Synthesis and Properties of Polyacetylene Films Prepared by $Ti(OEt)_4$–$AlMe_3$ Catalyst System[#]

Kazuo AKAGI,* Kazue MOCHIZUKI, Yoshifumi AOKI, and Hideki SHIRAKAWA*
Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305

(Received May 24, 1993)

Novel homogeneous catalyst system of composed tetraethoxytitanium–trimethylaluminum, $Ti(OEt)_4$–$AlMe_3$, is employed for synthesis of polyacetylene film. It is confirmed that the present system has a high catalytic activity for acetylene polymerization, and its activity is comparable to that of the representative Ti(O-*n*-Bu)$_4$–$AlEt_3$ catalyst system. Experimental conditions, especially for preparation and aging of the catalyst, are optimized in view of properties of polyacetylene film such as *cis* content, mechanical stretchability, and electrical conductivity. The homogeneity of the present catalyst aged at room temperature enables us to synthesize highly conductive non-stretched and stretched films whose electrical conductivities after iodine doping are 2.0×10^3 and 1.2×10^4 S cm^{-1}, respectively. Discussion has also been made in terms of the effect of high-temperature aging for the catalyst, the role of co-catalyst as a reductant, and the dependence of electrical conductivity on film thickness.

Tetrabutoxytitanium and triethylaluminum system, Ti(O-*n*-Bu)$_4$–$AlEt_3$, is a representative Ziegler–Natta catalyst and has been exclusively employed for synthesis of polyacetylene films owing to its profound solubility and homogeneity.[1,2] Since the high-temperature aging of the Ti(O-*n*-Bu)$_4$–$AlEt_3$ catalyst was found to give highly stretchable and highly conductive polyacetylene film with an order of 10^4—10^5 S cm^{-1},[3—6] it has been an urgent subject to elucidate an effect of the aging at various temperatures on the formation of catalytically active species and their structural changes.[7—10] However, due to an inherent complexity and instability of the catalytic species constructed with titanium and aluminum compounds,[11—13] crucial determination of the catalyst structure has not been put forward.

In order to make it easier to analyze the catalyst from aspects of both spectroscopic characterization and catalytic activity in the acetylene polymerization, we focused on a proto-type catalyst composed of tetraethoxytitanium and trimethylaluminum, $Ti(OEt)_4$–$AlMe_3$. Note that the tetramethoxytitanium, $Ti(OMe)_4$, is insoluble in organic solvent and hence can not be used as soluble and homogeneous catalyst that is prerequisite for synthesis of polyacetylene in a form of film.

Recent ESR studies[9,10] show that the $Ti(OEt)_4$–$AlMe_3$ catalyst gives a singular Ti^{3+} complex in the room-temperature aging, indicating a homogeneity of the catalyst at room temperature. While at higher temperature (80 °C) it becomes inhomogeneous with a drastic decrease of spin concentration of Ti^{3+} species. This is in quite contrast to the case of the Ti(O-*n*-Bu)$_4$–$AlEt_3$ catalyst system, in which there are three distinct signals due to the Ti^{3+} species even in the room-temperature aging; Whereas at the higher temperature of 150—200 °C a very broad and asymmetric signal is observed, suggesting a formation of bulky molecular aggregates of Ti^{3+} complex. Nowadays it may be allowed to assume that a trivalent titanium (Ti^{3+}) complex, detectable by ESR owing to its paramagnetic nature, is a catalytically active species for acetylene polymerization.[11—13] One can therefore anticipate that the $Ti(OEt)_4$–$AlMe_3$ catalyst would produce a high quality polyacetylene film by virtue of its catalytic homogeneity, when it is prepared under usual conditions such as the aging at room temperature followed by the polymerization at −78 °C. In the present study, we will systematically optimize experimental conditions for the preparation and aging of the $Ti(OEt)_4$–$AlMe_3$ catalyst. Through this, we will cultivate the present catalyst as a potential candidate for novel Ziegler–Natta catalyst available for acetylene polymerization.

Experimental

Acetylene gas of six-nine grade and trimethylaluminum, $AlMe_3$, were used without further purification. Tetraethyoxytitanium, $Ti(OEt)_4$, and hexane, toluene, and cumene, diglyme used as polymerization solvents were distilled under argon gas before use. Concentration of the catalyst was 0.1—0.5 mol dm^{-3} of $Ti(OEt)_4$, and the titanium/aluminum molar ratio, Al/Ti, was 0.1—4.0. A Schlenk flask containing the aged catalyst solution was connected to a vacuum line through a flexible joint. The solvent in the flask was dynamically pumped off with keeping the flask horizontal and simultaneously rotating it, until solvent was completely evaporated (practically below 0.01 Torr, 1 Torr = 133.322 Pa). This procedure, called *solvent evacuation method*,[4] gives rise to a catalyst layer homogeneously coated over the inner glass wall of the flask. At this stage, the concentration of the catalyst is increased by 2—3 times compared with the initial concentration before the evaporation of solvent, and hence the catalyst becomes viscous enough not to be flowed down along the glass wall of the flask. Polymerization was carried out at −78 °C by introducing acetylene gas onto the catalyst. Initial acetylene pressure was 680—750 Torr, and polymerization time of 1—20 h. After the polymerization, polyacetylene film was washed several times with toluene cooled by dry ice–ethanol solution (−78 °C) under argon gas.

[#] This paper is dedicated to the late Professor Hiroshi Kato.

The chemical doping of polyacetylene film was carried out by exposing the film to vapor of iodine at room temperature. Electrical conductivities of iodine-doped non-stretched and mechanically stretched films were measured using the four-probe method, as a function of doping time. For the stretched film, the conductivity parallel to an elongation direction was only focused. Hereafter, the conductivity means electrical conductivity of iodine-doped film, but not that of non-doped as-grown film, unless otherwise stated.

Results and Discussion

1. Preparation and Aging of Catalyst. Table 1 shows effects of aging condition of catalyst on both yield and properties of polyacetylene film. As properties of films, *cis* content, mechanical stretchability, and conductivities before and after stretching are examined. It is found that the optimum condition for preparation is to mix $Ti(OEt)_4$ with $AlME_3$ in hexane at −78 °C (dry ice–ethanol) and to age the catalyst solution at room temperature for 1 h.

On the other hand, the preparation (mixing and aging) of catalyst at −78 °C produces a less amount of catalytically active Ti^{3+} species, resulting in low yield of polyacetylene. However, the preparation at room temperature accelerates the aging itself owing to both exothermal heat and extremely high reactivity of the cocatalyst of $AlMe_3$. This should reduce the Ti^{3+} species into catalytically inactive Ti^{2+} and/or Ti^{1+} species. As a result, such a preparation also gives low yield of polyacetylene.

2. Al/Ti Ratio. Figure 1 shows changes of yield and *cis* content of polyacetylene film as a function of Al/Ti ratio that is a molar ratio between $Ti(OEt)_4$ and $AlMe_3$. The favorable Al/Ti ratio is in the range of 2—3, and especially the ratio of 2.5 gives the highest yield. Although the catalysts with the Al/Ti ratio of 1.5 and 4 provide free-standing films, they are nonstretchable. These results are also summarized in Table 2. It is well known that in the $Ti(O\text{-}n\text{-}Bu)_4$–$AlEt_3$ catalyst, the optimum Al/Ti ratios for the room-temperature[1,2] and high-temperature[3—6] agings are 3—4 and 2, respectively. The optimum Al/Ti ratio of 2—3 in the room-temperature aged $Ti(OEt)_4$–$AlMe_3$ catalyst is smaller than the corresponding value (3—4) in the $Ti(O\text{-}n\text{-}Bu)_4$–$AlEt_3$ catalyst. This is probably due to the stronger reducing power of $AlMe_3$. That is, the titanium compound (Ti^{4+}) is more easily reduced into catalytically active Ti^{3+} species by $AlMe_3$ than $AlEt_3$, provided that $Ti(OEt)_4$ and $Ti(O\text{-}n\text{-}Bu)_4$ have the same tendency for the reduction towards the cocatalytic AlR_3 compound.

Note that the film synthesized with the Al/Ti of 1.5 shows unexpectedly high electrical conductivity, which may be due to the thin film. The relationship between film thickness and conductivity will be discussed later.

3. Aging Temperature. In the $Ti(O\text{-}n\text{-}Bu)_4$–$AlEt_3$ catalyst, the aging of the catalyst at high temperature such as 120—200 °C is an essential factor to synthesize highly strechable and hence highly conductive polyacetylene films.[3—6] Here we examined effect of the high-temperature aging in the $Ti(OEt)_4$–$AlMe_3$ catalyst, by changing the aging temperature from 25 to 100 °C. It should be noted that the aging temperature was restricted below 100 °C because of the low boiling point of $AlMe_3$ (125.4 °C/760 mmHg, 1 mmHg=133.322 Pa) and its inclination to ignite easily in the atmosphere.

Figure 2 shows the results of polymer yield and *cis* content, as a function of aging temperature.

The yield drastically decreases above the temperature of 40 °C, although the *cis* content remains unchanged. Besides, the polyacetylene film synthesized with the catalyst aged at 80—100 °C shows no mechanical stretchability, which is different from the case (ca. 2.5 times stretchability) of lower-temperature aging (r. t. to 60 °C). These results indicate that the high-temperature aging is not effective to the present $Ti(OEt)_4$–$AlMe_3$ catalyst, in contrast to the $Ti(O\text{-}n\text{-}Bu)_4$–$AlEt_3$ catalyst, although both of them are composed of tetraalkoxytitanium and trialkylaluminum compounds, $Ti(OR)_4$–AlR'_3. In fact, the previous ESR results showed that the $Ti(OEt)_4$–$AlMe_3$ catalyst exhibits a single signal due to Ti^{3+} species at the room-temperature aging, but that it gives three complex signals at the temperature higher than 40 °C.[8,9] Although the spin density due to the Ti^{3+} species remains almost constant until the aging temperature of 60 °C, it decreases by one third at the higher-temperature (80 °C) aging. These ESR spectral changes well account for the above mentioned experimental results shown in Fig. 2 and Table 3.

4. Aging Time at Room Temperature. In the previous section, we confirmed that the high-temperature aging in the $Ti(OEt)_4$–$AlMe_3$ catalyst decreases the catalytic activity and therefore the room-temperature aging is rather more suitable for the synthesis of high-quality polyacetylene film. Then, we examined the optimum aging time for the room-temperature aging. Figures 3 and 4 show changes of the polymer yield and electrical conductivity of the film, respectively, as a function of aging time from 30 min to 48 h. The polymer yield increases notably with increasing of the aging time till 10 h and then it gradually decreases. However, the conductivities of non-stretched and three-times stretched films gradually decrease with increasing of the aging time. On the other hand, notable change was found in neither *cis* content nor mechanical stretchability. When the properties of the film are primarily concerned rather than the polymer yield, the aging time for 1 h is enough in the room temperature aging.

5. Concentration of Titanium Catalyst. We examined effect of the concentration of titanium catalyst on the catalytic activity and resultant polyacetylene film. The initial titanium concentration, [Ti], was changed from 0.05 to 0.5 mol dm^{-3}, keeping other experimental conditions constant, i. e., Al/Ti=2.5, poly-

Table 1. Effect of Aging Condition of Catalyst on Both Yield and Properties of Polyacetylene Films[a]

Mixing temp	Aging condition	Relative yield g/mmol Ti	*cis* Content %	Stretching ratio l/l_0	Conductivity[b] S cm^{-1}
−78°C	−78°C, 1 h	0.071	95.3	—[c]	1010
−78°C	r. t., 1 h	0.198	92.7	3—3.5	1980 [12000]
r. t.	r. t., 1 h	0.015	76.2	ca. 2	1790 [8710]

a) Polymerization condition: −78 °C, 20 h, Al/Ti=2, [Ti]=0.3 mol dm^{-3}, Solvent: hexane. b) Conductivities of stretched samples with the maximum draw ratio are shown in square parentheses. c) Unstrechable.

Table 2. Effect of Aluminum–Titanium Ratio on Both Yield and Properties of Polyacetylene Films[a]

Al/Ti	Relative yield g/mmol Ti	*cis* Content %	Stretching ratio l/l_0	Conductivity[b] S cm^{-1}
1				—[c]
1.5	0.095	73.2	—[d]	3900
2	0.198	92.7	3	2000 [12000]
2.5	0.391	92.0	3	2000 [9500]
3	0.081	93.1	3	2200 [13000]
4	0.039	78.7	—[d]	1100

a) Aging condition: r. t., 1 h. Polymerization condition: −78 °C, 20 h, [Ti]=0.3 mol dm^{-3}, Solvent: hexane. b) Conductivities of stretched samples with the maximum draw ratio are shown in square parentheses. c) No polymerized. d) Unstretchable.

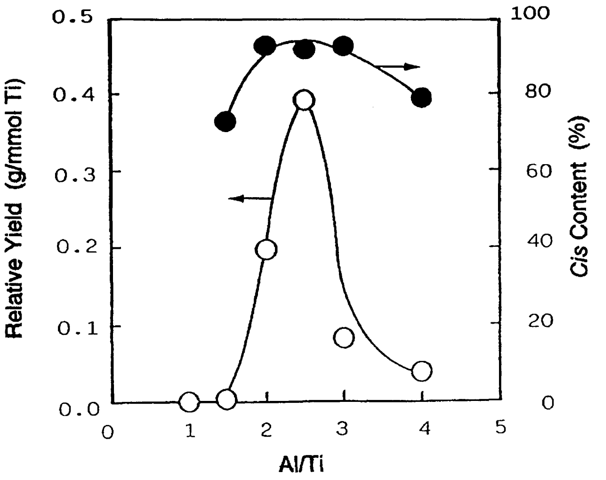


Fig. 1. Relative yield and *cis* content vs. aluminum–titanium ratio, Al/Ti. Polymerization conditions: −78 °C, 20 h. Solvent: hexane, [Ti]=0.3 mol dm^{-3}.

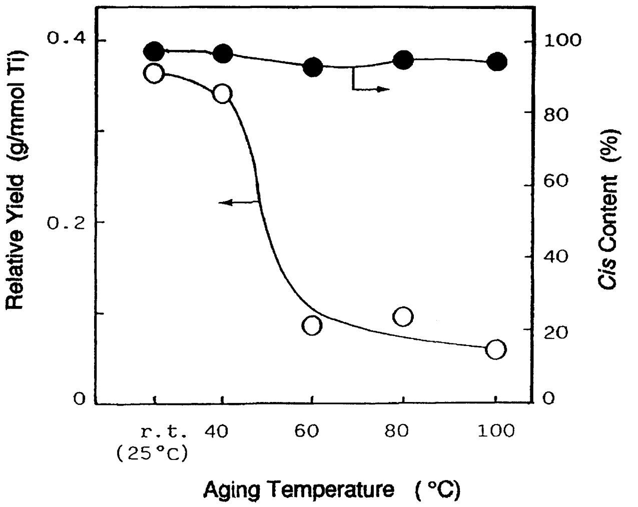


Fig. 2. Relative yield and *cis* content vs. aging temperature. Polymerization conditions: −78 °C, 20 h. Solvent: cumene, [Ti]=0.3 mol dm^{-3}.

merization at −78 °C for 1 h. and so on. In the case of [Ti]=0.05 mol dm^{-3}, the polymerization was carried out for 20 h, since the polymerization time of 1 h gave no sufficient amount of film. The results are summarized in Table 4.

As mentioned in the experimental section, the present polymerization is based on the *solvent evacuation method*, where the polymerization solvent such as hexane is completely evacuated by the dynamic pumping before the introduction of acetylene gas into the polymerization Schlenk flask. However, each titanium concentration after the solvent evacuation is 2.2 mol dm^{-3} even if the initial catalyst solution has different concentration, so far as Al/Ti ratio is kept to be 2.5. Nevertheless, as shown in Fig. 5, the polymer yield, *cis* content, and mechanical stretchability depend on the initial titanium concentration in preparing the catalyst. As a consequence, the initial titanium concentration of [Ti]=0.3 mol dm^{-3} is favored. This result suggests that

Table 3. Effect of Thermal Aging on Both Yield and Properties of Polyacetylene Films[a)]

Aging Temp	Relative yield g/mmol Ti	*cis* Content %	Stretching ratio l/l_0	Conductivity[b)] S cm^{-1}
40°C	0.341	97.1	2.5	2300 [9630]
60°C	0.085	93.1	2.5	2750 [12100]
80°C	0.096	94.8	—[c)]	823
100°C	0.058	94.3	—[c)]	1430
r. t. (25°C)	0.365	96.8	3	1740 [9130]

a) Polymerization condition: −78 °C, 20 h, Al/Ti=2.5, [Ti]=0.3, mol dm^{-3}, Solvent: cumene. b) Conductivities of stretched samples with the maximum draw ratio are shown in square parentheses. c) Unstretchable.

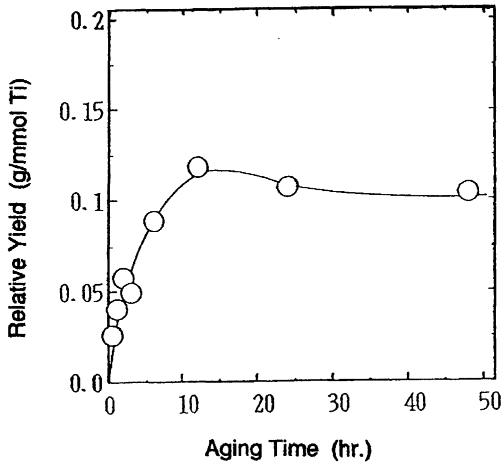


Fig. 3. Relative yield vs. aging time at room temperature. Polymerization conditions: −78 °C, 1 h. Solvent: hexane, Al/Ti=2.5, [Ti]=0.3 mol dm^{-3}.

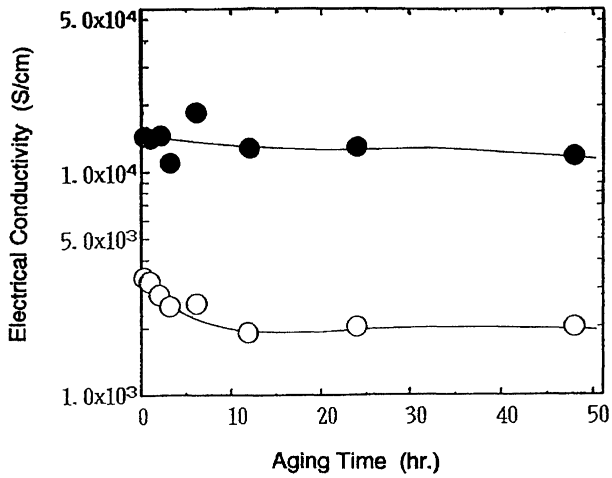


Fig. 4. Electrical conductivity of iodine-doped film vs. aging time at room temperature. Polymerization conditions: −78 °C, 1 h., Solvent: hexane, Al/Ti= 2.5, [Ti]=0.3 mol dm^{-3}. Open and closed circles in the figure indicate non-stretched and about three-times stretched films, respectively.

the initial titanium concentration largely affects a complexation between $Ti(OEt)_4$ and $AlMe_3$ and also an aging process of the catalytic complexes, enough to govern the properties of resultant polyacetylene film.

6. Solvent of Catalyst. As a solvent of the $Ti(O\text{-}n\text{-}Bu)_4$–$AlEt_3$ catalyst, hexane and toluene are usually used for the room-temperature aging, while cumene (isopropylbenzene), pentylbenzene, decalin, and tetradecane are used for the high-temperature aging. In the $Ti(OEt)_4$–$AlMe_3$ catalyst, hexane is employed since the room-temperature aging is more promising than the high-temperature aging and the solvent with low boiling point can be easily evacuated through the dynamic pumping. Here we examined three kinds of solvents, hexane, cumene, and diglyme (1,2-dimethoxyethane), that are representative aliphatic hydrocarbon, aromatic hydrocarbon, and aliphatic ether compounds, respectively. The result is shown in Table 5. Although no distinct difference is observed among these solvents in terms of polymer yield and *cis* content, the stretchability of the film synthesized by using diglyme is inferior to those by other solvents. In practice, the catalyst solution prepared with hexane or cumene shows dark brown color, as usually seen in the $Ti(O\text{-}n\text{-}Bu)_4$–$AlMe_3$ catalyst in toluene solvent. The polyacetylene films synthesized by these catalysts exhibit metallic luster. On the other hand, the catalyst solution with diglyme shows greenish black and the polyacetylene using by this catalyst exhibits dark gray or black color but not metallic luster. These results imply that the catalyst prepared with diglyme produces a polyacetylene with lower molecular weight and/or shorter conjugation length and hence less mechanical stretchability, compared with the case of hexane and cumene solvents. Such a relatively low activity of the catalyst in diglyme may be attributed to an existence of lone pair electrons of ether-type oxygen in diglyme. The diglyme molecule would coordinate to the titanium compound through an electrostatic interaction between the lone pair electrons and positively charged Ti^{4+} nucleus in $Ti(OEt)_4$. Thus generated associated complex between diglyme and titanium compounds should make it difficult for an alu-

Table 4. Effect of Titanium Concentration on Both Yield and Properties of Polyacetylene Films[a)]

[Ti]	Relative yield	*cis* Content	Stretching ratio	Conductivity[b)]
mol	g/mmol Ti	%	l/l_0	S cm^{-1}
0.05[c)]	0.620	97.4	1.5	2590 [10300]
0.1	0.075	94.8	1.5	4370 [4370]
0.3	0.133	94.3	3	1850 [11900]
0.5	0.025	74.3	1.5	1870 [3930]

a) Aging condition: r. t., 1 h. Al/Ti=2.5, Solvent: hexane. b) Conductivities of stretched samples with the maximum draw ratio are shown in square parentheses. c) This sample was polymerized for 20 h; others were for 1 h.

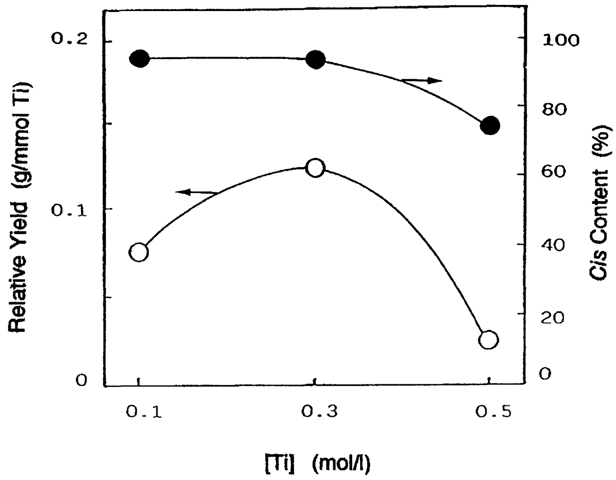


Fig. 5. Relative yield and *cis* content vs. initial titanium concentration. Polymerization conditions: −78 °C, 1 h. Solvent: hexane, Al/Ti=2.5, Aging condition: r. t. for 1 h.

minum molecule to approach the titanium molecule. This leads to a less amount of catalytic complexes between titanium and aluminum compounds. The suppress of the formation of Ti–Al complexes may be one of the reasons for the unusual results encountered in the usage of diglyme solvent.

Discussion

Through the present experiments, the optimum condition for synthesis of polyacetylene film by using the Ti(OEt)$_4$–AlMe$_3$ catalyst is as follows; (1) the catalyst is prepared at −78 °C so that the Al/Ti mole ratio is 2—3 and the initial titanium concentration, [Ti], is 0.3 mol dm^{-3}, (2) the catalyst is aged at room temperature for 1 h, (3) the polymerization is carried out at −78 °C for 1 h. The polyacetylene film synthesized under the optimum condition shows a three times mechanical stretchability, high *cis* content of more than 90%, high bulk density of 0.9—1.1 g cm^{-3}, and high electrical conductivities of 10^3 S cm^{-1} order in non-stretched film and 10^4 S cm^{-1} order in stretched film. The two of the above mentioned properties, i. e., *cis* content and electrical conductivity, are characteristics of polyacetylene films synthesized by using AlMe$_3$ as a co-catalyst.

Table 6 shows properties of polyacetylene films synthesized by several kinds of catalyst systems. Each catalyst is prepared under its optimum condition for the room-temperature aging. It is evident the trimethylaluminum, AlMe$_3$, is more feasible co-catalyst than the triethylaluminum, AlEt$_3$, as far as the room-temperature aged catalyst combined with the Ti(OEt)$_4$ or Ti(O-*n*-Bu)$_4$ is concerned. In fact, high conductivities of non-streched (2.0×10^3 S cm^{-1}) and three-times streched films (1.2×10^4 S cm^{-1}) are worthy to note, since these values are comparable to those of films synthesized by the high-temperature aged Ti(O-*n*-Bu)$_4$–AlEt$_3$ catalyst.

It is of keen interest to emphasize that the electrical conductivity of iodine-doped non-stretched film depends on the film thickness, as shown in Fig. 6. Actually, even non-stretched film shows a conductivity of more than 8.0×10^3 S cm^{-1} when it is less than 1.0 μm in thickness. Similar results have been observed in polyacetylene films synthesized by the Ti(O-*n*-Bu)$_4$–AlEt$_3$ catalyst, irrespective of the polymerization method.[10,14)] Polyacetylene film is known to have a randomly oriented fibrillar morphology. But as the film becomes thinner, the fibrillar morphology is suppressed to generate an in-plane alignment of fibrils. Such an in-plane alignment is confirmed to affect the electrical conductivity, as well as mechanically forced fibrillar alignment parallel to the stretching direction.[15)] The experimentally derived relationship shows that the electrical conductivity (σ) is proportional to an inverse of film thickness (d), i. e., $\sigma=a\cdot d^{-1}+\sigma_0$. Here a is the proportional constant, and σ_0 is the independent term of the conductivity on the film thickness which corresponds to the conductivity of film with a randomly oriented fibrillar morphology. In the present case, the upper limit of film thickness is about 20 μm, over which the film shows totally no in-plane alignment. Such an existence of upper limit of film thickness may be attributed to a so-called interfacial polymerization of acetylene in which free growth of polyne chains in an ambient direction is restricted; When the polymerization occurs in a limited thickness of catalyst layer, free growth of polyene chains and hence that of fibrils in three dimensional direction should be suppressed. One can imagine that the poly-

Table 5. Effect of Solvent on Both Yield and Properties of Polyacetylene Films[a)]

Solvent	Relative yield	*cis* Content	Stretching ratio	Conductivity[b)]
	g/mmol Ti	%	l/l_0	S cm^{-1}
Cumene	0.365	96.8	ca. 3	1740 [9130]
Diglyme	0.398	97.1	ca. 1.2	1310
Hexane	0.391	92.0	ca. 3	1490 [9460]

a) Aging condition: r. t., 1 h. Polymerization condition: −78 °C, 20 h, Al/Ti=2.5, [Ti]=0.3 mol dm^{-3}. b) Conductivities of stretched samples with the maximum draw ratio are shown in square parentheses.

Table 6. Comparison of Conductivity and Stretchability of Polyacetylene Films Synthesized by Several Kinds of Catalyst Systems, $Ti(OR)_4$–AR'_3.

$Ti(OR)_4$–AR'_3		Conductivity (S cm^{-1})		Mechanical
OR	R′	Non-stretched	Stretched	stretchability (%)
OEt	Me	2.0×10^3	1.2×10^4	2—3[a)]
O-*n*-Bu	Me	1.1×10^3	1.4×10^4	3[a)]
OEt	Et	1.0×10^3	8.5×10^3	3[b)]
O-*n*-Bu	Et	5.5×10^2	1.5×10^3	2—3[c)]

a) Al/Ti=2, [Ti]=0.3 mol dm^{-3}; Aged at r. t. for 1 h., b) Al/Ti=2, [Ti]=1.0 mol dm^{-3}; Aged at r. t. for 1 h., c) Al/Ti=4, [Ti]=0.3 mol dm^{-3}; Aged at r. t. for 1 h.

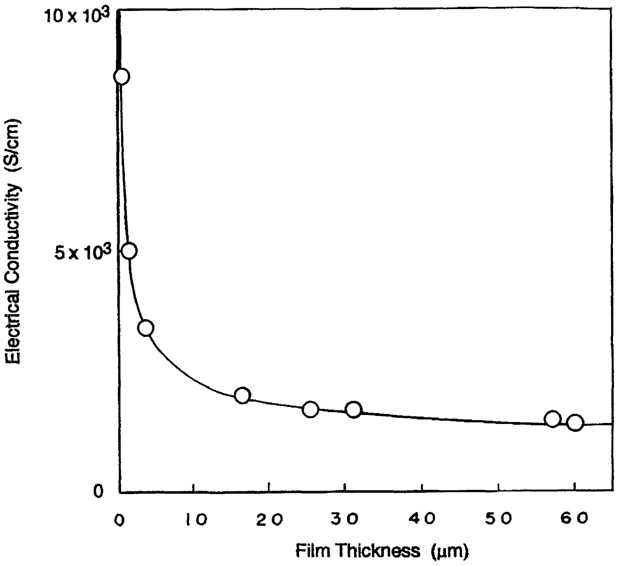
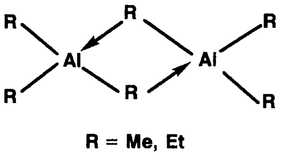


Fig. 6. Dependence of electrical conductivity of iodine-doped non-stretched film on film thickness. Polymerization conditions: −78 °C, 1 h. Solvent: hexane, Al/Ti=2.5, [Ti]=0.3 mol dm^{-3}.

merization would first occur on the surface of the catalyst solution. Then the polymerization proceeds into the inner part of the catalyst solution after the catalyst solution in the surface loses its activity. Thus thin film is formed near the surface of the catalyst solution at the initial stage of polymerization, since free growth of polyene chains is obstructed in thickness direction. Such restriction in polymerization field generates the in-plane alignment of polyacetylene film. However, when the polymerization is allowed to continue into the inner part of the catalyst solution, thick film with less in-plane alignment is formed owing to a weakening of interfacial effect. It follows that the above-mentioned upper limit of film thickness for the in-plane alignment may correspond to the region in which the interfacial polymerization becomes ineffective. In connection with this, it is worthwhile to note the following experimental results for polyacetylene films synthesized by the Ti(O-*n*-Bu)$_4$–$AlEt_3$ catalyst. Measurements of X-ray diffraction by irradiating X-ray beam into the lateral direction of a neat pile of as-grown films showed an arch with strong reflection in thickness direction. Such a diffraction pattern was still observed in the film of 20μm in thickness, and the thicker film gave a typical Debye–Sherrer ring in the diffraction photography.[16,17)]

Lastly we will focus on a role of trimethylaluminum used as a co-catalyst. It is known that trialkylaluminum, AlR_3, exists in a dimer, Al_2R_6, in which the electron-deficient and three-center bridging bonds are constructed (see, Scheme 1). One can expect that a triethylaluminum dimer, Al_2Et_6, is more stable than a trimethylaluminum dimer, Al_2Me_6, since the electron donating ability of ethyl group in Al_2Et_6 is stronger than that of methyl group in Al_2Me_6. This means that the Al_2Et_6 is less reactive to the titanium compound rather the Al_2Me_6, because the former is less easily dissociated into the monomer species owing to its superior stability than the latter. As a first step, the trialkylaluminum dimer has to be dissociated into monomer before a complexation with the titanium compound. It



Scheme 1.

follows that even a less amount of $AlMe_3$ can activate the titanium compound by reducing it into Ti^{3+} species at room temperature. The optimum Al/Ti ratio of 2—3 for the $Ti(OEt)_4$–$AlMe_3$ catalyst is smaller than that (3—4) for the Ti(O-*n*-Bu)$_4$–$AlEt_3$ catalyst. The result that the thermal treatment such as high-temperature aging deactivates the catalytic activity in the $Ti(OEt)_4$–$AlMe_3$ system is also accounted for by high reactivity and strong reducing power of $AlMe_3$. In other words, an exothermal heat occurring in the preparation and aging of the catalyst might give a sufficient aging effect even at room temperature.

Conclusion

The $Ti(OEt)_4$–$AlMe_3$ catalyst system is capable of producing highly conductive polyacetylene films under usual conditions such as the aging at room temperature for 1 h followed by the polymerization at −78 °C. The application of the higher temperature aging, however, leads to a notable decrease in catalytic activity, resulting in a lowering of mechanical and electrical properties of the films. These results are in marked contrast to those in the Ti(O-*n*-Bu)$_4$–$AlEt_3$ catalyst, although both catalysts are of the same type structure described by a general form as $Ti(OR)_4$–AlR'_3. Taking account of the present results as well as the previous ESR ones, it can be concluded that the homogeneity of the catalyst, characterized by singular catalytic active species, is essential in synthesizing high quality polyacetylene film.

The present work was supported by Grant-in-Aids for Scientific Research from Ministry of Education, Science and Culture, and TEPCO Research Foundation of Japan.

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