

Spectroscopic Investigation on the Reactions of Tin and Titanium Alkoxides with 3-Pentenoic Acid

Gamze Bulut and Asgar Kayan*

Department of Chemistry, Kocaeli University, İzmit, Turkey

Abstract: Tin and titanium pentenoate have been prepared from tin(IV) butoxide and titanium (IV) isopropoxide in alcohol and 3-pentenoic acid. Reactions of $\text{Sn}(\text{O}i\text{Bu})_4$ and $\text{Ti}(\text{OPr}^i)_4$ with 3-pentenoic acid in 1:1 molar ratio were studied in butanol and propanol solution at room temperature by sol-gel process. The complexations were investigated by ^{13}C , ^1H -NMR and FT-IR spectroscopy. $^{13}\text{C}\{^1\text{H}\}$, ^1H -NMR and FT-IR spectra showed that 3-pentenoic acid completely reacted with $\text{Sn}(\text{O}i\text{Bu})_4$ and $\text{Ti}(\text{OPr}^i)_4$. These new products were hydrolyzed by water in ratio of 1:4 $[\text{M}(\text{OR})_4/\text{H}_2\text{O}]$, M: Sn, Ti, R: butyl and isopropyl. The stability of hydrolyzed products was investigated by ^{13}C , ^1H NMR and FT-IR. After hydrolysis, it was seen that no 3-pentenoic acid was released from $[\text{Ti}(\text{OPr}^i)_3(\text{PA})]_n$ and but was released from $[\text{Sn}(\text{O}i\text{Bu})_3(\text{PA})]_n$ under the studied conditions.

Keywords: Oligomer gels, coatings, tin alkoxide, pentenoic acid, hydrolysis.

1. INTRODUCTION

Sol gel is an attractive synthetic method to metal oxide materials applied in a wide variety of fields such as ceramics, sensors, catalysts, optics, electronics and thin films [1-3]. Sol gel synthesis of materials from transition metal and silicon alkoxides has been extensively investigated [4-5]. Tin and titanium alkoxides are highly reactive to moisture and tend to form oxy-hydroxide precipitates [4-5]. Limiting metal alkoxides reactivity with the organic ligands such as organic acids and β -ketoesters inhibits precipitation formation and allows the preparation of oligomeric gels [6]. When these organic groups were added to metal alkoxides solution, some of the alkoxy groups from starting material were replaced with these chelate-organic groups [6-9]. Addition of water to these organically modified metal alkoxide complexes leads to hydrolysis of alkoxy groups and condensation reactions resulting in inorganic networks with high surface areas [10-12]. In this connection the hydrolytic stability of the unsaturated organic complex ligands is essential for the formation of organic-inorganic network structures. The concern of this work especially is to broaden the synthesis and hydrolytic stability of tin alkoxide complexes with 3-pentenoic acid.

2. EXPERIMENTAL SECTION

The $^{13}\text{C}\{^1\text{H}\}$ and ^1H -NMR spectra were recorded on Bruker AC300 spectrometer. Infrared spectra of products were recorded on Shimadzu 8201/86601 PC spectrometer.

The chemicals tin tetra-n-butoxides $[\text{Sn}(\text{O}i\text{Bu})_4]$, 99.99 % [Aldrich], titanium tetra isopropoxides $[\text{Ti}(\text{OPr}^i)_4]$, 98% [Merck], 3-pentenoic acid [PA, 97%, trans form > 90%, Fluka], propanol [99%, J.T. Baker] and butanol [99%,

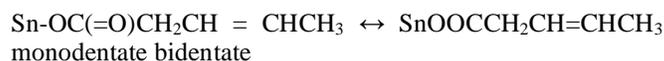
Fluka] were used in the experiments without further purification. Propanol and butanol were used as solvent for metal isopropoxide and metal butoxide studies, respectively.

Preparation of $[\text{Sn}(\text{O}i\text{Bu})_3(\text{PA})]_n$ (1)

0.01 mol $\text{Sn}(\text{O}i\text{Bu})_4$ was stirred in 10 g of butanol for 2 minutes and 0.01 mol 3-pentenoic acid (trans-form > 90%) was added to the solution. The mixture was stirred for two hours at room temperature. The solvent and liberated butanol were removed from the mixture under reduced pressure (~ 0 mbar) at about 50°C and orange polymer or oligomer gel was obtained. ^{13}C NMR (in CDCl_3) δ ppm(assignment): 14.0 (CH_3 , $\text{O}i\text{Bu}$), 19.1 (CH_3 , PA), 19.3 ($^3\text{CH}_2$, $\text{O}i\text{Bu}$), 35.1 ($^2\text{CH}_2$, $\text{O}i\text{Bu}$), 38.4 (CH_2 , PA), 64.7 (OCH_2 , $\text{O}i\text{Bu}$), 123.0 ($\text{CH}_3\text{-CH}=\text{P}$), 129.5 ($=\text{CH-CH}_2$, PA), 172.6 (COO-Sn , PA) (Fig. 1). ^1H NMR (in CDCl_3) δ ppm: (multiplicity, assignment): 0.92 (t, CH_3 , $\text{O}i\text{Bu}$), 1.30-1.65 (m, CH_2CH_2 , $\text{O}i\text{Bu}$), 1.70 (d, CH_3 , PA), 3.0 (d, CH_2 , PA), 3.65 (t, 2H, OCH_2 , $\text{O}i\text{Bu}$) 4.1 (t, 4H, OCH_2 , $\text{O}i\text{Bu}$), 5.57 (m, $\text{CH}=\text{CH}$, PA) (Fig. 2). FTIR (NaCl cell): 2965 (s), 2920 (s), 2859 (s), 1636(s), 1550 (s), 1439 (m), 1381-1368 (s, double), 1302 (m), 1242 (m), 1176 (w), 966 (s), 949 (w), 687 (s) 557 (br, s), cm^{-1} . NMR spectrum of Sn-complex shows that small amount of the solvent (butanol) remain in the product. The peaks at 62.4 ($\text{HO-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) and 32.2 ppm ($\text{HO-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) in ^{13}C NMR spectrum belong to solvent butanol. The other two carbon atoms peaks of solvent probably overlap with the complex peaks [Abbreviations. s: strong, m: medium, w: weak, br: broad, as: asymmetric, s: symmetric, brs: broad singlet, $^4\text{CH}_3^3\text{CH}_2^2\text{CH}_2^1\text{CH}_2\text{O-Sn}$].



Hydrolysis of $[\text{Sn}(\text{O}i\text{Bu})_3(\text{PA})]_n$ (2)



Compound-1 was prepared as mentioned in above procedure. Before removing the butanol, 4 moles water per mole

*Address correspondence to this author at the Department of Chemistry, Kocaeli University, İzmit, Turkey; Tel: + 90 (0)262-3032018; Fax: + 90 (0)262-3032002; E-mail: akayan@kocaeli.edu.tr

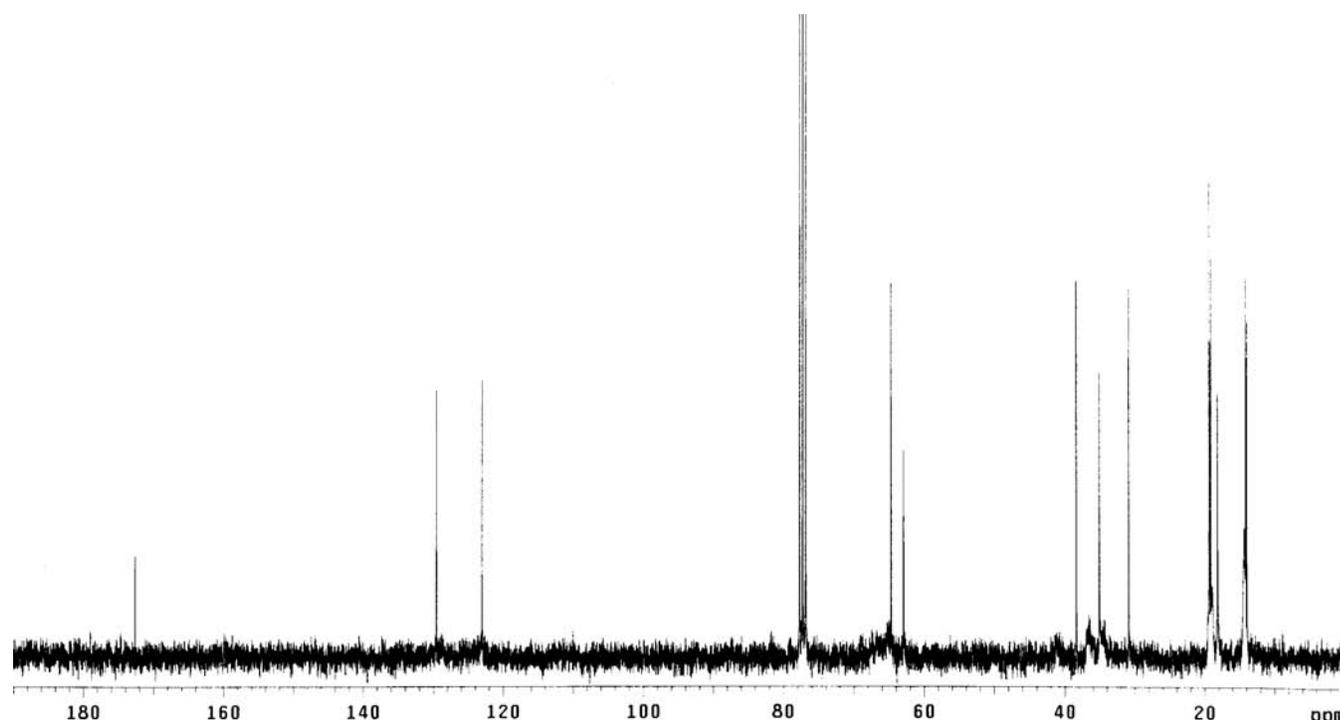


Fig. (1). $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of $[\text{Sn}(\text{OBu}^n)_3(\text{PA})]_n$.

$\text{Sn}(\text{OBu}^n)_4$ were added to solution and stirred for one more hour at room temperature. Then, solvent-butanol and liberated butanol were removed from the mixture under reduced pressure (~ 0 mbar) at 50°C and solid product was obtained. ^{13}C NMR (in $\text{CDCl}_3 + \text{DMSO}$) δ ppm(assignment): 14.0 (CH_3 , OBu), 18.1 (CH_3 , PA), 19.1 ($^3\text{CH}_2$, OBu), 35.0 ($^2\text{CH}_2$, OBu), 38.1 (CH_2 , PA), 64.4 (OCH_2 , OBu), 123.4 ($\text{CH}_3\text{-CH=}$, PA), 128.9 ($=\text{CH-CH}_2$, PA), 174.4 (COO-Sn , PA). ^1H NMR (in $\text{CDCl}_3 + \text{DMSO}$) δ ppm: (multiplicity, assignment): 0.90 (m, CH_3 , OBu), 1.35-1.65 (m, CH_2CH_2 , OBu), 1.705 (d, CH_3 , PA), 3.0 (d, CH_2 , PA), 3.58 (t, OCH_2 , OBu) 4.1 (t, OCH_2 , OBu), 5.54 (m, $\text{CH}=\text{CH}$, PA). FTIR (NaCl cell): 3416 (s), 2963 (s), 2920 (s), 2857 (s), 1740(m) 1626 (s), 1550 (s), 1437 (m), 1381-1371 (s, double), 1302 (m), 1244 (m), 1170 (w), 685 (s) 561 (br, s) (Fig. 3) [$^4\text{CH}_3^3\text{CH}_2^2\text{CH}_2^1\text{CH}_2\text{O-Sn}$].

Characteristic signals for released 3-pentenoic acid in amount of 15% (calculated from signal intensity) appear at $\delta = 122.9$ ($\text{CH}_3\text{-CH=}$, PA), 129.2 ppm ($=\text{CH-CH}_2$, PA).

Preparation of $[\text{Ti}(\text{OPr}^i)_3(\text{PA})]_n$ (3)

A preparative procedure analogous to the above (1) was performed in propanol. ^{13}C NMR (CDCl_3) δ , ppm: 18.2 (CH_3 , PA), 26.3 (CH_3 , OPr^i), 38.4 (CH_2 , PA), 64.9 (CH , OPr^i), 124.8 ($\text{CH}_3\text{-CH=}$, PA), 127.8 ($=\text{CH-CH}_2$, PA). ^1H NMR (in CDCl_3) δ ppm: (multiplicity, assignment): 1.2 (d, CH_3 , OPr^i), 1.6 (m, CH_3 , OPr^i and PA), 3.0 (brs, CH_2 , PA), 4.1-4.6 (brs, CH , OPr^i), 5.55 (brs, $\text{CH}=\text{CH}$, PA). FTIR (NaCl cell): 2961 (s), 2934 (s), 2874 (s), 1568-1556 (s), 1439-1400 (s), 1379 (m), 1321(w), 1258 (m), 1115 (s), 1080 (s), 1001 (s), 966 (s), 889 (w), 862(w), 787 (s) 764 (s), cm^{-1} . The ^1H -NMR spectrum of the complex indicates the presence of small quantity of the solvent remaining in the product (e.g., a peak at 0.9 ppm that belongs to the CH_3 carbon of n-propanol).



Hydrolysis of $[\text{Ti}(\text{OPr}^i)_3(\text{PA})]_n$ (4)

A preparative procedure analogous to the above (3) was performed. Propanol was used as solvent for this hydrolysis reaction. ^{13}C NMR ($\text{CDCl}_3 + \text{DMSO}$) δ , ppm: 18.0 (CH_3 , PA),

26.0 (CH_3 , OPr^i), 38.1 (CH_2 , PA), 63.9 (CH , OPr^i), 123.4 ($\text{CH}_3\text{-CH=}$, PA), 128.9 ($=\text{CH-CH}_2$, PA), 174.8 (broad signal, COO-Ti , PA). ^1H NMR (in $\text{CDCl}_3 + \text{DMSO}$) δ ppm (multiplicity, assignment): 1.4-1.8 (m, CH_3 , OPr^i and PA), 3.0 (brs, CH_2 , PA), 3.6 (brs, CH , OPr^i), 4.1 (CH , OPr^i), 5.5 (brs, $\text{CH}=\text{CH}$, PA). FT-IR (NaCl): 3412 (br., s), 2965 (m), 2936 (m), 2918 (m), 2857 (m), 1555 (broad singlet, strong intensity), 1437 (s), 1398 (s), 1321(m), 1258 (m), 1180 (w), 1112 (w), 966(m), 816 (br, s), 644-623 (br, s), 461 (s) cm^{-1} .

RESULTS AND DISCUSSION

Spectroscopic techniques were used to characterize tin and titanium complexes.

NMR spectroscopy: The ^{13}C NMR spectrum of free 3-pentenoic acid shows signals at $\delta = 17.7$ (CH_3), 37.8 (CH_2), 122.8 ($\text{CH}_3\text{CH=}$), 129.6 ($=\text{CH-CH}_2$) and 179 ppm (COOH). When 3-pentenoic acid was added to metal alkoxides compounds in 1:1 molar ratio of $\text{PA/M}(\text{OR})_4$, alkoxy group substitutes with PA . The ^{13}C NMR spectra of Sn and Ti complexes indicate that carbon groups of coordinated PA shift to different region in the ^{13}C NMR spectra. For example, the characteristic peaks for coordinated PA of compound $[\text{Sn}(\text{OBu}^n)_3(\text{PA})]_n$ come out at $\delta = 19.1$ (CH_3 , PA) 38.4 (CH_2 , PA), 123.0 ($\text{CH}_3\text{-CH}=\text{PA}$), 129.5 ($=\text{CH-CH}_2$, PA), 172.6 ppm (COO-Sn , PA) (Fig. 1). The ^1H NMR spectrum of $[\text{Sn}(\text{OBu}^n)_3(\text{PA})]$ gives peaks at 1.70 (d, CH_3 , PA),

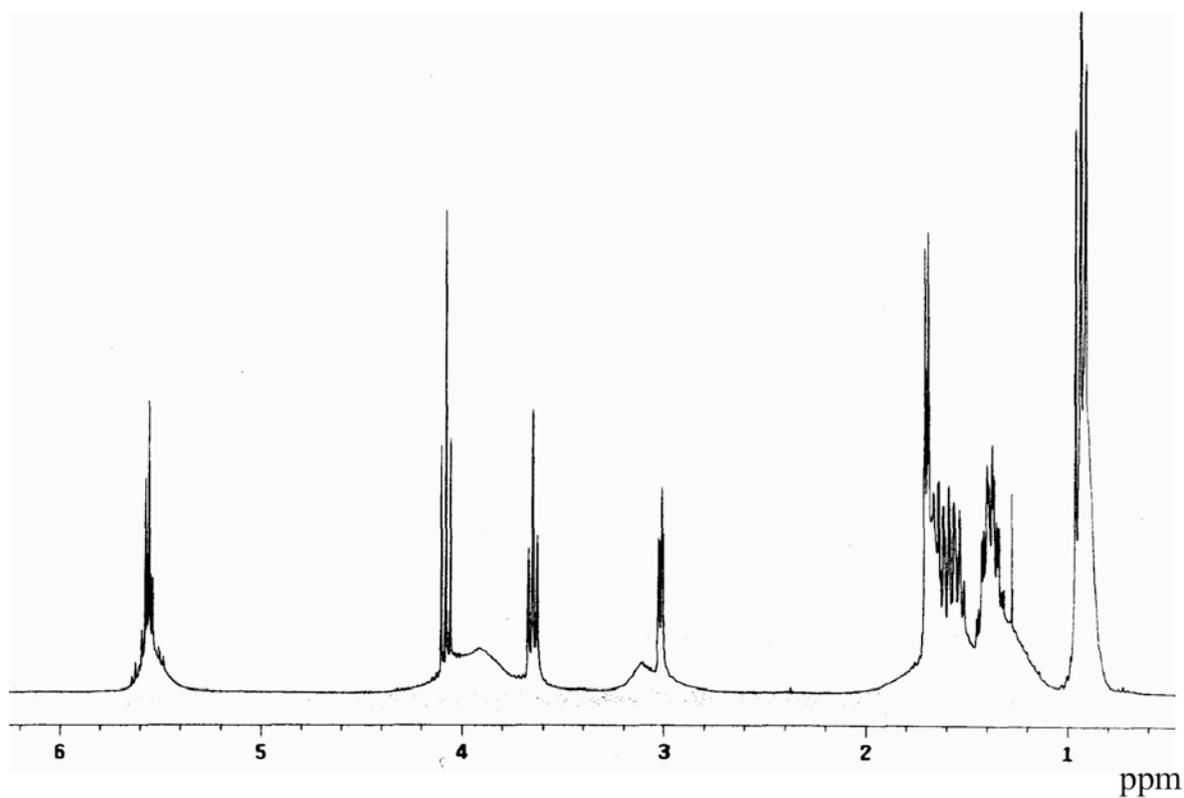


Fig. (2). ¹H-NMR spectrum of $[\text{Sn}(\text{OBu}^n)_3(\text{PA})]_n$.

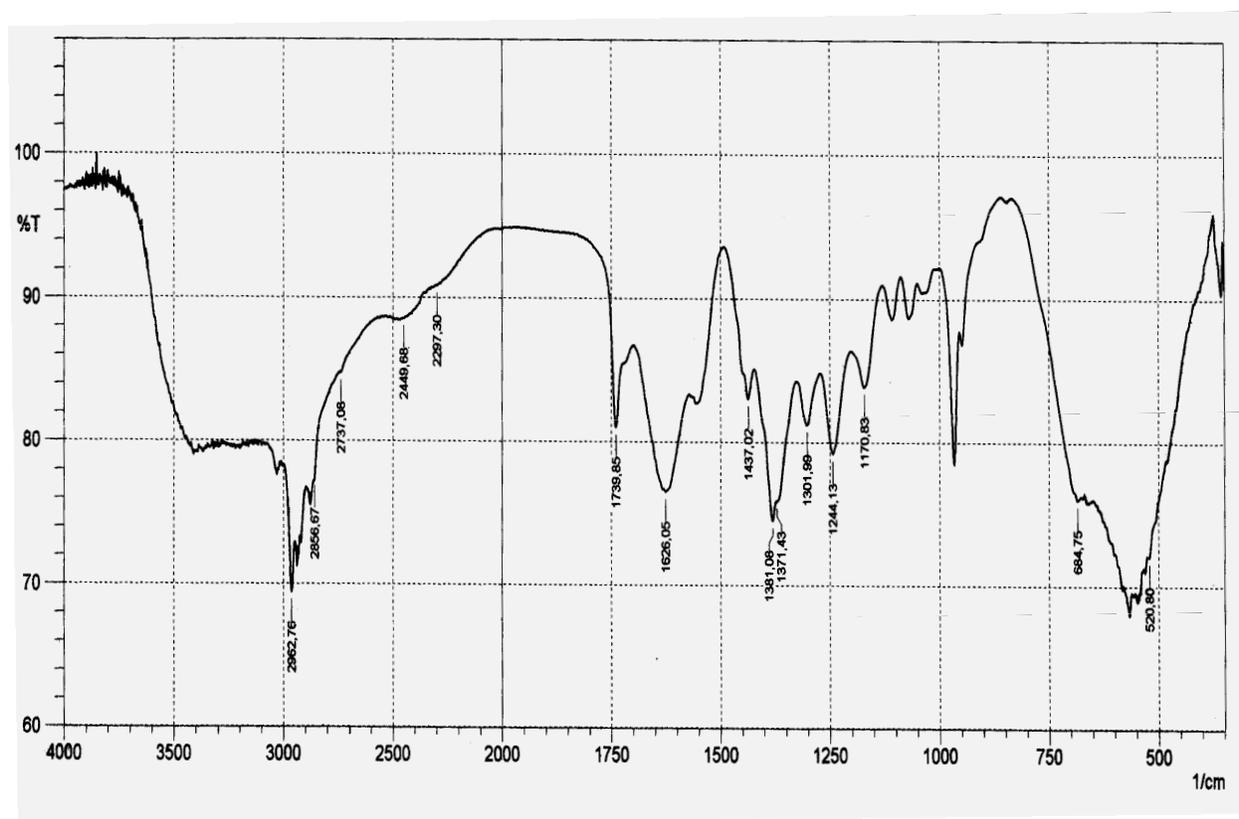


Fig. (3). FTIR spectrum of hydrolyzed product $[\text{Sn}(\text{OBu}^n)_3(\text{PA})]_n$.

3.0 (d, CH₂, PA), 5.57 ppm (m, CH=CH, PA) (Fig. 2). The signal for the -COOH proton in the ¹H-NMR spectrum is absent. Lack of a COOH proton signal indicates that 3-pentenoic acid is completely coordinated to tin. The OCH₂ protons of butoxy groups appear magnetically nonequivalent and occur at 3.65 ppm for one OCH₂ group and 4.1 ppm for two OCH₂ groups. Both NMR data which are given in text for [Ti(OPrⁱ)₃(PA)]_n are similar to that of tin complex.

When ¹³C-NMR spectrum of hydrolyzed-product of [Sn(OBuⁿ)₃(PA)]_n is taken, it shows that almost 15% 3-pentenoic acid is released from tin complex. The ¹³C-NMR spectrum of the Sn(OBuⁿ)₃(PA)-hydrolysate shows characteristic signals for released PA (~15%) at 122.9 (CH₃-CH =, PA), 129.2 (=CH-CH₂, PA) ppm. In contrast to above complex, ¹³C-NMR spectrum of the Ti(OPrⁱ)₃(PA)-hydrolysate shows no peaks for released pentenoic acid. Comparison of hydrolytic behaviour of tin and titanium complex indicate that the [Sn(OBuⁿ)₃(PA)]_n complex is more susceptible to hydrolysis than the [Ti(OPrⁱ)₃(PA)]_n complex. In other words, PA are strongly coordinated to titanium isopropoxide in the presence of water. The ¹³C-NMR spectrum of both complexes indicate the presence of small quantity of solvent remaining in the product (e.g., a peak at 64 ppm that belongs to the -CH₂OH carbon of n-propanol). The loss of the pentenoate or alkoxides by hydrolysis leads to the formation of oxo products, [M(O)(OR)(PA)]_n.

FTIR Spectroscopy: FT-IR spectrum of 3-pentenoic acid shows a strong absorbance at 1706 cm⁻¹ for asymmetric carboxyl stretch. The FTIR spectrum observed for an equimolar mixture of Sn(OBuⁿ)₄ and 3-pentenoic acid contains bands characteristic of both bidentate and monodentate pentenoate ligands. These bonding modes are not detected by NMR study. In the FTIR spectrum of compound 1, the formed pentenoate ligands have asymmetric carboxyl stretch vibrations between 1650-1500 cm⁻¹ and symmetric stretch bands at 1500-1250 cm⁻¹. The carboxylate coordination mode should be bidentate chelating which can be inferred from the frequencies of the ν_{as}(COO) at 1550 cm⁻¹ and ν_s(COO) at 1439 cm⁻¹. The frequency separation which is the difference between ν_{as}COO and ν_sCOO (111 cm⁻¹ for compound 1) shows that 3-pentenoate was bonded to tin as a bidentate chelating organic group. The broad band at around 1636 cm⁻¹ ν_{as}(COO) may be due to the monodentate coordination of 3-pentenoate [5]. In tin compounds, there are both monodentate and bidentate coordination modes. A strong broad band at 557 cm⁻¹ is attributed to ν(Sn-O). The other band at around 687 cm⁻¹ is attributed to ν(Sn-O-Sn), indicating the presence of oligomer-like structure.

FTIR spectrum obtained for hydrolyzed product (Sn(OBuⁿ)₄:PA :4H₂O) which includes peak for COOH at around 1739.85 cm⁻¹ indicates that water hydrolyzes some of the 3-pentenoate ligands (Fig. 3). In tin complex, reaction with water leads to lowering the intensity of the bidentate ν_{as}(COO) band. This shows that chelate pentenoate ligands hydrolyzed. The monodentate ν_{as}(COO) band has shifted from 1636 cm⁻¹ for Sn-complex to 1626 cm⁻¹ for hydrolyzed Sn-Complex. The hydrolyzed product includes strong peak at around 3416 cm⁻¹ for OH group. This shows that some of

the butoxy groups in tin complex were replaced with OH groups by hydrolysis (in a 1:4 ratio, Sn-alkoxides/H₂O). The unsaturated organic ligand, 3-pentenoic acid, in compound 4 is more stable than in 2 toward hydrolysis.

In the FTIR spectrum of titanium complex, the bands at 1555 and 1400 cm⁻¹ are due to asymmetric and symmetric COO stretches. This indicates only the presence of bidentate ligands. In other words, no evidence of monodentate pentenoate ligand was found in titanium isopropoxide complex. Since the hydrolyzed-products were less soluble in deuterated solvent, the product 4 was kept in deuterated solvent for a few hours before taking ¹³C-NMR.

CONCLUSIONS

These inorganic (Sn, Ti)-organic polymeric compounds were synthesized by sol-gel process. The complexation reactions (1 : 1) between metal alkoxides and 3-pentenoic acid were complete. The pentenoate ligand bonds to titanium alkoxide in only bidentate coordination mode while it bonds to tin alkoxide in both monodentate and bidentate coordination modes. The hydrolyzed product of tin complex was less stable than that of titanium complex under the used reaction conditions. 15% 3-pentenoic acid was released from hydrolyzed tin product. Both new complexes are suitable for sol-gel applications such as coating materials on glasses.

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