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Novel liquid-crystalline titanocene complexes with catalytic activity for polymerizations of acetylene and phenylacetylene

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We have synthesized a series of novel titanocene complexes with liquid-crystalline (LC) groups as coordination ligands, with the ultimate aim of developing LC catalytic species available for anisotropic polymerizations of acetylenes. The titanocene complexes were prepared by introducing LC groups into cyclopentadienyl ligands as substituents, $(PCH506Cp)_2TiCl_2$ (**1**), or coordinating them to a titanium atom as symmetric and asymmetric ligands, $Cp_2Ti(PCH5060)_2$ (**2**) and $Cp_2Ti(PCH5060)Cl$ (**3**) [where Cp = cyclopentadienyl, PCH506 = *p*-(*trans*-4-n-pentylcyclohexyl)phenoxyhexyl and PCH5060 = *p*-(*trans*-4-n-pentylcyclohexyl)phenoxyhexyloxy]. Polarizing optical microscope observations and differential scanning calorimetry measurements indicated that the titanocene complexes **2** and **3** are the first titanium complexes exhibiting LC behaviour. It is found that the titanocene complexes **1** and **2** can polymerize phenylacetylenes to give poly(phenylacetylene)s with the aid of triethylaluminium (Et_3Al) as cocatalyst. The molecular weights and degrees of polymerization of the poly(phenylacetylene)s prepared were comparable or superior to those prepared with titanocene dichloride and tetra-n-butoxytitanium [$Ti(O\text{-}n\text{-}Bu)_4$] catalysts. The LC titanocene complexes **2** and **3** were also confirmed to have catalytic activities for the polymerization of acetylene. Electron spin resonance spectra of the catalyst systems gave signals of trivalent titanium (Ti^{3+}) with no hyperfine structure, suggesting that the catalytically active species is a mononuclear complex consisting of Ti^{3+} rather than a binuclear or trinuclear one. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: titanocene complex; liquid crystalline ligand; catalytic activity)

INTRODUCTION

Macroscopic alignment of conjugated polymer chains is responsible for high electrical conductivity and significant electrical anisotropy. Several methods have been established to align conducting polymers, i.e. mechanical stretching of polymer films endowed with profound Young's modulus and tensile strength[1], anisotropic polymerization field by using a liquid crystal as solvent[2], and the introduction of liquid-crystalline (LC) substituents into the side chain[3].

Transition metal complexes with LC ligands are known as metallomesogens. They have the potential to be used for display devices, anisotropic polymerization catalysts and advanced materials exhibiting peculiar physicochemical properties such as mixed-valence metal complexes. Among them, the titanium complex with liquid crystallinity has not been reported so far, mainly because of its extreme instability in air and moisture. However, such instability of the titanium complex implicitly suggests its activity as a catalyst for some polymerizations. It is anticipated that an LC titanium complex would serve as an anisotropic polymerization catalyst for acetylene. This is because it is spontaneously oriented and also macroscopically aligned to generate an anisotropic reaction field under external forces such as shear stress, electric and magnetic force fields, as in the case of ordinary LC molecules. Recently, we briefly reported the preparation of LC titanocene complexes **1** and **2** and their catalytic activities for the polymerizations of acetylene and mono-substituted acetylene derivatives[4].

The purpose of this study is to synthesize a series of novel LC titanocene complexes to be used as anisotropic polymerization catalysts. As a primary step, we examined their catalytic activities for polymerizations of acetylene and phenylacetylene.

EXPERIMENTAL

General

All procedures were performed under an argon atmosphere by using the Schlenk technique and glove-box treatment. Particular attention was paid to exclude oxygen and moisture. Tetrahydrofuran and n-hexane were dried over calcium hydride, and toluene was dried over sodium. These solvents were distilled prior to use. Titanium(IV) chloride was available commercially and distilled under vacuum before use. Triethylamine was dried over barium oxide. Sodium cyclopentadienylide, titanocene dichloride and chloroform-*d* were used as purchased. Phenylacetylene was used as purchased without further purification. Acetylene gas of six-nine grade and Et_3Al were used without further purification.

Scheme 1 and *Scheme 2* show the synthetic routes for the precursors, PCH506Br, PCH506Cp and PCH5060H, and the complexes **1**, **2** and **3**. The phase transition behaviour of these complexes was measured by means of a Nikon polarizing optical microscope equipped with a Linkam

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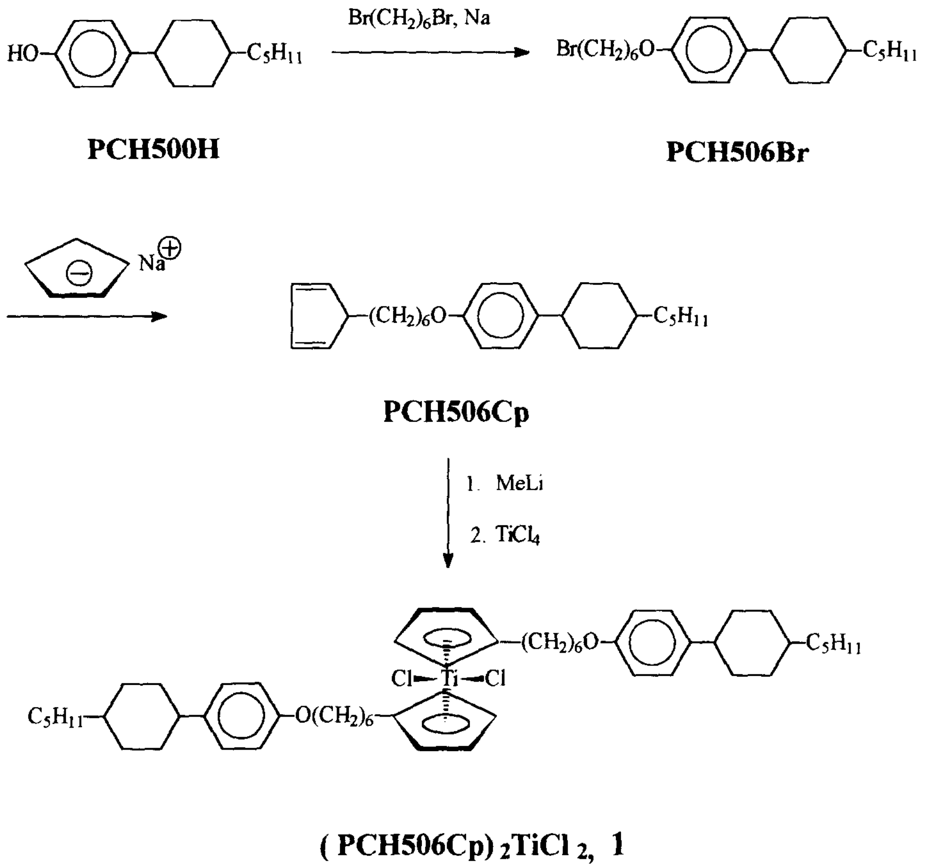
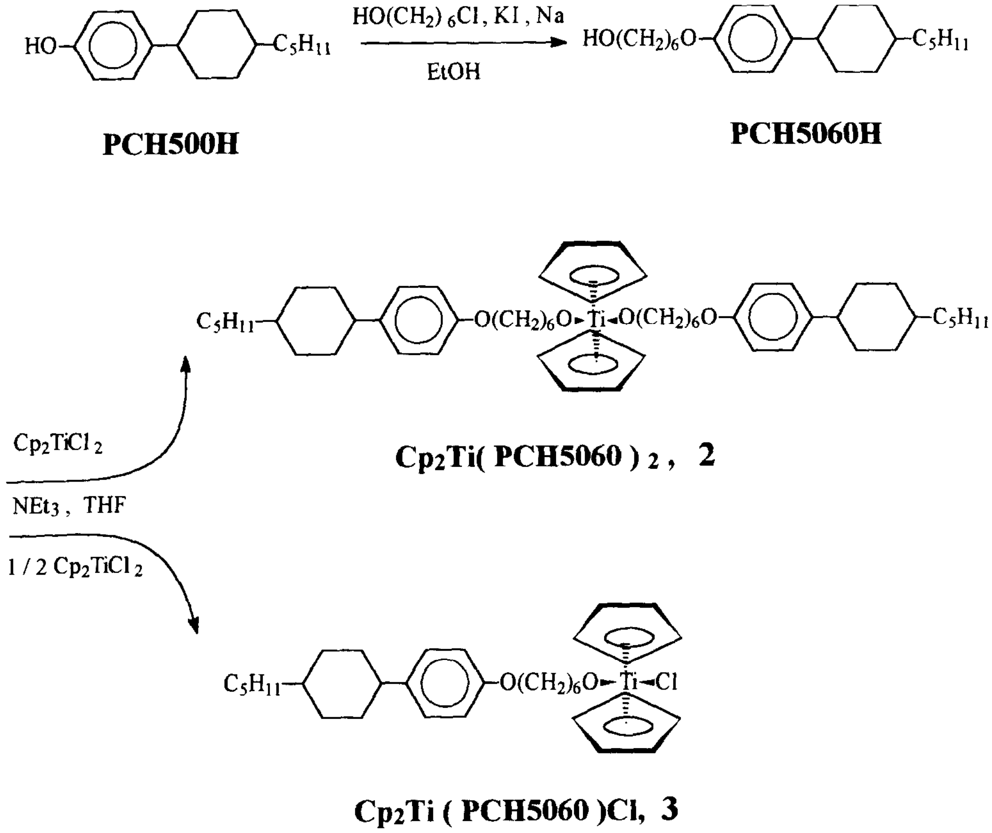


Scheme 1



Scheme 2

THMS 600 hot-stage and controller. Thermal transition characteristics were determined with a Perkin–Elmer differential scanning calorimeter (DSC 7) at a rate of 10°C min^{-1} under argon atmosphere. Room-temperature electron spin resonance (e.s.r.) spectra were measured on solution samples with a JES-TE200 ESR spectrometer. Throughout the measurements we adopted the following spectroscopic conditions: microwave frequency 9.230 ± 0.005 GHz (X band), central magnetic field 335 mT, swift range 15 mT, magnetic modulation frequency 100 kHz, width 1 mT, magnetic swift time 30 s, time constant 0.03 s and amplitude 200.

1-[p-(trans-4-Pentylcyclohexyl)phenoxy]-6-bromohexane (PCH506Br)

Sodium metal (4.4 g, 0.19 mol) was added to 200 ml of ethanol in a flask at room temperature with stirring. Then *p*-(*trans*-4-pentylcyclohexyl)phenol (PCH500H) (37 g, 0.15 mol) was added to the solution and stirred at room temperature for 24 h. Subsequently, 1,6-dibromohexane (96 ml, 0.60 mol) was added slowly from a dropping funnel. The mixture was stirred with a magnetic stirrer at 60°C for 7 h, allowed to cool to room temperature and then an excess of water was added. The organic material was extracted into ether and the combined organic extracts were washed with water. The organic layer was collected and the solvent was removed under reduced pressure. The crude product was recrystallized from ethanol and dried *in vacuo* to give a white powder. Yield: 58 g, 94%.

Infra-red (i.r.) ν (cm^{-1}): 3039 (w), 2955 (s), 2919 (s), 2847 (s), 1613 (m), 1581 (m), 1515 (s), 1469 (s), 1447 (m), 1390 (w), 1304 (m), 1282 (m), 1246 (s), 1180 (s), 1111 (m), 1075 (m), 966 (m), 836 (s), 812 (s), 722 (w), 624 (w), 565 (m), 541 (s).

Elemental analysis—calc. for $C_{23}H_{37}OBr$: C 67.47, H 9.11, Br 19.51; found: C 68.94, H 9.62, Br 16.62.

6-[p-(trans-4-Pentylcyclohexyl)phenoxy]-hexylcyclopentadiene (PCH506Cp)

PCH506Br (41 g, 0.10 mol) was added to 200 ml of tetrahydrofuran in a flask with stirring and then sodium cyclopentadienylide (50 ml, 0.10 mol) was added slowly from a dropping funnel at room temperature. The mixture was stirred at room temperature for 30 min and then at 60°C for 20 h. It was allowed to cool to room temperature and then an excess of water was added. The organic material was extracted into ether and the combined organic extracts were washed with water. The organic layer was collected and the solvent was removed under reduced pressure. The crude product was recrystallized from a mixture of tetrahydrofuran and methanol (tetrahydrofuran:methanol = 1:5) and dried *in vacuo* to give a milky white powder. Yield 22 g, 55%.

I.r. ν (cm^{-1}): 3091 (w), 3045 (m), 2921 (s), 2850 (s), 1702 (w), 1610 (s), 1581 (w), 1513 (s), 1466 (s), 1444 (s), 1378 (m), 1286 (m), 1247 (s), 1178 (s), 1114 (m), 1068 (w), 1032 (s), 969 (m), 896 (m), 836 (s), 809 (s), 766 (m), 725 (m), 684 (w), 638 (w), 541 (s).

Elemental analysis—calc. for $C_{28}H_{41}O$: C 85.21, H 10.73; found: C 84.62, H 10.74.

6-[p-(trans-4-Pentylcyclohexyl)phenoxy]-1-hexanol (PCH5060H)

Sodium metal (3.0 g, 0.13 mol) was added to 400 ml of ethanol in a flask at room temperature with stirring. Next PCH500H (26 g, 0.10 mol) was added to the solution and then 6-chlorohexanol (28 ml, 0.20 mol) and potassium iodide (1.7 g, 10 mmole). The mixture was refluxed for 36 h with stirring, allowed to cool to room temperature and then evaporated to dryness to remove the excess of ethanol. The organic material was extracted into ether and the combined organic extracts were washed with water. The organic layer was collected and the solvent was removed under reduced pressure. The crude product was recrystallized from n-hexane and dried *in vacuo* to give white needle crystals. Yield 14 g, 40%.

I.r. ν (cm^{-1}): 3367 (m), 3033 (w), 2916 (s), 2849 (s), 1612 (m), 1581 (w), 1513 (s), 1466 (m), 1446 (m), 1394 (m), 1246 (s), 1109 (w), 1026 (s), 914 (w), 824 (s), 808 (s), 725 (w), 624 (w), 542 (s).

Elemental analysis—calc. for $C_{23}H_{38}O_2$: C 79.71, H 11.05; found: C 79.76, H 10.87.

(PCH506Cp)$_2$TiCl$_2$ (**1**)

PCH506Cp (9.8 g, 25 mmol) dissolved in 100 ml of n-hexane was added slowly to 18 ml of a 1.4 M (25 mmol) solution of methyllithium in ether at room temperature with stirring, yielding a yellow solution with a white precipitate. To this suspension were added, with stirring, titanium(IV) chloride (2.4 ml, 13 mmol) and 50 ml of n-hexane. During the stirring for 8 h, 250 ml of toluene was supplemented. After continuous stirring for 48 h, the solution was filtered off and the solvent of the filtrate was evacuated under reduced pressure. A brown solid was produced after freeze-drying. Yield 10.6 g, 47%.

I.r. ν (cm^{-1}): 3104 (w), 2917 (s), 2846 (s), 1616 (m), 1513 (m), 1471 (m), 1255 (s), 1184 (m), 1033 (w), 833 (m), 820 (m).

Elemental analysis—calc. for $C_{56}H_{82}O_2Cl_2Ti$: C 74.24, H 9.12, Cl 7.83; found: C 67.52, H 8.81, Cl 8.91.

Cp$_2$Ti(PCH5060)$_2$ (**2**)

PCH5060H (1.9 g, 5.6 mmol) and titanocene dichloride (0.70 g, 2.8 mmol) dissolved in 50 ml of tetrahydrofuran were added to triethylamine (1.0 ml, 7.1 mmol) with stirring, yielding an yellowish orange solution with a white precipitate. After stirring at room temperature for 4 h, the solution was filtered off and the solvent of the filtrate was evacuated under reduced pressure to give an orange solid. Yield 2.1 g, 85%.

I.r. ν (cm^{-1}): 3367 (m), 3100 (w), 2917 (s), 2849 (s), 1611 (m), 1581 (w), 1513 (s), 1475 (m), 1445 (m), 1394 (w), 1247 (s), 1176 (m), 1061 (m), 1014 (m), 833 (s), 807(s), 727 (m), 624 (w), 593 (w), 544 (m).

Elemental analysis—calc. for $C_{56}H_{84}O_4Ti$: C 77.39, H 9.74; found: C 72.82, H 9.20.

Cp$_2$Ti(PCH5060)Cl (**3**)

PCH5060H (0.59 g, 1.7 mmol) and titanocene dichloride (0.43 g, 1.7 mmol) dissolved in 50 ml of tetrahydrofuran were added to triethylamine (0.3 ml, 2.14 mmol) with stirring, yielding an yellowish orange solution with a white precipitate. After stirring at 60°C for 24 h, the solution was filtered off and the solvent of the filtrate was evacuated under reduced pressure to give an yellowish orange solid. Yield 0.72 g, 76%.

I.r. ν (cm^{-1}): 3367 (w), 3100 (w), 2922 (s), 2852 (s), 1611 (m), 1511 (s), 1447 (m), 1246 (s), 1177 (m), 1070 (s), 1025 (m), 806 (s), 637 (w), 585 (w), 549 (m).

Elemental analysis—calc. for $C_{33}H_{47}O_2ClTi$: C 70.90, H 8.50, Cl 6.30; found: C 66.91, H 8.69, Cl 3.45.

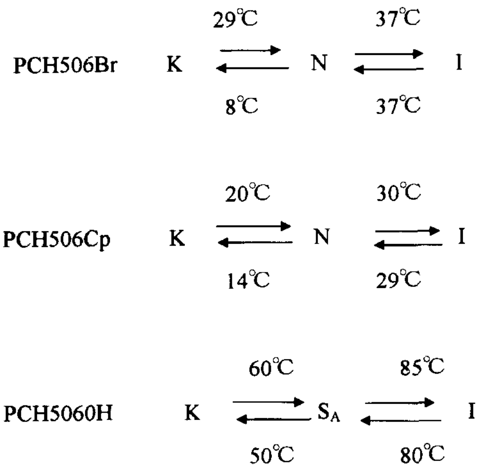
RESULTS AND DISCUSSION

Liquid crystallinity

The precursors, PCH506Br and PCH506Cp, showed nematic phases and the free ligand, PCH506OH, showed a smectic phase in both heating and cooling processes, indicating an enantiotropic nature. Transition temperatures for the precursors and the free ligand are collected in *3 3*.

The titanocene complex **1**, $(PCH506Cp)_2TiCl_2$, showed an optical texture in the polarizing optical microscope but it showed no distinct peak in differential scanning calorimetry (d.s.c.), probably owing to insufficient purification. Thus the liquid crystallinity of **1** still remains unconfirmed. On the other hand, the titanocene complexes **2**, $Cp_2Ti(PCH5060)_2$, and **3**, $Cp_2Ti(PCH5060)Cl$, exhibited fan-shaped texture in the polarizing optical microscope as shown in *Figure 1*, indicating a thermotropic smectic LC mesophase.

D.s.c. measurements and polarizing optical microscope observations showed that the mesophases of **2** and **3** are in the range 65–95°C and 67–90°C, respectively. *Figure 2* shows d.s.c. curves of the titanocene complex **2**, $Cp_2Ti(PCH5060)_2$. As far as we know, the present complexes **2** and **3** are the first titanium complexes that show LC behaviour. Note that heating to a temperature higher than 150°C caused decomposition of the complexes as a consequence of oxidation, giving no mesophase in the next cooling process of the d.s.c. measurement.



Scheme 3

Catalytic activity

Polymerization of phenylacetylene. We examined the capability of the present titanocene complexes to polymerize a phenylacetylene that is a representative mono-substituted acetylene. Et_3Al and toluene were used as cocatalyst and solvent, respectively. Concentrations of the monomer and catalyst were 10.5 M and 5 mM, respectively. The [cocatalyst]/[catalyst] ratio was 6. Polymerizations were carried out at room temperature for 12–38 h. The results are summarized in *Table 1*. It is clear that both the titanocene complexes **1** and **2** have catalytic activity for the polymerization of phenylacetylene. In particular, the molecular weight, degree of polymerization and yield of the polymer prepared with the catalyst including **2** are much higher than those of the polymers prepared with other catalysts including titanocene dichloride and $Ti(O\text{-}n\text{-}Bu)_4$.

Polymerization of acetylene. We also examined the catalytic activities of the titanocene complexes **2** and **3** for acetylene polymerization, using Et_3Al as cocatalyst. The ratio [cocatalyst]/[catalyst] was 10. The catalyst systems

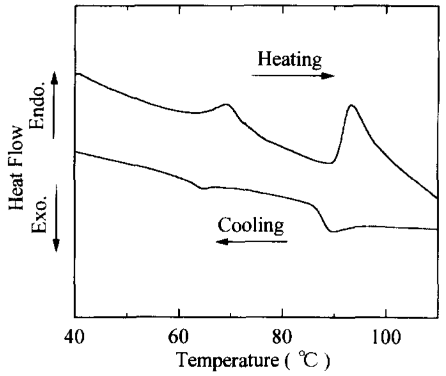
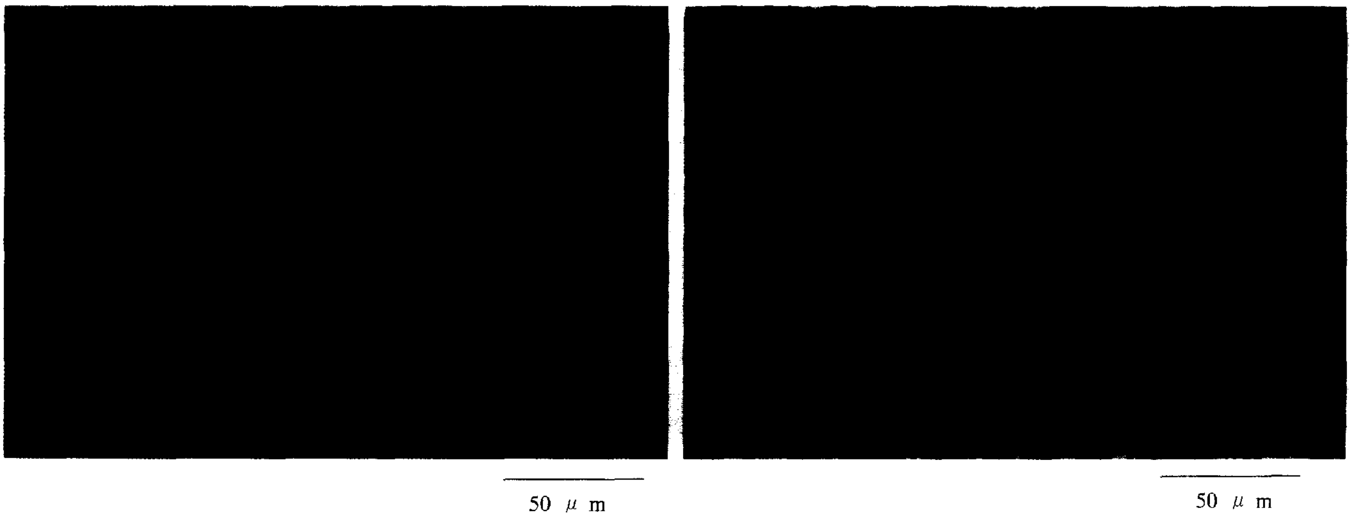


Figure 2 D.s.c. curves of $Cp_2Ti(PCH5060)_2$ (**2**)



$Cp_2Ti(PCH5060)_2$ (2)

$Cp_2Ti(PCH5060)Cl$ (3)

Figure 1 Polarizing micrographs of the titanocene complexes of **2** and **3**

Table 1 Polymerization of phenylacetylene with titanium-based catalysts

Catalyst[a]	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	*DP*[b]	Yield (%)
1	5.2×10^3	8.3×10^3	1.6	51	3
2	1.3×10^4	3.4×10^4	2.7	126	84
Cp_2TiCl_2	4.1×10^3	5.7×10^3	1.4	40	14
$Ti(O\text{-}n\text{-}Bu)_4$	4.1×10^3	4.9×10^3	1.2	41	14

1: $(PCH506Cp)_2TiCl_2$; **2**: $Cp_2Ti(PCH5060)_2$

[a] Catalyst molar ratio, $[Ti]/[Et_3Al]$, was 6

[b] Degree of polymerization was evaluated from the number-average molecular weight ($\bar{M}_n$)

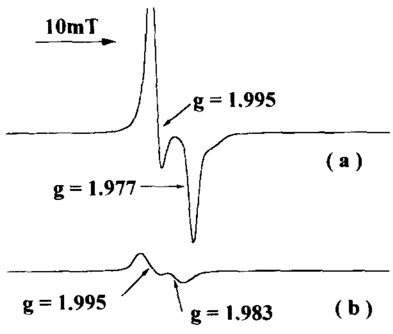


Figure 3 E.s.r. spectra of $Cp_2Ti(PCH5060)_2$–Et_3Al catalyst aged at room temperature for 1 h (a) and followed by heating to 140°C for 1 h (b)

were aged at room temperature for 1 h. The polymerizations were carried out at −76°C according to the solvent evacuation method[1], where cumene, used as the solvent, was evacuated through vacuum pumping just before the introduction of acetylene gas into the catalyst system. As a consequence, by using the titanocene complex **2** we obtained a free-standing polyacetylene film where the *cis* content and electrical conductivity upon iodine doping were 94% and 4.9×10^3 S cm^{-1}, respectively. However, the application of high-temperature ageing (room temperature for 1 h and 140°C for 1 h) unexpectedly results in a substantial decrease in catalytic activity, leading to a lowering of the mechanical properties of the film. On the other hand, the titanocene complex **3**—which contains an electronegative chlorine atom—gave a fragile film. Thus the titanocene complex **2** aged at room temperature yields *cis*-rich and highly conducting polyacetylene films.

E.s.r. spectra. It has been considered so far that the catalytically active species for acetylene polymerization is trivalent titanium, Ti^{3+}, generated from the tetravalent titanium of $Ti(OR)_4$ through a reduction by Et_3Al[5]. The trivalent titanium has an unpaired electron in the 3*d* orbital (valence electronic configuration of $3s^2 3p^6 3d^1$) and hence it is detectable by means of e.s.r. spectroscopic measurement. In fact, extensive e.s.r. studies of the $Ti(O\text{-}n\text{-}Bu)_4$–$Et_3Al$ catalyst have been carried out by varying the Al/Ti molar ratio under conditions of room-temperature and high-temperature ageing[5–11].

As mentioned above, the novel titanocene complex **2** has a high catalytic activity for the polymerizations of acetylene and mono-substituted acetylene after ageing at room temperature. However, high-temperature ageing resulted in a substantial decrease in the catalytic activity, indicating that high-temperature ageing is not effective for the present catalyst system. Such an apparently contradictory difference between the $Ti(O\text{-}n\text{-}Bu)_4$–$Et_3Al$ and $Cp_2Ti(PCH5060)_2$–Et_3Al catalysts promotes us to elucidate the latter catalyst in more detail.

Thus we examined the structural changes of Ti^{3+} species in the $Cp_2Ti(PCH5060)_2$–Et_3Al catalyst system by means of e.s.r. measurements. *Figure 3* shows e.s.r. spectra of the $Cp_2Ti(PCH5060)_2$–Et_3Al catalyst dissolved in cumene, aged at room temperature for 1 h and at 140°C for 1 hour. In the spectrum of the catalyst aged at room temperature, two signals are observed with *g* values of 1.995 and 1.977. On the other hand, in the spectrum of the sample treated at higher temperature, the integrated intensity correlated with total spin concentration of the Ti^{3+} species exhibited a drastic decrease, as shown in *Figure 3b*. This observation is consistent with the above-mentioned experimental result that high-temperature ageing of the $Cp_2Ti(PCH5060)_2$–Et_3Al catalyst decreases the catalytic activity. The signal of 1.995 observed in the room-temperature-aged catalyst showed no shift after high-temperature ageing; however, the signal of 1.977 shifted to a lower magnetic field to give a *g* value of 1.983. It is important to note that, in both cases of room-temperature and high-temperature ageing, no hyperfine structure appeared in the e.s.r. spectra. This is quite a contrast to the case of the $Ti(O\text{-}n\text{-}Bu)_4$–$Et_3Al$ catalyst, which gives a hyperfine structure[5–11]. This may be ascribed to the effect of coordination of the bulky LC ligands. That is, these ligands restrict the formation of a binuclear or trinuclear complex with a 'bridging structure', where one or two aluminium nuclei are connected with a Ti^{3+} nucleus through ligands of butoxy and/or ethyl groups, as seen in the $Ti(O\text{-}n\text{-}Bu)_4$–$Et_3Al$ catalyst. In other words, the structure of the present active species can be regarded as a mononuclear complex consisting of Ti^{3+} rather than a binuclear or trinuclear one, since no hyperfine structure was observed. The results mentioned above are stimulating for further studies to develop LC catalysts for the anisotropic polymerizations of acetylene and mono-substituted acetylene.

CONCLUSIONS

A series of LC titanocene complexes has been synthesized with the ultimate goal of developing LC catalytic species feasible for the anisotropic polymerization of acetylenes. The titanocene complexes were prepared by introducing LC groups into cyclopentadienyl ligands as substituents, $(PCH506Cp)_2TiCl_2$ (**1**), or by coordinating them to a titanium atom as symmetric and asymmetric ligands, $Cp_2Ti(PCH5060)_2$ (**2**) and $Cp_2Ti(PCH5060)Cl$ (**3**). Titanocene complexes **1** and **2** can polymerize phenylacetylenes to give poly(phenylacetylene)s with the aid of Et_3Al used as cocatalyst. The molecular weights and degrees of polymerization of the resulting poly(phenylacetylene)s were comparable or superior to those prepared by catalysts of Cp_2TiCl_2 and $Ti(O\text{-}n\text{-}Bu)_4$. The LC titanocene complexes **2** and **3** were also confirmed to have catalytic activity for acetylene polymerization. E.s.r. spectra of the catalyst systems gave signals of trivalent titanium (Ti^{3+}) with no hyperfine structure, suggesting that the structure of the catalytically active species is a mononuclear complex consisting of Ti^{3+} rather than a binuclear or trinuclear one.

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