APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2007; **21**: 652–660
DOI:10.1002/aoc.1233

Synthesis of ultra-low-molecular-weight polyethylene wax using a bulky Ti(IV) aryloxide–alkyl aluminum catalytic system

Prashant S. Umare[1], Ajaykumar J. Tiwari[2], Robin Antony[2], Gopal L. Tembe[2]* and Bhavna Trivedi[1]

[1]Department of Chemistry, The M.S. University of Baroda, Vadodara 390 002, India
[2]Research Centre, Indian Petrochemicals Corporation Limited, Vadodara 391 346, India

Received 10 November 2006; Accepted 23 February 2007

Complexes of titanium(IV) with bulky phenolic ligands such as 2-*tert*-butyl-4 methylphenol, 2, 4-di-*tert*-butyl phenol and 3,5-di-*tert*-butyl phenol were prepared and characterized. These catalyst precursors, formulated as $[\mathrm{Ti(OPh^*)}_n(\mathrm{OPr}^i)_{4-n}]$ (OPh* = substituted phenol), were found to be active in polymerization of ethylene at higher temperatures in combination with ethylaluminum sesquichloride ($Et_3Al_2Cl_3$) as co-catalyst. It was observed that the reaction temperature and ethylene pressure had a pronounced effect on polymerization and the molecular weight of polyethylene obtained. In addition, this catalytic system predominantly produced linear, crystalline ultra-low-molecular-weight polyethylenes narrow dispersities. The polyethylene waxes obtained with this catalytic system exhibit unique properties that have potential applications in surface coating and adhesive formulations. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: titanium–phenolate catalysts; ethylene polymerization; polyethylene wax; ethylaluminum sesquichloride

INTRODUCTION

There has been an immense interest in the use of non-cyclopentadienyl catalysts for olefin polymerization over the past few years.[1–4] The replacement of ubiquitous 'Cp' ligand with hard donor ligands such as amido,[5,6] alkoxide,[7] siloxide[8] and aryl oxide[9–11] groups has tremendously expanded the scope of organometallic chemistry at early d-block metal centers.[12,13] One particular area of focus has been the application of titanium alkyloxides and aryloxides as precatalysts for novel types of α-olefin polymerizations.[14–17] These titanium-based catalysts have also found extensive use in organic transformations such as oxidation,[18] epoxidation[19] and carbon–carbon bond formation.[20] Further, the diversity of these titanium complexes stems from the fact that $Ti(OR)_4$-type compounds are easily accessible and possess the ability to stabilize unusual coordination polyhedra, which have lead to the synthesis of two- and three-dimensional metal–organic frameworks.[21–23]

Industrial manufacture of polyethylene is primarily concerned with conventional grades such as low-density, high-density and linear-low-density polyethylenes (LDPE, HDPE and LLDPE). Nevertheless, new types of polyethylene as building blocks in chemical industry catalyst systems that are more active and selective are constantly being sought to meet the demand for polymer properties and minimize the cost of production. A potentially emerging segment of the global polyethylene business involves the production of specialty low-molecular-weight polyethylene wax, which is gaining importance for many applications.[24–27] Polyethylene wax (PE wax) can be made by direct polymerization of ethylene under controlled conditions. Another route involves breaking down high-molecular-weight polyethylene into lower-molecular-weight fractions. A third method involves separation of the low-molecular-weight PE fraction from high-molecular-weight polymer.

Commercial PE waxes, because of their unique physicochemical properties, serve as aids in a variety of plastics processing applications to enhance lubricity, control the set/softening point of hot melt adhesives, impart slip and rub resistance in printing inks and improve the fusing properties

*Correspondence to: Gopal L. Tembe, Research Centre, Indian Petrochemicals Corporation Limited, Vadodara 391 346, India.
E-mail: gopal.tembe@ipcl.co.in

in toner formulations, etc.[28–30] Wax producers like Clariant (Licowax), Dow (Insite catalyst) and Mitsui (Excerex process) employ proprietary metallocenes and methyl alumoxane as co-catalysts for polymerizing ethylene to highly crystalline low-molecular-weight polyethylene.[31–34] Synthetic PE waxes are generally characterized by low melt temperatures, high crystallinity, molecular weights from 1000 to 3000 g/mol and mean particle size around 10–30 μm. Compared with the relatively expensive metallocene technology, the design and development of non-metallocene homogeneous catalysts that are easily accessible, less expensive and tolerant to moisture and air for producing specialty PE wax, constitutes an useful research objective. However, there has been no systematic effort to study catalysts containing aryl oxides of group 4 metals, in particular those derived from sterically hindered phenols in ethylene polymerization. The aryloxides of titanium and zirconium described by the formulation $[(\mathrm{OR})_n\mathrm{MX}_{4-n}$, where R = substituted phenol, X = labile ligand and M = Ti(IV) or Zr(IV)] are relatively ineffective in presence of MAO as co-catalyst for producing low-molecular-weight polyethylene.[35–40] In a recent finding we reported that titanium complexes of 1,1′-bi-2-aryl oxide, such as BINOL (1,1′-binaphthalene-2,2′-diol), which is an important c_2 symmetric chiral auxiliary ligand, promoted the polymerization of ethylene to predominantly low-molecular-weight product having high crystallinity and narrow polydispersity.[41] In order to gain further insight into the interesting behavior of bulky aryloxy derivatives of Ti(IV) in polymerization, in the present work, catalyst precursors containing sterically bulky phenols have been prepared and evaluated for catalytic ethylene polymerization in combination with ethyl aluminum sesquichloride as co-catalyst.

RESULTS AND DISCUSSION

Synthesis of aryloxide complexes of titanium

The preparation of Ti–phenolate complexes was carried out via the stoichiometric reaction between $\mathrm{Ti(OPr^i)_4}$ and the phenolic ligands [1 : 2 mole ratio in the case of **1** and 1 : 4 mole ratio in the case of **2–4**] and removal of liberated isopropanol azeotropically. The reaction in toluene afforded dark orange colored complexes.

Catalyst characterization

The titanium complexes **1–4** described by the empirical formula $\mathrm{Ti(OPh^*)_n(OPr^i)_{4-n}}$ are generally soluble in aromatic and chlorinated aromatic solvents but only sparingly so in aliphatic hydrocarbons. Catalysts **1–4** have been characterized by microanalysis, IR, ^{1}H NMR, FAB mass spectra and thermal analysis. In a typical IR spectra of **1**, the low intensity broad peaks in the 3000–3500 cm^{-1} region indicate deprotonation of the phenolate ligand on complexation to the titanium center.

The ^{1}H NMR spectra are generally simple and were primarily used as a diagnostic tool for ascertaining the purity of the complexes (Fig. 1). A set of multiplets in the region 7.0–7.3 ppm for the aromatic protons is a common feature in addition to signals due to methyl proton at 2.36 ppm and the tertiary butyl group $\{-\mathrm{C(CH_3)_3}\}$ at 1.3 ppm. In the FAB mass spectra of **3** a prominent peak for ligand fragment (phenolate ion) appeared at 206. However, the parent ion was not detected. Fragment ions originating from other species were difficult to establish due to the complexity of the spectrum beyond m/z values of 400. Such band patterns were also noted in the EI-MS of other titanium alkoxide complexes.[42–45]

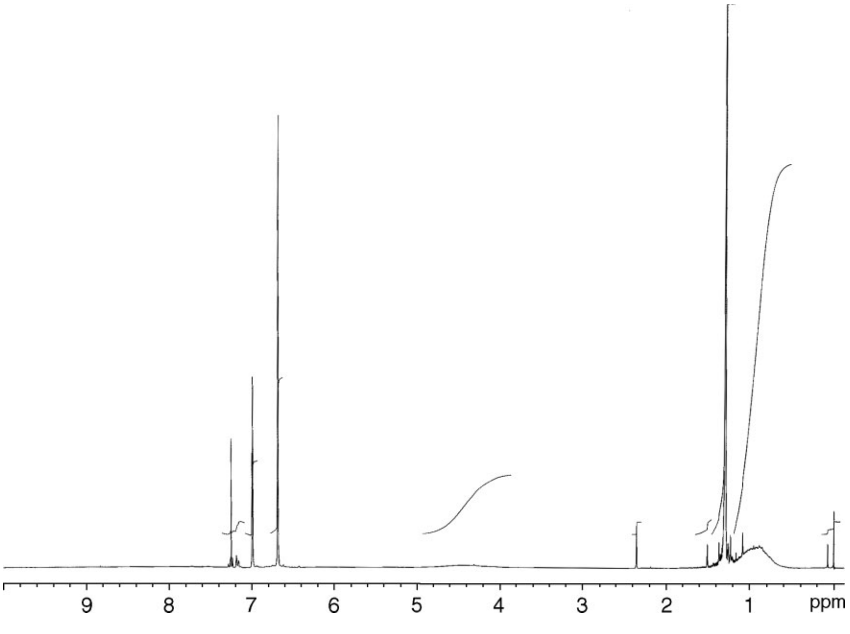
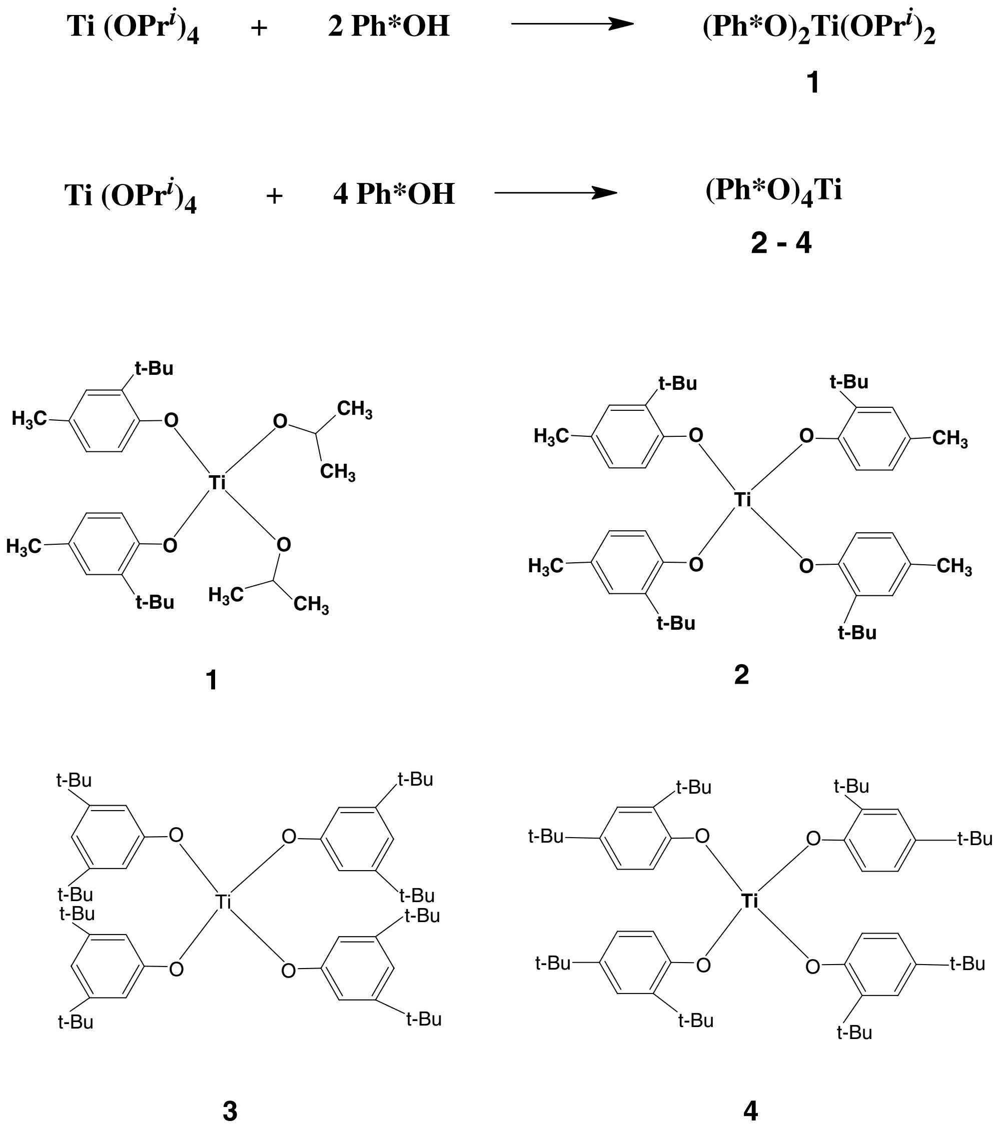


Figure 1. ^{1}H NMR of catalyst **3**.

DOI: 10.1002/aoc



Scheme 1. Catalyst synthesis. Ph*OH = 2-*tert*-butyl-4 methyl phenol (**1** and **2**); 3,5-di-*tert*-butyl phenol (**3**); 2,4-di-*tert*-butyl phenol (**4**).

In general the Ti catalysts are quite stable, as is apparent from the thermal degradation profile (Fig. 2), which indicates major degradation peaks in the 200–400 °C region. However, complete degradation to the dioxide, TiO_2, was noted beyond 480 °C. Typical TG results for **1** (observed 16.8%; calculated 16.2%) and **3** (observed 8.9%; calculated 9.2%) support the solid-state stoichiometry of the complexes inferred from microanalysis.

Polymerization of ethylene

The results of ethylene polymerization using catalyst precursors **1**–**4** are shown in Table 1. The efficiency of catalysts was compared with known metallocenes such as Cp_2TiCl_2 and Cp_2ZrCl_2 in the presence of EASC as co-catalyst. The polymerization was carried out under different reaction conditions such as temperature, pressure, solvent and co-catalysts. Initial examination of catalysts indicated that, amongst the different substituted phenols, titanium complexes of 2-*tert*-buyl-4 methylphenol and 3, 5 di-*tert*-butyl phenol generally display higher activity in polymerization than the titanium complex of 2, 4 di-*tert*-butyl phenol (Table 1, entries 1–4). The metallocenes on the other hand are practically inactive under these reaction conditions (Table 1, entries 5 and 6). The activity is also predominantly dependent on the nature of the co-catalyst. Ethylaluminum sesquichloride uniquely favors the polymerization. Other chlorinated alkylaluminums, $EtAlCl_2$ (EADC; Table 1, entry 11), are also active but show lower productivities. This rather exclusive combination of Ti–phenolate precursor and EASC co-catalyst in polymerization suggests formation of active

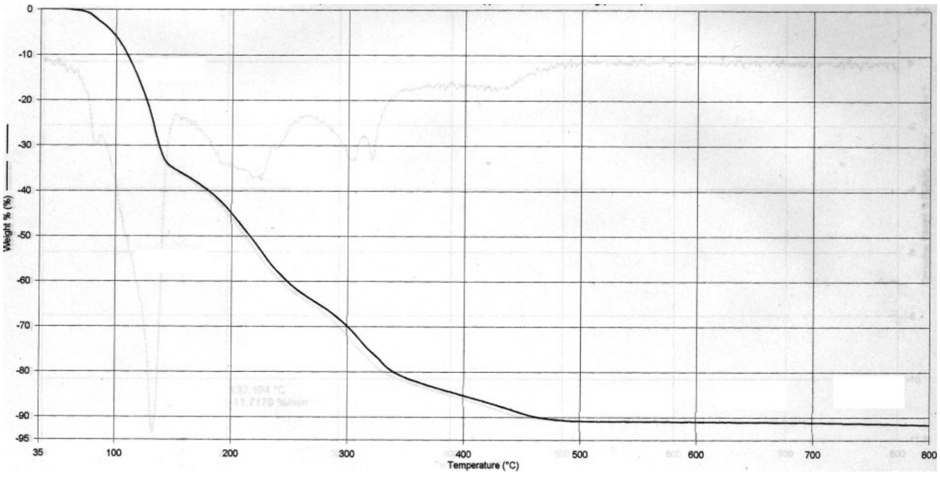


Figure 2. Typical TG of catalyst **3**.

Table 1. Results of ethylene polymerization with Ti–phenolate catalytic system[a]

Entry	Catalyst	Temperature, °C	Pressure, psi	Co-catalyst	Activity, kg PE/g Ti	M_w	PD	T_m (°C)	d (g cm^{-3})
1	**1**	100	500	EASC	19.9	1290	1.5	118	0.952
2	**2**	100	500	EASC	24.7	1170	1.5	124	0.954
3	**3**	100	500	EASC	18.5	930	1.4	128	0.958
4	**4**	100	500	EASC	4.7	840	1.4	125	0.954
5	Cp_2TiCl_2	100	500	EASC	0.2	—	—	—	—
6	Cp_2ZrCl_2	100	500	EASC	1.0	—	—	—	—
7[b]	2	100	250	EASC	9.5			116	
8[c]	3	50	500	EASC	2.6			—	
9[d]	3	30	500	EASC	0.3			—	
10	3	100	500	MAO	1.5			132	
11	3	100	500	EADC	4.2			123	
12	3	100	500	TEAL	0.2			—	
13[e]	3	100	500	EASC	23.5			116	
14[f]	3	100	500	EASC	0.1			—	

[a] All reactions were carried out in a 600 ml SS reactor at 100 °C and 500 psi ethylene pressure for 1h in toluene.
[b] (C_2H_4) = 250 psi; temperature = 50 °C[c], 30 °C[d]; [e] solvent = chlorobenzene;
[f] hexane.
EADC = $EtAlCl_2$, TEAL = Et_3Al.

intermediates responsible for polymerization, as will be discussed in the following section. Interestingly conventional co-catalysts for polyolefin production such as methyl alumoxane (MAO) and triethylaluminum (TEAL, Et_3Al; entries 10 and 12) displayed poor activity while the isolated polymer was found to be largely coarse and inhomogeneous. A noteworthy feature of polyethylene obtained with these Ti–phenolate catalysts is the invariably low molecular weight (M_w) of the polymer, as revealed by GPC analyses. In all cases the PEs display narrow molecular weight distribution ($M_w/M_n = 1.4–1.5$). It is however, pertinent to point out that the tetra aryloxides of unsubstituted phenol such as $Ti(OR)_4$ essentially lead to low molecular weight linear alpha olefins in the $C_4–C_{20}$ carbon range in sharp contrast to exclusive formation of solid PE wax with [Ti $(OPh^*)_n$ $(OPr^i)_{4-n}$]-type complexes employed in the present study.[46,47] This can be qualitatively interpreted as the chain propagation rates, $r_p \approx r_t$ in the case of the $Ti(OR)_4$–EASC catalyst system, resulting in oligomer formation whereas with the $[Ti(OPh^*)_n(OP^i)_{4-n}]$–EASC system $r_p > r_t$, giving polyethylene under identical conditions. The absence of α-olefins was also confirmed by gas chromatographic analysis of reaction mixture after separation of polymer. Detailed studies on the effect of temperature (entries 3, 8 and 9) and pressure (entries 3 and 7) were then carried out employing complex **3** and EASC as the co-catalysts. From the results summarized in Tables 1 it is evident that increasing the reaction temperature from ambient to

DOI: 10.1002/aoc

100 °C has a marked effect on the activity as seen by the approximately 10-fold increase in polymer yield. Applying higher pressure while maintaining constant temperature led to higher productivity. Generally a combination of higher Al : Ti ratio and higher temperature led to an improvement in the productivity of the catalyst. A brief study of the effect of different solvents (Table 1, entries 13 and 14) indicated that a chlorinated aromatic solvent such as chlorobenzene showed a nearly 25% increase in productivity of polyethylene over toluene. Interestingly, this increase was accompanied by a slight increase in M_w. However, aliphatic hydrocarbon solvents such as hexane resulted in poor activity, which may be due to low solubility of catalysts in these solvents.

In order to ascertain the level of branching in the 'as synthesized' polymer reported in Table 1, the IR spectrum was compared with a standard PE wax sample using the following equation.[48] The branching degree of PEs was determined by taking the value of absorbance of the 1378 cm^{-1} peak (νs CH$_3$)

$$\frac{n}{1000C} = \frac{(A_{1378}/l\rho)\ 5.4}{0.691}$$

From the spectrum shown in Fig. 2 the reference material indicated a branching degree of **4** compared with **1.9** for the sample. These values are consistent with generally fewer short chain branches (SCB) observed for most linear high density polyethylenes (~1–2/1000*C*).

To investigate the molecular properties of polyethylenes further, they were characterized by GPC (Fig. 3). A commercial PE wax sample was also included as a reference for comparison. The GPC of this material also displays similar distribution in the low-molecular-weight region. As discussed earlier, one of the striking feature of these PEs is the exceptionally low molecular weights ($M_w = 840–1290$) and narrow polydispersities (PD = 1.4–1.5). In no case was high-molecular-weight PE ($M_w \geq \sim 10^5$) obtained, although these catalysts resemble typical Ziegler–Natta systems. As briefly mentioned in the Introduction, polyethylene waxes with interesting applications have similar molecular weights and molecular weight distributions. The DSC (Fig. 4) also reveals lower T_m than that observed for conventional HDPE or LDPE. A known sample of micronized PE wax was used as benchmark for comparison of polymer properties with that obtained in this work (The commercial samples employed in this work, MPP123 and MPP 635 are a micronized, high-melting-point, crystalline form of polyethylenes and were supplied by M/s Micro Powders Inc., USA. The products have a T_m of 125-135 °C, molecular weight 2000, *d* (25 °C) 0.96 and maximum particle size = 31 μm. These and other grades of polyethylene waxes have been designed to increase the abrasion resistance and anti-blocking characteristics in flexographic inks as well as industrial paints and coatings. More details can be found at www.micropowders.com).

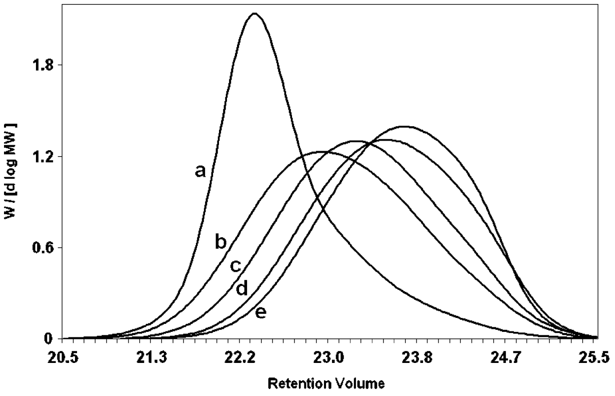


Figure 3. GPC profile of polymer listed in Table 1: (a) commercial sample; (b) Table 1, entry 3; (c) Table 1, entry 2; (d) Table 1, entry 4; (e) Table 1, entry 1.

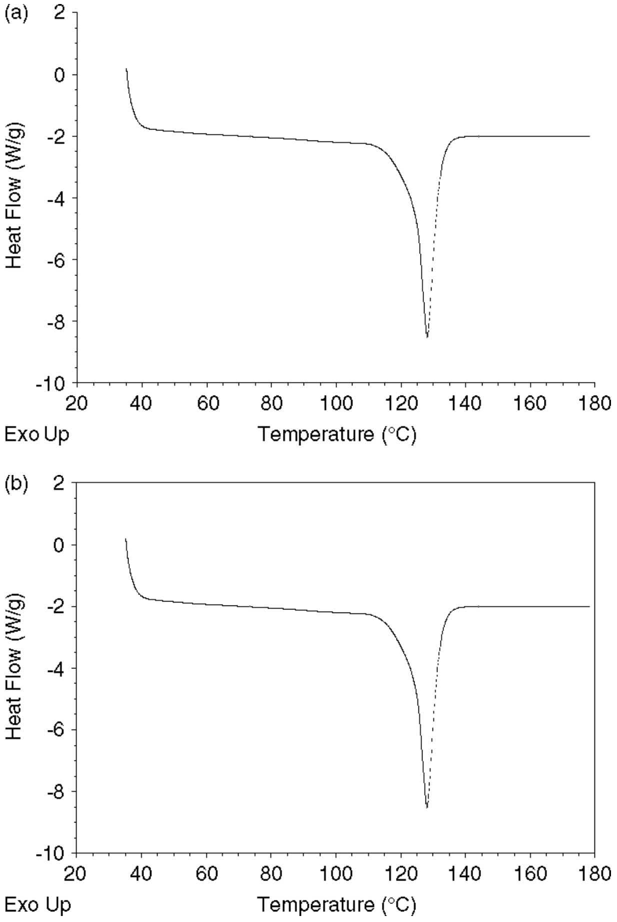


Figure 4. DSC of PE wax, Table 1: (a) entry 2; (b) entry 3.

The intensity of the equatorial peaks in the X-ray diffractogram (Fig. 5) for the 110 ($2\theta = 21.5°$) and 200 ($2\theta = 23.5°$) reflection planes for the experimental sample closely match the intensity of the reference sample and the pattern is indicative of orthorhombic crystallinity in these samples.

The crystalline nature of these polymers was also estimated by integration of the X-ray diffraction peaks observed for the

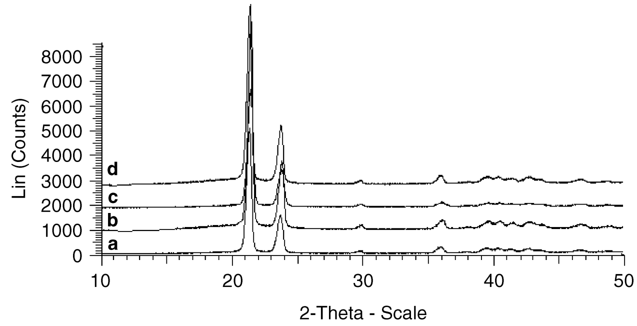
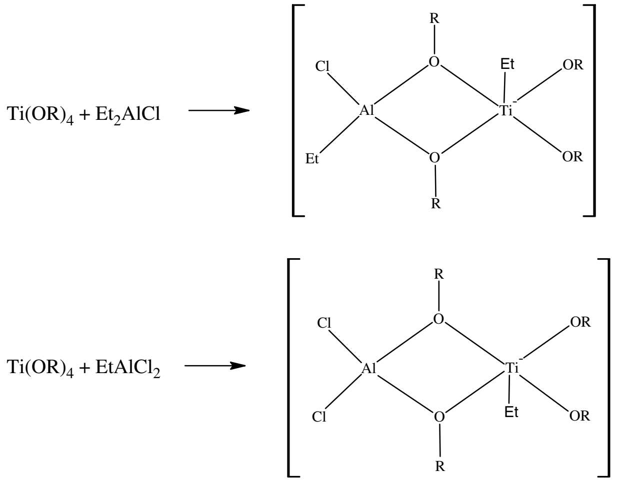


Figure 5. XRD of PE wax (a) commercial sample; (b) Table 1, entry 1; (c) Table 1, entry 2; (d) Table 1, entry 3.

wax samples. A high degree of crystallinity is indicated in all cases, generally in the range 80–88%. The polymer particles appear as well separated crystalline blocks having sharp plate-like features, as seen by a scanning electron micrograph. A common feature of these waxes is that the average particle size of the polymer as measured during post-reactor work-up was typically <400 μm. In Fig. 6 is shown the SEM of one of the PE samples obtained in this study. The unique polymer properties exemplified by these titanium phenolate–EASC catalyst system can be fine-tuned to tailor the M_w and polydispersities for the end use application.

Catalytic pathway

Treatment of mononuclear $Ti(OR)_4$-type alkoxides with alkylaluminum halides has been reported to yield active intermediates (see below) responsible for the polymerization of ethylene to low-molecular-weight dimers and oligomers, which essentially follow Schulz–Flory-type distribution.[49–53]



We believe that a similar type of active species may be involved in the present Ti–phenolate system. Moreover, as EASC is derived from an equimolar mixture of EADC and DEAC,[54] we have

$$2\,Et_3Al_2Cl_3 \rightleftharpoons (EtAlCl_2)_2 + (Et_2AlCl)_2$$

Since EASC can dissociate as Et_2AlCl and $EtAlCl_2$ in solution, it is reasonable to expect the formation of two types of catalytic species on interaction with Ti–phenolate catalyst. The reduction of Ti(IV) in the presence of EASC will generate catalytically active Ti-alkyl intermediates.

Qualitative information on the course of reaction was followed with the help of UV–vis spectra at different stages of mixing of the catalyst precursor and EASC in toluene. For example, in Fig. 7 the peak at 365 nm after immediate addition of EASC to catalyst **1** disappears (intensity is reduced). The introduction of ethylene leads to a new peak at around 460 nm (LMCT band). Similar evidence for the formation of active Ti-alkyl species was proposed for ethylene polymerization using a metallocene Cp_2TiCl_2 and MAO by Kaminsky and others.[55,56]

As shown in Scheme 2 the active catalysts in polymerization need to retain monomeric four or five coordinate geometry to allow for olefin insertion and subsequent propagation.[57]

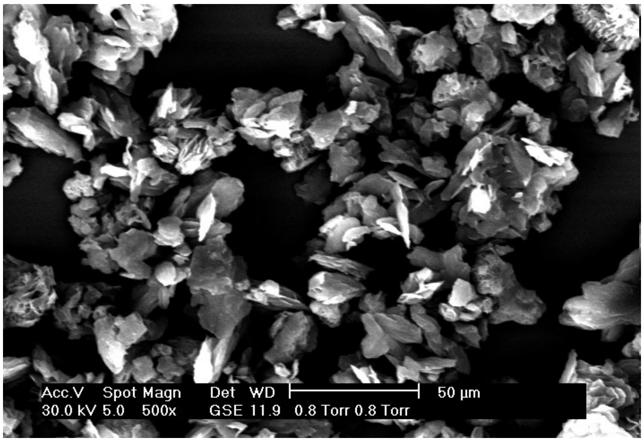
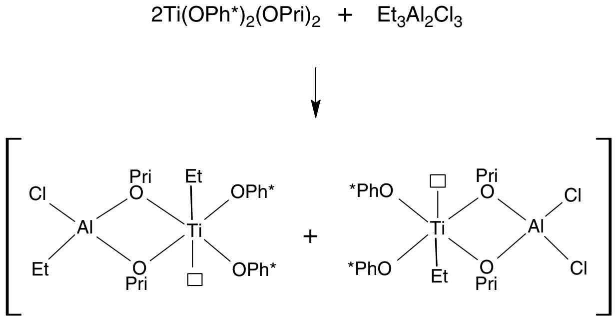


Figure 6. SEM of PE wax (Table 1, entry 1).



Scheme 2. Reaction of catalyst **1** with EASC.

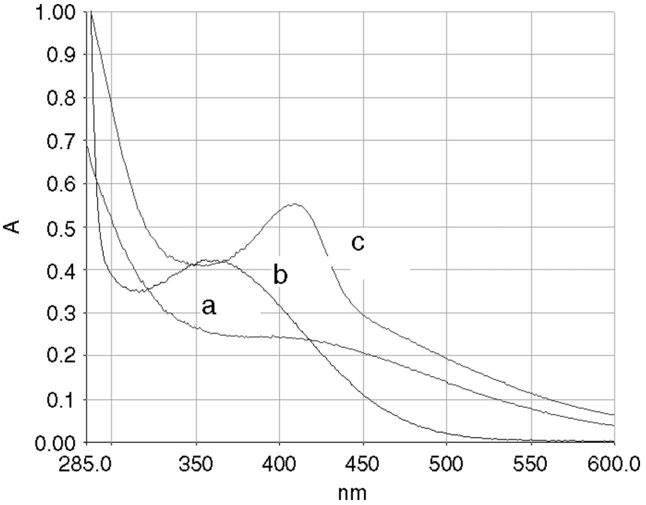
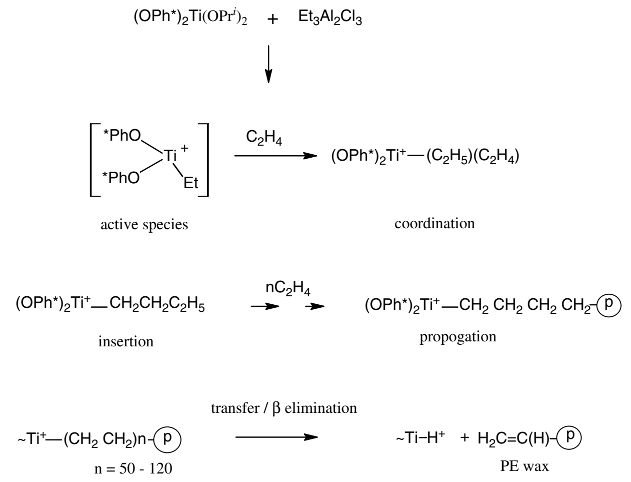


Figure 7. UV spectrum, (a) catalyst **1** + EASC; (b) catalyst **1;** (c) catalyst **1** + EASC + C_2H_4.



Scheme 3. Proposed mechanism of ethylene polymerization by Ti–phenolates.

In the present Ti–phenolate catalytic system, higher temperatures tend to favor formation of active intermediates responsible for polymerization.

Mechanistic aspect

From the information collected in Table 1 it follows that for the different Ti–catalyst precursors examined in this study, the activities and molecular weight dependence are primarily governed by (1) the nature of the substituents; (2) the type of alkyl aluminum co-catalyst; and finally (3) the reaction conditions of polymerization.

Based on a theoretical study by Morokuma[58,59] on the catalytic polymerization by chelating bridged and non-bridged Titanium aryloxides, it is possible to predict the possible course of ethylene polymerization for the present Ti–phenolate–EASC catalytic system. The active cationic species generated from the '*pre* catalyst' intermediates shown in Scheme 2 will facilitate the insertion of ethylene (rate determining step) into the growing chain, which ultimately leads to the desired polyethylene via propagation and termination steps. A modified Cossee–Arlmann-type mechanism[60–62] can thus be extended to rationalize the polyethylene formation with these catalysts (Scheme 3).

Although chain transfer can occur by other reactions as well, however, the relative inactivity of these catalysts with MAO & Et_3Al indicates that termination is unlikely to proceed by transfer to Al-alkyl or by H_2 under the reaction conditions. It is obvious that steric factors in phenols and the coordination geometry around the Ti atom contribute significantly towards productivity and *inter alia* molecular weight regulation.[63,64] This implies that the ligands that generate the highest molecular weights do so by slowing down β-hydrogen abstraction. Although the structure of active intermediates is as yet unknown, the mechanism leading to these linear low-molecular-weight polyethylenes is consistent with those reported previously for solution phase olefin polymerization using titanium alkoxides and aluminum alkyls.[58,59,65,66] Efforts are underway to investigate the detailed kinetics of this reaction.

CONCLUSIONS

The complexes of titanium(IV) with bulky phenolic ligands in presence of ethylaluminum sesquichloride as co-catalyst are highly effective for the synthesis of specialty low-molecular-weight polyethylene with good productivity. The catalyst activity is significantly influenced by the reaction temperature and Al : Ti ratios. The physical properties exhibited by these polyethylenes such as low molecular weights, high crystallinity and narrow dispersities suggest single-site catalytic behavior of Ti-aryloxy precursors. The close resemblance of polymer properties to commercially important synthetic waxes holds promise for developing alternative cheaper catalysts for this process.

EXPERIMENTAL

Materials

The synthetic work involving air- and/or moisture-sensitive compounds was carried out using standard high vacuum Schlenk or dry box (VAC) technique. AR-grade toluene was refluxed over sodium for 4 h and freshly distilled prior to use. High-purity ethylene (polymer grade) was collected in a cylinder from the commercial plant, the pressure of which was adjusted with a two-stage regulator. Co-catalysts were purchased from Ethyl Corporation or Crompton GmbH and used without further purification. Titanium iso-propoxide and the different substituted phenols were purchased from Aldrich and used as received.

Elemental analysis

Elemental analyses was carried out on a Perkin Elmer Model 2400 instrument. Titanium content in catalysts was determined gravimetrically as TiO_2.

IR spectra

A Perkin Elmer FT-IR spectrometer model Spectrum BX was used to obtain the IR spectra of samples pressed into KBr pellets over the 4000–400 cm^{-1} range.

NMR analysis

^1H NMR spectrum of catalysts was recorded in $CDCl_3$ solvent on a Varian NMR 300 MHz spectrometer using TMS as an internal reference.

FAB mass spectra

FAB mass spectral analysis of catalysts was carried out on a Jeol SX 102/DA-6000 mass spectrometer/data system using argon/xenon as the FAB gas. The accelerated voltage was 10 kV and the spectra were recorded at room temperature. *m*-Nitrobenzyl alcohol was used as the matrix.

UV–vis spectra

UV–vis spectra of Ti–catalyst and EASC were separately taken in toluene solutions and sealed in 1 cm airtight quartz cells under nitrogen atmosphere. The spectra were then recorded on a Perkin-Elmer Lambda 19 UV–vis–NIR spectrophotometer in the 200–800 nm range at ambient temperature; 2.0×10^{-4} mmol solution of the catalyst in toluene was taken for recording the spectra.

Gel permeation chromatography

Molecular weights of polyethylene were determined using size exclusion chromatography (SEC). The high-temperature GPC analysis of the polymers was carried out using Polymer Lab's PL-GPC 220 chromatograph. A set of PL Gel three Mixed B columns were used. 1,2,4-Trichlorobenzene was used as the mobile phase at 135 °C. Irganox, 0.0125%, was added to the mobile phase prior to filtration. A sample preparation unit, PL-SP260, was used to dissolve and filter the samples at 135 °C; 0.2% solutions were injected with the help of an auto sampler to record the chromatogram. Viscotek's Trisec conventional software was used to analyze the chromatograms which were matched with polystyrene calibration curve. The following MHK constants were used to construct an universal calibration curve. For PS: $K = 1.2105 \times 10^{-4}$; $a = 707$; PE: $K = 4.055 \times 10^{-4}$; $a = 725$.

Differential scanning calorimetry

Differential scanning calorimetry was performed under continuous nitrogen purge on a Mettler–Toledo DSC 822 instrument from 30 to 200 °C at a scan rate of 10 °C/min. Indium was used to perform the calibration.

Thermogravimetry

TGA/DTA of catalysts were recorded in air (heating rate 10 °C/min) from ambient to 800 °C on a TA Instrument (Universal V2).

Density of polymer

The density of polymers was determined in *n*-butyl acetate medium at 23 °C as per ASTM method D 792-00.

X-ray diffraction

X-ray experiments were carried out on a Brüker AXS model D8 advanced diffractometer. Scattering patterns were obtained with Ni-filled CuKα radiation ($\lambda = 1.5406$ Å, generator voltage = 45 kV, current = 40 µA) in the reflection mode, detected by a scintillation counter. Samples were pressed films approximately 400 µm thick and were scanned into 2θ ranges from 10–50° at a rate of 1 deg/min. Measurements were recorded at steps of 0.02°.

Scanning electron microscopy

Scanning electron micrographs of powdered polymer samples were taken on a Jeol JFC 1100 instrument ion sputter water. They were observed on a Jeol 5600 CV scanning electron microscope in Hv mode with operating voltage of 20 kV.

Catalyst 1 preparation

To a solution of 1 mmol (284.3 mg) of $Ti(OPr^i)_4$ in toluene (25 ml) was added slowly 2 mmol (324.5 mg) of 2-*tert*-butyl-4 methyl phenol in warm toluene (30 ml) under nitrogen atmosphere and heated at 60 °C for 3 h. The contents were then stirred for 24 h at room temperature. The solvent was carefully removed, the precipitated solid washed with small portions of toluene and finally the dark orange-colored complex was isolated. The remaining catalysts **2**–**4** were prepared in an analogous manner by using the corresponding amount of substituted phenol as the case may be. Anal calcd for catalyst **1** ($C_{28}H_{44}O_4Ti$), C, 68.3; H, 9.0; Ti, 9.7; found: C,68.2; H 8.8; Ti, 9.8. Catalyst **2** ($C_{44}H_{60}O_4Ti$), C, 75.4; H, 8.6; Ti, 6.8; found: C,75.8; H 8.6; Ti, 6.9. Catalyst **3** ($C_{56}H_{84}O_4Ti$), C, 77.4; H, 9.7; Ti, 5.5; found: C,77.8; H 10.1; Ti, 5.5. Catalyst **4** ($C_{56}H_{84}O_4Ti$), C, 77.4; H, 9.7; Ti, 5.5; Found: C,77.5; H 9.8; Ti, 5.8.

Procedure for ethylene polymerization

Ethylene polymerization was conducted in an high-pressure stirred autoclave (600 ml, Parr, USA) connected to a model 4850 microprocessor controller. Prior to polymerization, the reactor was baked at 150 °C under nitrogen for 2 h and then cooled to room temperature. In a typical experiment catalyst **1** (13.8 mg, 0.028 mmol) dissolved in toluene (50 ml) and $Et_3Al_2Cl_3$ (1.28 ml, 5.6 mmol) in toluene (200 ml) were carefully charged into the reactor under a nitrogen blanket. The Al : Ti molar ratio was 200. The reactor temperature was set at 100 °C and then pressurized with ethylene to 500 psi. The polymerization was continued for 1 h. After the end of the

DOI: 10.1002/aoc

reaction the autoclave was cooled to ambient, excess ethylene vented and the slurry slowly poured into acidic methanol (5%, v/v) to precipitate the polymer. The white polyethylene powder was filtered, washed several times with methanol followed by acetone and finally dried under reduced pressure at 70 °C for 2 h.

Acknowledgments

One of the authors (P.S.U.) gratefully acknowledges the management of Indian Petrochemicals Corporation Limited for technical facilities and the Head, Department of Chemistry, MS University of Baroda, for supporting the project. A.J.T. thanks the Department of Chemical Engineering, DD University, Nadiad, for the project work at IPCL. The authors thank the Regional Sophisticated Instrumentation Centre, IIT Mumbai and Central Drug Research Laboratory, Lucknow for NMR and FAB mass spectral analysis.

REFERENCES

1. Bristvsek GJP, Gibson VC, Wass DF. *Angew. Chem Int. Edn* 1999; **38**: 428.
2. Gibson VC, Spitzmesser SK. *Chem. Rev.* 2003; **103**: 283.
3. Ittel SD, Jhonson LK, Brookhart M. *Chem. Rev.* 2000; **100**: 1169.
4. Coates GW, Hustad PD, Reinartz S. *Angew. Chem Int. Edn* 2002; **41**: 2236.
5. Chisholm MH, Rothwell IP. *Polyhedron* 1998; **17**: 623.
6. Volkis V, Lisovskii A, Tumanskii B, Shuster M, Eisen MS. *Organometallics* 2006; **25**: 2656.
7. Chisholm MH, Rothwell IP. *Polyhedron* 1995; **14**: 3177.
8. Wolczanski PT. *Polyhedron* 1995; **14**: 3335.
9. Rothwell IP. *Chem.Commun.* (feature article) 1997; 1331.
10. Thorn MG, Hill JE, Waratuke SA, Johnson ES, Fanwick PE, Rothwell IP. *J. Am. Chem. Soc.* 1997; 8630.
11. Thorn MG. Etheridge ZC, Fanwick PE, Rothwell IP. *J. Organomet. Chem.* 1999; **591**: 148.
12. Gibson VC. *Angew. Chem. Int. Edn Engl.* 1994; **33**: 1565.
13. Lavanant L, Toupet L, Lehmann CW, Carpentier JF. *Organometalics* 2005; **24**: 5620.
14. Oakes DCH, Krmberley BS, Gibson VC, Jones DJ, White AJP, Williams DJ. *Chem. Commun.* 2004; 2174.
15. Kretschmer WP, Dijkhuis C, Meetsma A, Hessen B, Teuben JH. *Chem. Commun.* 2002; **608**.
16. Chen EYX, Marks TJ. *Chem Rev.* 2000; **100**: 1391.
17. Coates GW. *Chem. Rev.* 2000; **100**: 1223.
18. Fujiwara M, Xu Q, Souma Y, Kobayashi T. *Mol. Catal. A Chem.* 1999; **142**(1): 77.
19. Ramon DJ, Yus M. *Chem. Rev.* 2006; **106**: 2126.
20. Chen Y, Yekta S, Yudin AK. *Chem. Rev.* 2003; **103**: 3155.
21. Tanski JM, Wolczanski PT. *Inorg. Chem.* 2001; **40**: 2026.
22. Tanski JM, Vaid TP, Lobkovsky EB, Wolczanski PT. *Inorg. Chem.* 2000; **39**: 4756.
23. Vaid TP, Tanski JM, Pette JM, Lobkovsky EB, Wolczanski PT. *Inorg. Chem.* 1999; **38**: 3394.
24. Luker H. US Patent 5 023 388, 1991.
25. Tavares B, Gambino J. US Patent 6 409 811, 2002.
26. Hohner G, Spaleck W, Voigt H, Bohm L, Herrmann HF. US Patent 5 723 705, 1998.
27. Spaleck W, Rohrmann J, Antberg M, Dolle V, Winter A. US Patent 5 962 719, 1999.
28. Borsinger G, Cawley C. US Patent 6 639 003, 2003.
29. Eguchi A, Sakai H, Kigami T, Suzuki C, Aoki T. US Patent 5 928 825, 1999.
30. Technical Product Literature, 2005; from Noveon Inc., USA at www.noveoncoatings.com.
31. Hohner G, Herrmann HF. US Patent 6 080 902, 2000.
32. Finlayson MF, Guerra RF, Garrison CC, Guest MJ, Kolthammer BWS, Ueligger SM, Parikh DR. US Patent 6 335 410, 2002.
33. Tomoshige T. US Patent 4 039 560, 1977.
34. Toyoda H, Tjaden EB, Swenson DC, Jordon RF, Petersen JL. *Organometallics* 1995; **11**: 371.
35. Tjaden EB, Swenson DC, Jordon RF, Petersen JL. *Organometallics* 1995; **11**: 371.
36. Sobota P, Przybylak K, Utko J, Jerzykiewicz LB, Pombeiro AJL, da Silva M, Szczegot K. *Chem. Eur. J.* 2001; **7**: 951.
37. Nakayama Y, Miyamoto K, Ueyama N, Nakamura A. *Chem. Lett.* 1999; 391.
38. Nakayama Y, Watanabe K, Ueyama N, Nakamura A, Harada J, Okuda J. *Organometallics* 2000; **19**: 2498.
39. Manivannan R, Sundararajan G. *Macromolecules* 2002; **35**: 7883.
40. Fokken S, Saniol TP, Okuda J. *Organometallics* 1997; **16**: 4240.
41. Umare PS, Antony R, Gopalakrishnan K, Tembe GL, Trivedi B. *J. Mol. Catal. A Chem.* 2005; **242**: 141.
42. Lorca M, Kuhn D, Kurosu M. *Tetrahedron Lett.* 2001; **42**: 6243.
43. Kobayashi S, Kusakabe K, Komiyama S, Ishitani H. *J. Org. Chem.* 1999; **64**: 4220.
44. Mikami K, Korenaga T, Matsumoto Y. Veki M, Terada M, Matsukawa S. *Pure Appl. Chem.* 2001; **73**: 255.
45. Yamashita Y, Ishitani H, Shimizy H, Kobayashi S. *J. Am. Chem. Soc.* 2002; **124**: 3292.
46. Tembe GL, Ravindranathan M. *Ind. Engng Chem. Res.* 1991; **30**: 2247.
47. Tembe GL, Pillai SM, Satish S, Ravindranathan M. US Patent 6 013 850, 2000.
48. Panin AN, Sukhova TA, Bravaya NM. *J. Polym. Sci.* 2001; **39**: 1901.
49. Hirai H, Hiraki K, Noguchi I, Makishima S. *J. Polym. Sci. Part A* 1970; **8**: 47.
50. Shilov AE, Dzhabiev TS, Sabirova RD. *Kinet. Catal. Engl. Transl.* 1964; 5385.
51. Moyer PH. *J. Polym. Sci. A* 1965; **3**: 199.
52. Angelescu E, Nicolau C, Simon Z. *J. Am. Chem. Sci.* 1966; **88**: 3910.
53. Rothenburg RA. *J. Polym. Sci. A* 1965; **3**: 3038.
54. Kaminsky W. *Transition Metal Catalyzed Polymerizations—Alkenes and Dienes*. Hardward Academic NW: 1981; 233.
55. Mole T, Jeffery EA. *Organoaluminum Compounds*. Elsevier: New York, 1972; 9.
56. Brandt J, Hoffman EG. *Brennstoff. Chem.* 1962; **45**: 200.
57. Olivé GH, Olivé S. *Coordination and Catalysis*. Verlag Chemie: Weinheim, 1977; 193.
58. Froese RDJ, Musaev DG, Matsubara T, Morokuma K. *J. Am. Chem. Sci.* 1997; **119**: 7190.
59. Froese RDJ, Musaev DG, Matsubara T, Morokuma K. *Organometallics* 1999; **18**: 373.
60. Cossee P. *J. Catal.* 1964; **3**: 80.
61. Arlman EJ, Cossee P. *J. Catal.* 1964; **3**: 99.
62. Brookhart M. Green MLH. *J. Organomet. Chem.* 1983; **250**: 395.
63. Sernetz FG, Mulhaupt R, Fokken S, Okuda J. *Macromolecules* 1997; **30**: 1562.
64. Capacchione C, Proto A, Ebeling H, Mülhaupt R, Möller K, Manivannan R, Spaniol TP, Okuda J. *J. Mol. Catal. A Chem.* 2004; **213**: 137.
65. Watenpaugh K, Caughlan CN. *Inorg. Chem.* 1966; **5**: 1782.
66. Frazer MJ, Goffer Z. *J. Inorg. Nucl. Chem.* 1966; **28**: 2410.

DOI: 10.1002/aoc