Poly-alkoxides as Functional Polymer Photocatalyst[†]

Hisashi UEDA

*National Institute of Materials and Chemical Research,
1-1 Higashi, Tsukubashi, Ibaraki 305, Japan.*

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ABSTRACT: Metal alkoxides polymerize to form metal-oxygen polymers. In the present work polymers and co-polymers of metal alkoxides were prepared and their physical and chemical properties were investigated using tetra-hydrofuran (THF) as solvent. One of the properties is photocatalytic activity and another is visible light excited ESR absorption. Tetrabutyl orthotitanate, pentaethyl niobate, and other alkoxides which dissolve in THF were polymerized under fluorescent lamps. ESR spectra were recorded while the polymer was illuminated by a halogen lamp. Catalytic activity was measured using visible light and gas chromatograph. All polymers gave visible light excited ESR spectra. The analysis of ESR intensity change caused by the light-on and light-off procedure have elucidated that there are more than two excited states, the shorter lived one of which is the reaction intermediate of photocatalysis. Among the copolymers of (—TiO—O—NbO—O—) copolymers, Nb 10—20% copolymers gave the highest catalytic activity. It has also been found that the copolymer which has the largest number of Ti₃O₂ unit has the highest activity. These results seem to indicate that the catalyst polymer is a linear polymer. The merit of using alkoxide polymers and copolymers as photocatalyst lies in the facts that in these stable radical type molecules the absorption of visible light is made possible and that in these molecules the catalytic reaction sites are more accessible to the reaction substrate than 3-dimensional crystalline materials.

KEY WORDS Poly-alkoxides / Inorganic Copolymer / Photocatalyst / Photolysis by Visible Light / Visible Light Excited ESR / Stable Free Radical Polymer /

Little is known about 3-dimensional organic natural polymers except those foodstuff polymers as devil's tongue paste or bean-curd. On the other hands, inorganic crystals such as silicates or alumino-silicates are considered to be 3-dimensional polymers. Synthetic 3-dimensional polymers are rather scarce except bakelite or cross-linked rubber.

If we use those polymers, natural or synthetic, by their macroscopic mechanical virtue, it matters little whether their structures are within the boundary of a conjectured specifications. In other words, it matters little whether the material is consisted of linear molecules or 3-dimensional molecules under the condition that the final mechanical properties satisfy our needs. Let us consider

the case of photocatalytic materials. The entire reaction process may be divided into three steps. First, the catalyst must absorb light energy. Secondly, it must provide an environment in which the reaction substrate molecule is excited to a reactive state. Thirdly, the substrate molecules must reach the reaction site and must leave that site after reaction.

For all these steps, a linear molecule is superior to 3-dimensional materials because it has higher probability to meet the reaction substrate molecules than atoms in a 3-dimensional materials. Therefore, a linear synthetic molecular photocatalyst is not only a synthetic substitute of a natural, 3-dimensional, and crystalline photocatalyst, but photocatalytic material of better choice.

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EXPERIMENTAL

Reagents

n-Butyl orthotitanate (Tokyo Chemical Industries), Pentaethyl Niobate (Mitsubishi Metal Co.) were used as received.

Polymerization Method

The polymerization method is almost identical to the one used in the previous reports.¹⁻¹¹ 18.5 mM equivalent amount of the metal alkoxide was dissolved in 500 ml of tetrahydrofuran (THF) in a Pyrex container. To this solution 2 g of silica gel powder, finer than 100 mesh, were added and mixed well. The container was covered with a glass dish and placed in the center of two 30 W circular fluorescent lamps, so that lighting and warming of the solution occurred simultaneously. Co-polymers of metal alkoxides were obtained using a mixture of two metal alkoxides.

Co-polymers of Ti and Nb alkoxides

Nb 100 mol%, Ti 10 mol%–Nb 90 mol%, Ti 20 mol%–Nb 80 mol%, Ti 30 mol%–Nb 70 mol%, Ti 40 mol%–Nb 60 mol%, Ti 50 mol%–Nb 50 mol%, Ti 60 mol%–Nb 40 mol%, Ti 70 mol%–Nb 30 mol%, Ti 80 mol%–Nb 20 mol%, Ti 90 mol%–Nb 10 mol%, and Ti 100 mol% polymer samples were prepared. Their compositions were verified by fluorescent X-rays as within $\pm 10\%$ of the designated value in error.

Measurement of Catalytic Activity

0.30 g of the polymer or a copolymer of metal alkoxides was placed in a Pyrex glass cell with two glass tube branches. The diameter of the main section of the glass cell was 20 mm in diameter and 150 mm in length. The main section was kept in the horizontal position and the side arms, in vertical position, were used as the N_2 gas inlet and outflow tubes. The light source was a Toshiba UV lamp (H400P type) with yellow filters which pass light having wave lengths longer than 480 nm. Therefore, the light

of 480–700 nm region was actually illuminated on the catalyst. As the reaction substrate ethanol (99.5% with 0.5% H_2O) was used. The reaction products, hydrogen and other volatile species, were washed by nitrogen and was analyzed by Okura 701 type gas chromatograph using Porapac-q column at 150°C with N_2 carrier.

Spectroscopic Data of the Polymers

ESR spectra of the polymer were recorded with RE1X type spectrometer of JEOL. IR spectra were recorded by type 102 spectrometer of Japan Spectroscopic Co., Ltd. Reflectance spectra were recorded by a type-240 spectrometer of Shimadzu Co. using a type-180/190 attachment.

RESULTS

Hydrogen Generated from Ethanol by (Ti–O–Nb) Copolymers

Figure 1 indicates the relative activities of the Ti–Nb copolymers when used as photocatalysts to decompose ethanol with visible light. Catalytic activity was the highest when 10–20 mol% of Nb existed in the copolymer.

Figure 1. Photocatalytic activities of (–Ti–O–Nb–) copolymers when used for photolysis of ethanol.

Reflectance Spectra of Polymers

Figure 2 indicates the reflectance spectra of the polymers thus obtained. These spectra show that the relatively stronger visible light absorption region of Ti–O–Nb copolymers is more extended toward 600–800 nm than either Ti 100% polymer or Nb 100% polymer.

Figure 2. Reflectance spectra of (–Ti–O–Nb–) copolymers.

Figure 3. IR spectra of (–Ti–O–Nb–) copolymers.

Infrared Spectra of Polymers

Figure 3 shows the IR spectra of Ti–O–Nb copolymers. The metal–OH bonds linearly increase with the Ti atom increase. Ti_3O_2 units sharply decreases when Ti content reaches 100%. The $-\text{CH}_2-$ and $-\text{CH}_3$ groups due to butyl or ethyl groups increase when Ti content is above 90%. Therefore, free radical content ($\cdot\text{Ti}-\text{O}-\text{Bu}(=\text{O})$) is large when Ti content is almost 100%. Thus, the number of surface OH groups is proportional to the Ti content. In a 50:50 molar mixture (Ti:Nb) of (Ti–O–Nb) copolymer, Ti_3O_2 and Nb_3O_2 units still exist to a considerable extent.

ESR Spectra of the Copolymers

Figure 4 shows the ESR spectra of Ti–O–Nb copolymers when no light is illuminated on them. These spectra indicate that these polymers are stable free radicals. The differences in the shapes of the spectra indicate that

Figure 4. ESR spectra of (–Ti–O–Nb–) copolymers when light is not illuminated.

Figure 5. ESR spectra of (Ti-O-Nb) copolymers when illuminated by visible light.

Figure 6. ESR intensity change with time, with and without light.

the unpaired electron has spin density on several metal atoms. Figure 5 shows the ESR spectra of these polymers when visible light is illuminated.

ESR Intensity Change during and after Visible Light Illumination

Figure 6 shows ESR intensity change (the intensity across $g=2.0021$ of the spectrum for

Table I. Decay rate constants of excited species

Ti:Nb	$k_{11}/10^{-2}$	$k_{12}/10^{-2}$	$k_2/10^{-3}$
100:0	4.969	4.969	1.799
90:10	5.768	5.768	3.200
50:50	7.730	3.896	2.833
10:90	14.65	6.244	3.293
0:100	10.86	3.259	4.894

Ti=100% case in Figure 5, the shape of the spectrum did not change during formation and decay), *versus* time, when the visible light is illuminated and turned off. When the light is turned on, the ESR signal increases until total intensity comes to a saturation value. After attaining this saturation value, if the light is turned off, the intensity decreases at a semilogarithmic-linear rate. The decay rate constants observed for five different samples of (Ti-O-Nb) copolymers are listed in Table I. In Table I, k_{11} and k_{12} are two components of $k(d_1)$, k_{11} being the first section and k_{12} being the second section of a growing curve as shown in Figure 6. k_2 is identical to $k(d_2)$ in Figure 6. The decay rate constant in the growing section of light-on experiment has two components, k_{11} and k_{12} , if the Nb content is 50%, 90%, and 100%. It seems that these two decay components are related to Nb atom.

DISCUSSION

Structure of the Obtained Polymer

Polymers of metal alkoxides obtained by partial-hydrolysis-polymerization have been described by Bradley.^{1,2} According to him, there are five directions in which polymerization reactions proceed.³ Those partial-hydrolysis-methods employed water as a component of the solvent. In the present work, dry THF was used and, therefore, the polymerization reaction seemed to proceed only in one direction, in which the polymerization took place most easily. As a result, the rate of polymerization is relatively slow compared to

Figure 7. The chemical structures of alkoxide polymers. Top, titanium 100% polymer; Bottom, Ti/(Ti + Nb) = 50% polymer.

hydrolysis cases. Evidence to prove this one directional polymerization has been given by X-ray diffraction and IR absorption spectra.⁴ By X-ray data, the polymer obtained was found to be an amorphous material. Elementary analysis results indicated that the composition of the polymer obtained has the molecular formula approximately that of TiO_2 but with considerable amounts of carbon and hydrogen. The presence of a considerable amount of Ti_3O_2 units in the polymer molecule was concluded from IR spectra.⁴ These data will allow to draw a structural picture as shown in Figure 7.

Reaction Diagram

The light excited intensity of ESR absorption, x , changes as shown in Figure 6. The curves in Figure 6 consists of three component curves, (a), (b), and (c). (a) is the growing curve which has k (formation), (b) is the decay curve

Figure 8. Block diagram of the excitation and reaction scheme of catalysis reactions.

which appears only during light illumination and has a decay constant $k(d_1)$. (c) is the decay curve which appears during light-on and light-off periods and has a decay constant $k(d_2)$. Therefore,

$$\frac{dx}{dt} = k(\text{formation}) \cdot I \cdot y - \{k(d_1) + k(d_2)\} \cdot x \quad (1)$$

$$\frac{dx}{dt} = -k(d_2)x \quad (2)$$

(1) is for a light-on case and (2) is for a light-off case. I is the visible light intensity illuminated on the catalyst. y is the concentration of the ground state catalyst molecule, Y . The light excited catalyst molecule X has two subspecies, X_1 and X_2 . X_1 is a short lived species and X_2 is a long lived species and can be observed even after light is turned off. The decay constant of X_1 is $k(d_1)$ and the decay constant of X_2 is $k(d_2)$. X_2 corresponds to the metastable state in Figure 8. Since $k(d_1) \gg k(d_2)$, (1) may be approximated by (1'),

$$\frac{dx}{dt} = k(\text{formation}) \cdot I \cdot y - k(d_1) \cdot x \quad (1')$$

By integration,

$$x = x_\infty [1 - \exp\{-k(d_1) - k(d_2)t\}] \quad \text{light on case,}$$

$$x = x_\infty \cdot \exp[-k(d_2)t] \quad \text{light off case,}$$

are obtained, x_∞ being $\{k_f/(k_1 + k_2)\} \cdot I \cdot y$. From the curves in Figure 6, these rate

constants are determined, and shown in Table I. In the table, $k(d_1)=k_{11}$ and k_{12} , $k(d_2)=k_2$. From these results, it is possible to draw a reaction scheme as shown in Figure 8. In Figure 8, the ground state of the catalyst molecule Y is excited to the excited state of the catalyst molecule X_1 by visible light. Therefore,

In Figure 8, the shadowed portions in the block diagram vaguely denote the energy states of the electrons: the ground state, metastable state, and excited state.

The original structure of $-\text{Ti}(\text{OC}_4\text{H}_9)_2-$ is a tetrahedral configuration as shown in Figure 9A. An energy level diagram as shown in Figure 9B is drawn upon this structure, if one electron exists in the 3d orbital of Ti atom. Therefore, if one OC_4H_9 groups is eliminated, the d^2 orbitals, x^2-y^2 and z^2 , will be used to form hybrid orbitals d^2s sigma bonds. Then the extra Ti electron will occupy one of the 4p orbitals. Dark ESR absorption corresponds to this $4p^1$ (Ti) electron (Figure 9C). When visible light is illuminated, one of the d^2s electrons is excited to 4p orbital to make a $4p^2$ (Ti) structure and the resulting unpaired spin density is mainly in 4s orbital of Ti. The narrow line width of the light-excited ESR spectra in Figure 5 is explained by this structure. The $-\text{CH}_2-\text{CH}_3$ hyperfine structure observed in the light excited ESR spectrum of Ti-alkoxide polymer⁴ may be explained well by this 4s-spin density model, because $=\text{Ti}-\text{O}-\text{C}-\text{C}-\text{CH}_3$ seems to form a hexagonal ring structure in which (Ti, 4s) orbital and $(\text{CH}_3, \text{C}-\text{H}, \sigma)$ orbitals overlap each other.

Figure 9. Configuration of titanium atom. A: Two OC_4H_9 groups not eliminated by condensation. B: Electronic state of Ti $3d^1$, assuming tetrahedral environment. C: Structure when one OC_4H_9 group is taken away.

Mechanism of Visible Light Absorption

Figure 10 illustrates the visible light absorption of alkoxide polymer catalyst. In case of an ordinary diamagnetic type crystalline catalyst, the light absorption leads to an excitation of a valence band electron to the conduction band. In the case of stable paramagnetic molecules, the ground state has $M_s=1/2$ spin state and therefore there are several spin-excited states having similar energy. The actual ground state is, therefore, a hybrid of these spin-excited states and so the ground state energy level goes up compared to the diamagnetic case. The light-excited state is also composed of a hybrid of spin-excited states having ($M_s=1/2$ and $M_s=3/2$), whose lowest orbital component has considerably lower energy than diamagnetic case. As a result, the energy difference between a ground state orbital and excited state orbital is far smaller than the diamagnetic case. Thus, light with a wavelength 480–700 nm can be used to photolyse ethanol.

In a continuous solid, it is convenient to

Figure 10. Molecular orbital energy levels (ground and photoexcited states) of diamagnetic and paramagnetic inorganic polymer molecules.

describe the behavior and energy state of electrons by the band theory. The band theory is based on the idea that all electrons contained in the solid are exchangeable. In the case of a low-dimensional solid, the extent of the exchangeable region is somehow narrowed. For this reason, a molecular orbital approach seems to be better to analyse a linear molecule photocatalyst system.

Special Functions of Inorganic Polymers and Copolymers

The most characteristic point of an inorganic polymer is it can be a stable free radical polymer and a linear polymer. If these two conditions are simultaneously satisfied, they make the polymer catalyst work in the visible wavelength region. Stable free radical, $M_s = 1/2$ state, makes the energy difference between the ground state and the excited state small. This resembles the case of impurity doped semiconductor in which the energy band is bent around an impurity ion. The linear polymer

makes the reaction substrate more accessible to the charge transfer site at which electric charge with higher electrostatic energy is transferred from the catalyst to the reaction substrate molecule. In the case of a three dimensional crystalline catalyst, the rigid crystalline structure prevents the penetration of the substrate into catalyst body and therefore only the crystal surfaces can be used. Therefore, the efficiency is low.

Such an advantage of a linear structure is more significant in the case of co-polymers. In a $(-\text{NbO}-\text{O}-\text{TiO}-)$ copolymer with 10–20% Nb/(Nb+Ti) and 90–80% Ti/(Nb+Ti), the catalyst has a substructure like $-\text{O}-(\text{TiO}_2)_{9-x}(\text{TiO}_2\text{R})_x-\text{NbO}-\text{O}-$ or like $-\text{O}-\text{NbO}-\text{O}-(\text{TiO}_2)_{8-x}(\text{TiO}_2\text{R})_x-\text{NbO}-\text{O}-$, which works as an effective catalytic unit. This, it seems, establishes a molecular orbital with member atoms limited to one of the substructures. An electron, light-excited to an unoccupied molecular orbital having relatively small member atoms, will have a higher flat-band potential.¹² For these reasons, a study of inorganic copolymers or inorganic–organic copolymers of metal alkoxide give important data when these polymers are chosen for photocatalysts.

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