. Foà and F. Francalanci, *J. Mol. Cat.*, **41**, 89 (1987); F. Francalanci, A. Gardano, and M. Foà, *J. Organomet. Chem.*, **282**, 277 (1985); R. A. Sawicki, *J. Org. Chem.*, **40**, 5382 (1983).
 - G. C. Tustin and R. T. Hembre, *J. Org. Chem.*, **49**, 1761 (1984); S. Hashiba, T. Fuchigami, and T. Nonaka, *ibid.*, **54**, 2475 (1989); S. C. Shim, W. H. Park, C. H. Doh, and H. K. Lee, *Bull. Korean Chem. Soc.*, **9**, 61 (1988).
 - M. M. Tāqū Khan, S. B. Halligudi, and S. H. R. Abdi, *J. Mol. Cat.*, **44**, 179 (1988).
 - C. Buchan, N. Hamel, J. B. Woell, and H. Alper, *J. Chem. Soc., Chem. Commun.*, 167 (1986); H. Alper, S. Antebi, and J. B. Woell, *Angew. Chem. Int. Ed. Engl.*, **23**, 732 (1984); J. B. Woell and H. Alper, *Tetrahedron Lett.*, **25**, 4879 (1984); J. B. Woell, S. B. Fergusson, and H. Alper, *J. Org. Chem.*, **50**, 2134 (1985).
 - T. Kobayashi and M. Tanaka, *J. Mol. Cat.*, **47**, 41 (1988); H. Alper, K. Hashem, and J. Heveling, *Organometallics*, **1**, 775 (1982); S. C. Shim, W. H. Park, C. H. Doh, and J. O. Baeg, *Bull. Korean Chem. Soc.*, **9**, 185 (1988).
 - U. Prange, M. Elchahawi, H. Richtzenhain, and W. Vogt, *German Patent* 2509017 (1976).
 - S. C. Shim, C. H. Doh, W. H. Park, Y. G. Kwon, and H. S. Lee, *J. Organomet. Chem.*, **382**, 419 (1990).
 - S. C. Shim, C. H. Doh, and C. S. Cho, *Bull. Kor. Chem. Soc.*, **11**, 474 (1990).
 - A. Wojcicki, *Adv. Organometal. Chem.*, **11**, 87 (1973).
 - R. B. King, *ibid.*, **2**, 157 (1964).
 - H. Alper, K. Denis Logbo, and H. des Abbayes, *Tetrahedron Lett.*, 2861 (1977).
 - A. Miyashita, K. Nomura, S. Kaji, and H. Nohira, *Chem. Lett.*, 1983 (1989).

¹³C and ⁵¹V Nuclear Magnetic Resonance Studies of Vanadium (V) Complexes of Iminodiacetate Analogues

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The solution structures of the vanadium (V) complexes of iminodiacetate analogues, such as iminodiacetate (IDA), methyliminodiacetate (MeIDA), ethyliminodiacetate (EtIDA), benzyliminodiacetate (BzIDA), pyridine-2,6-dicarboxylate (DPA), and 2-hydroxyethyliminodiacetate (HEIDA), have been studied by ¹³C- and ⁵¹V-NMR spectroscopy. Assuming that the complexes have a *cis*-VO₂ core, IDA, MeIDA, EtIDA, and BzIDA act as facial tridentate ligands to form octahedral complexes, whereas DPA coordinates to VO₂⁺ as a meridional tridentate. And one water molecule fulfills the remaining site to satisfy the coordination number of six. But HEIDA coordinates to VO₂⁺ through one IDA moiety and one hydroxyl group, acting as a tetradentate.

Introduction

There is increasing evidence that vanadium plays an important role in biological reactions.¹⁻⁵ Especially vanadium is an important trace element that has potent biological effects in mammals. But the chemistry of vanadium (V) is not much well known because of the complexity of vanadium (V) species in solution and the strong oxidizing power of the metal ion.

Amos and Sawyer⁶ first reported ¹H-NMR studies of vanadium (V) of aminopolycarboxylates such as ethylenediaminetetraacetate (EDTA), ethylenediaminediacetate (EDDA), and N,N'-dimethylethylenediamine-N,N'-diacetate (DMEDDA). In the previous study⁷ we reported the solution structures of vanadium (V) complexes of some aminopolycarboxylates, such as ethylenediaminetetraacetate (EDTA), *trans*-cyclohexanediaminetetraacetate (CDTA), 1,2-propylenediaminetetraacetate (PDTA), ethylenediaminediacetate (EDDA), 2-hydroxyethylthylenediaminetriacetate (HEDTA), diethylenetriaminepentaacetate (DTPA), and nitrilotriacetate (NTA) by ¹³C-

and ⁵¹V-NMR spectroscopy. All of these ligands acted as tetradentates to form octahedral complexes containing a *cis*-VO₂ core.

Iminodiacetate (IDA)-type ligands which can act as tridentates have been reported to form 1 : 1 complexes with vanadium (V) in the acidic solution by their kinetic studies,⁸⁻¹⁰ but the structures of the complexes have not been studied. It is hoped to obtain more information about the solution structures of the vanadium (V) complexes of IDA-type ligands. In this paper we report the results on ¹³C- and ⁵¹V-NMR studies of vanadium (V) complexes of IDA analogues, such as iminodiacetate (IDA), methyliminodiacetate (MeIDA), ethyliminodiacetate (EtIDA), benzyliminodiacetate (BzIDA), pyridine-2,6-dicarboxylate (DPA), and 2-hydroxyethyliminodiacetate (HEIDA), in aqueous solution.

Experimental

All chemicals were of reagent grade (Aldrich etc.) and used without further purification. ¹³C-NMR spectra were

Table 1. ⁵¹V Chemical Shifts of Vanadium (V) Complexes

Complex	δ (ppm) ^a	Half-width (Hz)
V-IDA	-513.7	ca. 300
V-MeIDA	-516.7	330
V-EtIDA	-515.0	ca. 500
V-BzIDA	-519.4	ca. 500
V-DPA	-534.2	260
V-HEIDA	-512.5	650

^aRelative to external VOCl₃.

measured at 25.16 MHz on a Varian XL-100 FT spectrometer and ⁵¹V-NMR spectra were obtained at 67.76 MHz on a Bruker WM-250 FT spectrometer. Sample solutions for NMR measurements were prepared by dissolving the weighed amounts of NH₄VO₃ and ligand into 20% D₂O/80% H₂O to provide concentration of 0.5 M in ligand. The pH of the solution was adjusted to 3 for IDA, MeIDA and BzIDA, and 6 for DPA and HEIDA with addition of 50% NaOH solution or concentrated H₂SO₄. EtIDA solutions were saturated at somewhat lower molarity because of its low solubility in water. NMR spectra of the complexes were measured at the temperature of 283 K immediately after preparing solutions to reduce decomposition to a negligible rate. ¹³C chemical shifts were measured to internal dioxane and referenced to external TMS using the relation δ_{TMS} = δ_{dioxane} + 67.73 ppm. ⁵¹V chemical shift were measured to external VOCl₃ and referenced to it.

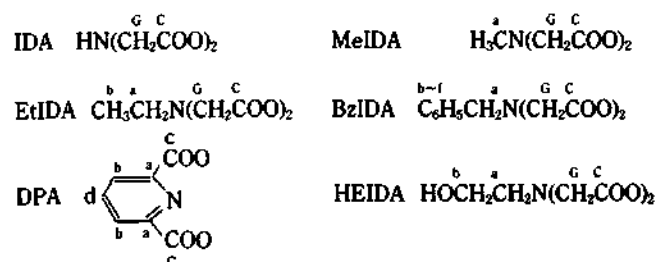
Results and Discussion

Vanadium (V) was reported to be reduced in an acidic medium in the presence of excess aminopolycarboxylate.⁸ Aqueous solutions of the vanadium (V) complexes of IDA analogues except DPA turned slightly green within a few hours, indicating reduction of vanadium (V) by ligand to give a paramagnetic blue VO⁺ species. Of the ligands studied IDA was most easily oxidized in the complexes. The oxidation was acid-catalyzed and, thus, the color change of the solution was pronounced at pH 3. The pH of the solution can affect the stability of the complex formed. IDA, MeIDA, EtIDA, and BzIDA formed complexes at pH 3, whereas DPA and HEIDA formed complexes more easily at pH 6. Complexes of IDA-type ligands might easily be hydrolyzed and are not stable at pH 6.

⁵¹V- and ¹³C-NMR chemical shifts of the vanadium (V) complexes are shown in Table 1 and 2, respectively. The new ⁵¹V signal appeared in the vanadium solution when complexation occurred. The ⁵¹V chemical shifts and linewidths of the complexes are comparable to those observed in octahedral V(V)-EDTA complex.^{7,14} Also the complex formation was easily detected by the appearance of a set of new ¹³C signals which were distinct from those of free ligand. Upon complexation the ligands generally showed downfield shifts in ¹³C-NMR spectra, caused by the displacement of the protons in amine sites. Protonation shifts in amines¹⁵ and aminoacids¹⁶ are generally upfield, due to the local electric field of protonated species and the net effect of complexation to the less

Table 2. ¹³C Chemical Shifts (in ppm) of Free and Complexed Ligands

Complex	Assignment ^a					
	C	G	a	b	d	e f
IDA	172.15	49.85				
V-IDA	181.79	57.04				
MeIDA	171.46	59.64	43.70			
V-MeIDA	180.04	66.26	49.97			
EtIDA	171.72	57.40	52.79	10.12		
V-EtIDA	180.46	63.08	57.40	10.62		
BzIDA	171.22	57.00	60.14	131.52	130.55	132.40 130.25
V-BzIDA	180.04	62.67	60.20	133.93	130.08	132.40 130.08
DPA	173.41		153.52	126.38	140.32	
V-DPA	170.27		149.13	128.07	148.36	
HEIDA	171.45	58.48	58.06	56.79		
V-HEIDA	181.30	64.92	64.92	62.39		

^aStructural assignment:

acidic VO₂⁺ moiety is usually downfield shift. Although ⁵¹V has a nuclear spin (I) of 7/2, no coupling was observed between the metal and the ligand carbons in any of the complexes studied.

IDA, MeIDA, EtIDA, and BzIDA. The formation constants of IDA and MeIDA complexes are reported to be 10^{11.70} and 10^{10.29}, respectively.^{8,9} The formation constant¹¹ of EDTA complex is 10^{15.64}, indicating that the stability of complexes of multidentate ligands increases with the number of chelate rings formed.

IDA, MeIDA, EtIDA and BzIDA can react with VO₂⁺ at pH 3 as a tridentate ligand whose one amine nitrogen and two acetate oxygens coordinate to the metal ion. A water molecule might fulfill the vacant position in the octahedral complexes as follows:



where HY⁻ represents mono-protonated IDA-type ligand. Mono-protonated forms of the ligands predominate at pH 3 in the solution.^{8,9} At a higher pH than 4.5 the hydrolysis of VO₂Y(H₂O)⁻ occurs.¹⁰ In acidic solution (pH > 2.5), vanadium exists as the VO₂⁺ ion. This ion hydrolyses to H₂VO₄⁻, HVO₄²⁻, VO₄³⁻, V₃O₉³⁻, and HV₂O₇³⁻ in alkaline solutions and polymerizes in moderately acidic solutions.^{12,13} It was suggested that MIDA formed the complex VO₂Y(H₂O)⁻, with VO₂⁺ in the acidic solution by the thermodynamic studies.⁹

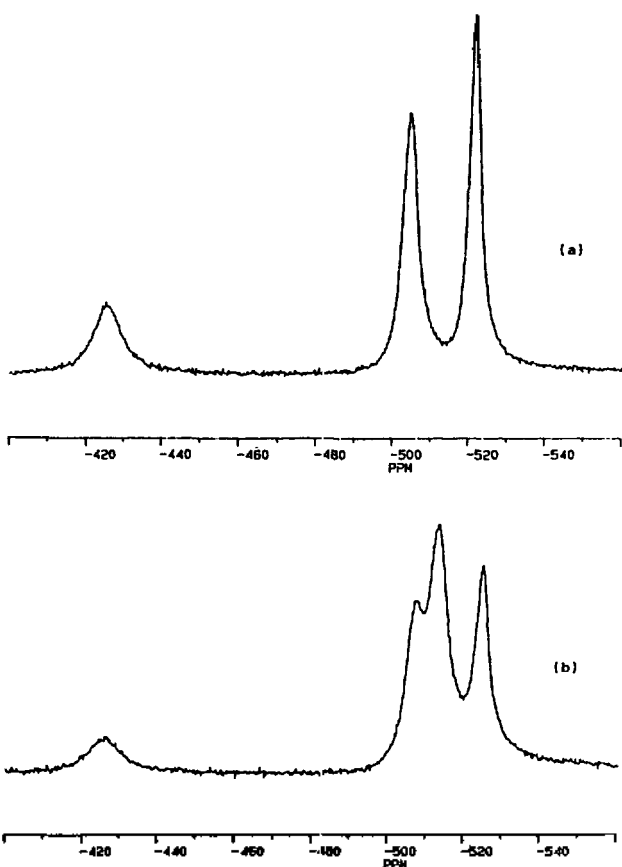
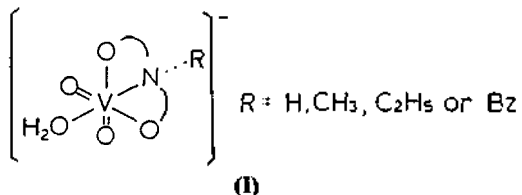


Figure 1. ^{51}V -NMR spectra of (a) NH_4VO_3 and (b) V-EtIDA (1:1) in D_2O - H_2O (20:80) at pH 3.

^{51}V -NMR spectra of NH_4VO_3 and V-EtIDA (1:1) solutions are shown in Figure 1. The signal at -515.0 ppm is attributed to octahedral complex and the remaining signals (-426.1 , -506.8 , and -524.5 ppm) are from protonated decavanadate ion, $\text{H}_n\text{V}_{10}\text{O}_{28}^{-(6-n)}$ ($n=1$ or 2).¹³ The complex formation of these ligands with vanadium (V) is not quantitative, because ^{13}C -NMR lines of the free ligands are superimposed on those of the complexes. ^{13}C -NMR spectra of EtIDA and its vanadium complex are shown in Figure 2. When the complex formation occurs, ^{13}C chemical shifts of the ligands are shifted to downfield. In Figure 2(b) the signal of carbon (a) in EtIDA complex is supposed to overlap with that of carbon (G) in free EtIDA at 57.40 ppm. The four available coordination sites of VO_2^+ ion are occupied by one nitrogen and two acetate oxygen. In addition, one water molecule might fulfill the remaining site to satisfy the coordination number of six in octahedral complex. The structure of the complexes is proposed as shown in (I). The manner of binding of ligand



to metal is a facial tridentate coordination. Aspartic acid and histidine whose structures are shown in (II) and (III), respec-

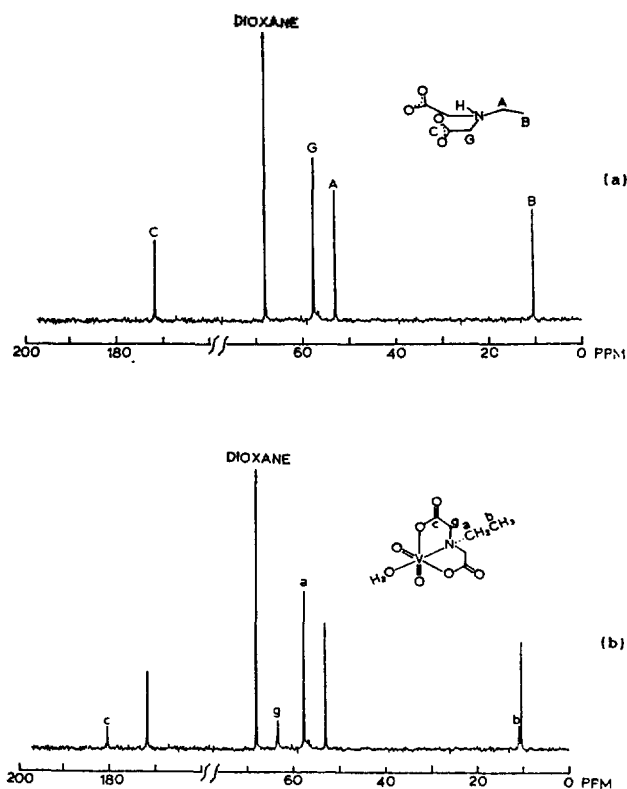


Figure 2. ^{13}C -NMR spectra of (a) EtIDA and (b) V-EtIDA (1:1) in D_2O - H_2O (20:80) at pH 3.

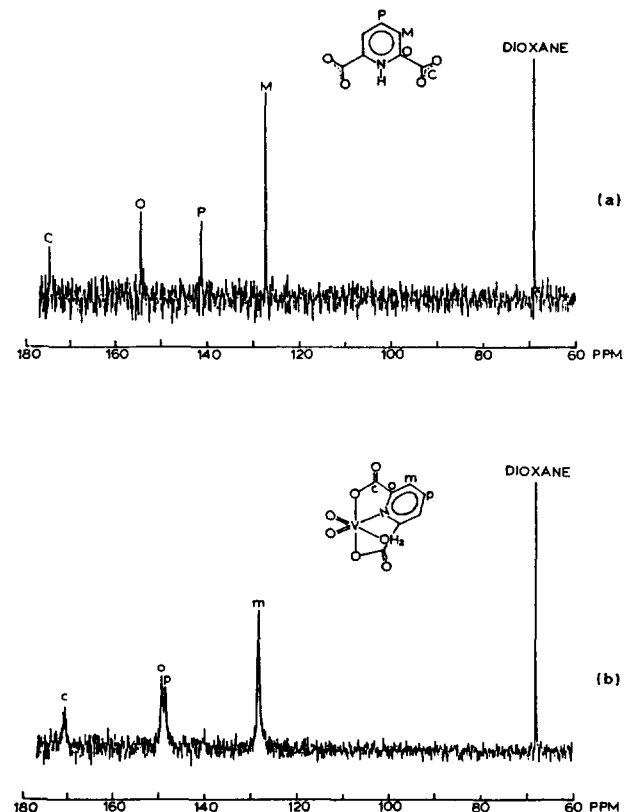


Figure 3. ^{13}C -NMR spectra of (a) DPA and (b) V-DPA (1:1) in D_2O - H_2O (20:80) at pH 6.

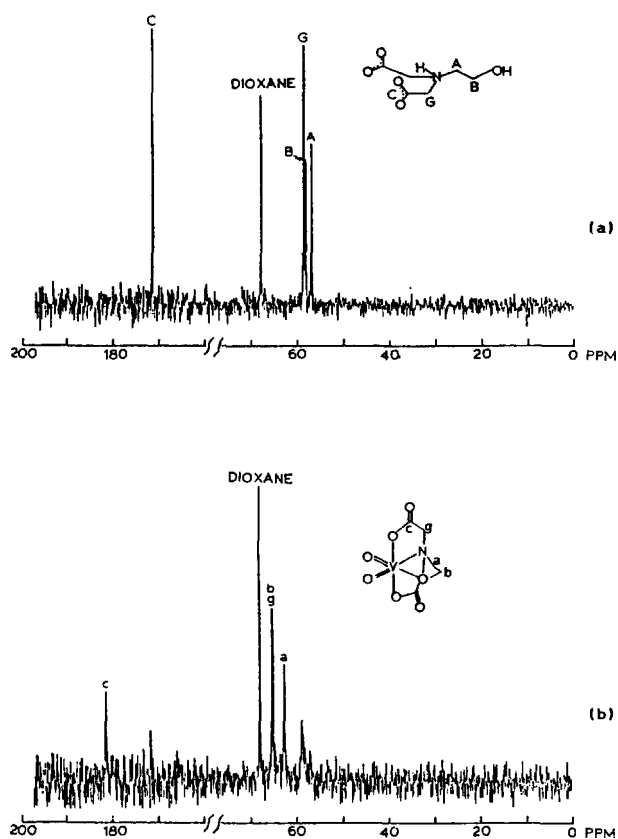
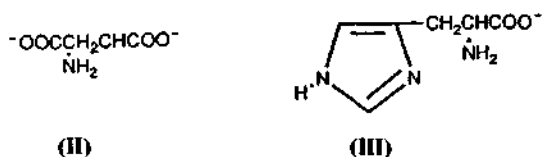


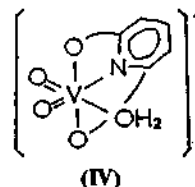
Figure 4. ¹³C-NMR spectra of (a) HEIDA and (b) V-HEIDA (1:1) in D₂O-H₂O (20:80) at pH 6.



tively, fail to form complexes with VO₂⁺ ion, even though these ligands can form facial tridentate complexes. Two chelate rings in these complexes would be five- and six-membered and therefore less stable than two five-membered rings formed in IDA-type complexes.

DPA. DPA can also act as a tridentate ligand which contains one heterocyclic nitrogen and two carboxylate oxygens. It is interesting to investigate whether DPA coordinates to VO₂⁺ or not, because DPA can not coordinate in a facial tridentate manner due to the structure of the ligand as does IDA-type ligand. DPA has been used for colorimetric determination of vanadium (V).¹⁷ ⁵¹V- and ¹³C-NMR data indicate the formation of an octahedral complex. The high-field ⁵¹V chemical shift (−534.2 ppm) of DPA complex may be due to the increased electron density on metal, derived from electron-donating character of the heterocyclic ring. ¹³C-NMR spectra of DPA and its vanadium (V) complex are shown in Figure 3. The signals of 149.13 and 148.36 ppm in the complex are tentatively assigned to *o*- and *p*-carbons of heterocyclic ring, respectively. There is no signal of free ligand in V-DPA (1:1) solution, indicating complete complex formation of DPA with vanadium (V). A protonated form of the ligand predominates in the pH 6 but nonzwitter form would

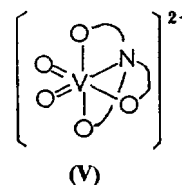
be expected to occur in some quantities.¹⁸ It is suggested that the structure of DPA complex is as shown in (IV). In



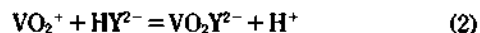
this structure three donor atoms (two oxygens and one nitrogen) are in the same plane of the heterocyclic ring. This coordination manner, so-called meridionally tridentate coordination, is different from that of IDA-type ligands which coordinate facially to VO₂⁺ ion. The complex-formation reaction of DPA ligand is same as Eq. (1).

HEIDA. Alcohols have been reported to form esters with vanadate.¹⁵⁻¹⁷ HEIDA is a potentially quadratentate ligand which contains one IDA moiety and one hydroxyl group.

⁵¹V signal at −512.5 ppm corresponds to vanadium complex. The ¹³C chemical shifts (56.79, 58.06 ppm) of hydroxyethyl (CH₂CH₂OH) group in the free ligand are shifted to large value (62.39, 64.92 ppm) in the complex. In Figure 4(b) the signal of carbon (b) overlap with that of carbon (g) at 64.92 ppm. The large downfield shift of hydroxyethyl group, especially about 7 ppm shift of the hydroxy-bearing carbon, indicates the coordination of the hydroxyethyl group in the complex. The structure of the complex is proposed as shown in (V).



Deprotonation of OH group in HEIDA is needed to form complexes with vanadium (V). The hydroxyl group might be less favored than carboxylate group in the complex formation.⁷ The binding of hydroxyl group in the ligand is consistent with the result in alcohols.¹⁵⁻¹⁷ The complex-formation reaction is suggested to be same as Eq. (2).



In Eq. (2) HY²⁻ represents fully dissociated HEIDA ligand. In summary, HEIDA coordinates to VO₂⁺ through one IDA moiety and one hydroxyl group, acting as a quadratentate.

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References

1. B. R. Nechay, L. B. Nannainga, P. S. E. Nechay, R. L. Post, J. J. Grantham, I. G. Macara, L. F. Kubena, T. D. Phillips, and F. H. Nielsen, *Fed. Proc. Fed. Am. Soc. Exp. Biol.*, **45**, 123 (1986).
2. N. D. Chasteen, *Bonding (Berlin)*, **53**, 105 (1983).
3. D. W. Boyd and K. Kustin, *Adv. Inorg. Biochem.*, **6**, 311 (1984).
4. T. Ramasarma and F. L. Carane, *Top. Cell. Regul.*, **20**,

- 247 (1981).
5. E. Maschitelli-Coriandoli and C. Citterio, *Nature (London)*, **193**, 1527 (1959).
 6. L. W. Amos and D. T. Sawyer, *Inorg. Chem.*, **11**, 2692 (1983).
 7. Man-Ho Lee and Tae-Sub O., *J. Korean Chem. Soc.*, **27**, 117 (1983).
 8. K. Zare, P. Lagrangee, and J. Lagrange, *J. Chem. Soc., Dalton Trans.*, 1372 (1979).
 9. S. Yamada, J. Nagase, S. Funahashi, and M. Tanaka, *J. Inorg. Nucl. Chem.*, **38**, 617 (1976).
 10. S. Yamada, Y. Ukei, and M. Tanaka, *Inorg. Chem.*, **15**, 964 (1976).
 11. J. Lagrange and P. Lagrange, *Bull. Soc. Chim. France.*, **1**, 13 (1972).
 12. M. T. Pope and B. W. Dale, *Quart. Rev., Chem. Soc.*, **22**, 527 (1968).
 13. E. Heath and O. W. Howarth, *J. Chem. Soc., Dalton Trans.*, 1105 (1981).
 14. S. E. O'Donnell and M. T. Pope, *J. Chem. Soc., Dalton Trans.*, 2290 (1976).
 15. J. E. Sarneski, H. L. Suprenant, F. K. Molen, and C. N. Reilley, *Anal. Chem.*, **47**, 2116 (1975).
 16. H. L. Suprenant, J. E. Sarneski, R. R. Key, J. T. Byrds, and C. N. Reilley, *J. Mang. Reson.*, **40**, 231 (1980).
 17. G. A. Pearse, *Anal. Chem.*, **34**, 536 (1962).
 18. J. C. Cassatt and R. G. Wilkins, *J. Am. Chem. Soc.*, **90**, 6045 (1968).
 19. J. H. Ferguson and K. Kustin, *Inorg. Chem.*, **12**, 3349 (1985).
 20. M. J. Gresser and A. S. Tracey, *J. Am. Chem. Soc.*, **107**, 4215 (1985).
 21. M. J. Gresser and A. S. Tracey, *J. Am. Chem. Soc.*, **108**, 1935 (1986).

Synthesis and Characterization of Poly(alkoxy- and aryloxyphosphazene) Copolymers

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Copolymers with two different side groups, 2,2,2-trifluoroethoxy and *p*-chlorophenoxy groups, have been synthesized by reaction of poly(dichlorophosphazene) with their sodium salts, and characterized by elemental analysis, gel permeation chromatography, IR and NMR spectroscopies. The molecular weight measurement has shown that the weight average molecular weight, \bar{M}_w of the copolymers are all above 10^6 and their molecular weight distributions are monomodal and narrow ($\bar{M}_w/\bar{M}_n < 4$). Thermal properties of these copolymers measured by DSC and TGA exhibited to be intermediate between those of the two corresponding homopolymers.

Introduction

Since hexachlorocyclotriphosphazene, $(\text{NPCl}_2)_3$, was first thermally polymerized to a soluble high molecular weight poly(dichlorophosphazene), $(\text{NPCl}_2)_n$, by Allcock,¹ many different types of poly(organophosphazenes) were prepared by nucleophilic substitution of the chlorine atoms with various organic groups.²⁻⁶ A wide variety of chemical and physical properties of poly(organophosphazenes) is given depending on the kinds of the organic substituents. It is known that, in particular, poly(organophosphazenes) with alkoxy and/or aryloxy groups, $[\text{NP}(\text{OR})(\text{OR}')]_n$, exhibit excellent elastomeric properties.^{6,7} In general, when R and R' are the same aromatic groups, the homopolymers are microcrystalline and thermally stable but show low tensile strength. On the other hand, when R and R' are not the same and one or both of them are aliphatic, the copolymers exhibit noncrystalline and flexible properties but are thermally unstable.⁸⁻¹⁰ In an attempt to prepare an elastomer with improved mechanical and thermal properties we have prepared copolymers by substitution of poly(dichlorophosphazene) with trifluoroethoxy and *p*-chlorophenoxy groups, and characterized by means of

elemental analysis, gel permeation chromatography and various spectroscopic techniques.

Experimental

Chemicals. Hexachlorocyclotriphosphazene (Aldrich) used for polymerization was purified by sublimation at 50°C under vacuum (~0.1 mmHg). Sodium (Nakarai), reagent grade *p*-chlorophenol and 2,2,2-trifluoroethanol (Aldrich) were used as received. 1,4-Dioxane (Kento) and all other solvents were thoroughly dried by distillation over sodium and benzophenone under nitrogen atmosphere before use.

Measurements. IR spectra of polymers were recorded on Analect FX-6160 FT-IR spectrometer in thin film between NaCl disks. ¹H-NMR and ³¹P-NMR were measured using Bruker AM-60 and Bruker AM-200 spectrometers, respectively. The chemical shifts for ³¹P-NMR are relative to reference of 85% aqueous phosphoric acid solution. Solution viscosity measurements were made with a Cannon-Ubbelohde Type No. 526 viscometer at 25°C (± 1) using DMF or THF as solvent for copolymers and acetone for homopolymers. Gel permeation chromatography data were obtained with the