# Highly dispersed clay–polyolefin nanocomposites free of compatibilizers, *via* the *in situ* polymerization of α-olefins by clay-supported catalysts†

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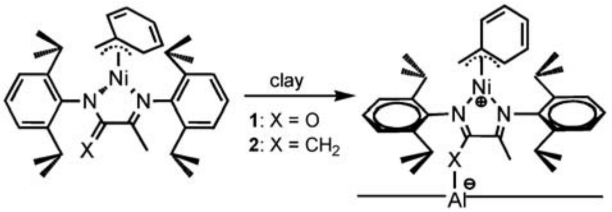
***In situ* polymerization by certain transition metal catalysts supported on and activated by acid-treated montmorillonite produces well-dispersed clay–polyolefin nanocomposites, without requiring either organic surfactants to be present in the clay phase or modification of the polyolefin structure.**

Reports of much improved physical properties in polymer–clay nanocomposite materials consisting of a polar polymer such as Nylon-6 and the delaminated form of a clay such as montmorillonite[1] have inspired many efforts to produce analogous clay nanocomposites with polyolefins.[2–11] However, dispersing the clay in a non-polar polyolefin matrix has proven difficult. One successful strategy relies on organic modification of the clay *via* ion-exchange with a long-chain alkylammonium or related surfactant,[2,3,7,8] followed by *in situ* polymerization of the α-olefin with an intercalated catalyst. Alternatively, the clay can be dispersed by melt-blending with a modified polyolefin containing polar side-chains or end-groups.[5,12] Unfortunately, the same compatibilizers (*e.g.*, surfactants or maleated polymers) that facilitate dispersion of the clay may also degrade the physical properties, and hence the usefulness, of the nanocomposite material. For example, the presence of organic modifiers reduces the barrier effect of the clay on gas permeability by inducing the formation of a secondary crystal phase in the polyolefin adjacent to the modified clay.[13] Organic modifiers can decompose under processing conditions,[4,13,14] at temperatures as low as 105 °C.[4] As a result, the exfoliation of the clay in the nanocomposite may become unstable, causing the platelets to reaggregate. Finally, formation of volatile decomposition products at low temperatures may enhance the flammability of these materials.[15]

We sought to develop a method for the production of well-dispersed polyolefin–clay nanocomposites without the use of compatibilizing agents in either the clay or polymer phases.



**Scheme 1** Proposed mechanism of clay activation for nickel precatalysts.

Many single-site olefin polymerization catalysts are activated by Lewis acids,[16,17] while clays are inherently Lewis acidic due to the presence of coordinatively-unsaturated Al.[18] Initially, we focused on late transition metal catalysts since they tend to be more tolerant of water and other polar groups found in clays than their early transition metal analogues. Thus [*N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)-propanamidato-κ$^2$-*N,N*]Ni(η$^3$-CH$_2$Ph), **1**, can be activated for ethylene polymerization by binding a Lewis acid such as B(C$_6$F$_5$)$_3$ at the carbonyl group on the ligand backbone, generating a Zwitterionic adduct.[19–21] An analogous activation mechanism is proposed for the complex interacting with the surface of clay, Scheme 1.

Pretreatment of montmorillonite with a mineral acid increases its Lewis acidity and causes extensive disruption of the layered structure,[22] as shown by the loss of intensity in the basal reflection *d*(001) of the clay at *ca.* 7° 2$\theta$, Fig. 1a. When 4 mg **1** was stirred with 100 mg acid-treated montmorillonite, most of the yellow color of the toluene solution was transferred to the clay. The resulting Ni-modified clay was active for ethylene polymerization (965 kg PE (mol Ni)$^{-1}$ h$^{-1}$) without addition of any other co-catalyst or need for passivation of the clay surface (*e.g.*, by pretreatment with an alkylaluminium). The basal reflection of the clay is completely absent in the product, Fig. 1a (iii). A TEM image of a composite material (3 wt% clay) produced in this way confirms that the clay is both well-distributed and highly exfoliated; no tactoids (large aggregates) are visible, Fig. 1b. To evaluate whether the specific interaction between the carbonyl group in the ligand backbone of **1** and the clay surface is critical to achieving high clay dispersion, we also tested [*N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)-1-methylenepropylamido-κ$^2$-*N,N*]-Ni(η$^3$-CH$_2$Ph), **2**. It differs from **1** only in the replacement of the carbonyl group by a methylene. This catalyst was also activated by the clay (1340 kg PE (mol Ni)$^{-1}$ h$^{-1}$), and produced a composite material with a clay dispersion similar to that found for clay-activated **1** (see ESI). We infer that a Lewis acid–base interaction exists

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† Electronic supplementary information (ESI) available: Clay treatment, polymerization procedures, measurement of flexural modulus and additional TEM images. See DOI: 10.1039/b718241d

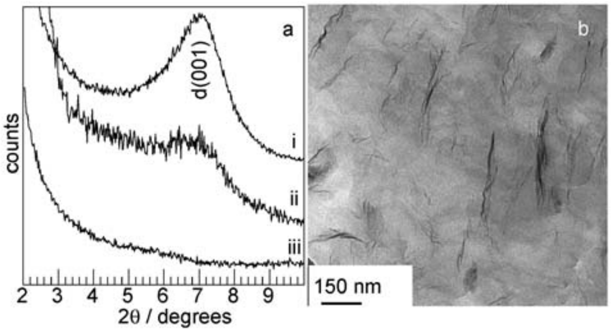

**Fig. 1** (a) Powder XRD of montmorillonite: (i) as raw clay; (ii) after treatment with mineral acid; and (iii) incorporated into a 3 wt% clay–polyethylene nanocomposite generated by clay-activated **1**. (b) TEM image of PE–montmorillonite nanocomposite (3 wt% clay).

between the methylene group in the ligand backbone and Al sites in the clay surface; a similar interaction has been reported between **2** and $B(C_6F_5)_3$.[21]

Since acid pretreatment of the clay causes extensive disruption of the layered structure before polymerization takes place, we sought further evidence for the importance of direct clay–catalyst bonding in forming the nanocomposite. Acid-treated montmorillonite has been reported to activate certain metallocene polymerization catalysts, even in the absence of alkylaluminium scavengers.[22–24] However, we found the activity of these supported catalysts towards ethylene to be very low. When a solution of $Cp_2ZrMe_2$ was added to a slurry of acid-modified montmorillonite, followed by addition of ethylene, we observed little uptake of the monomer. Furthermore, in the small quantity of gel-like material recovered from the reactor, very little clay was incorporated into the polymer phase; the two phases (polyethylene and clay) were visually distinguishable.

We speculated that the low catalytic activity of the clay-supported metallocene may be due to extensive decomposition of this protolytically-sensitive catalyst on the strongly Brønsted-acidic clay surface. Polymerization activity was much higher after passivation of the clay with an alkylaluminium co-catalyst. Thus when clay pretreated with methylaluminoxane (MAO) was used to support $Cp_2ZrMe_2$, the resulting catalyst was very active towards ethylene. However, polymerization still took place mostly in the solution phase: the clay was recovered, separate from the polyethylene product, at the bottom of the reactor. Leaching of MAO from the clay surface *via* ligand metathesis presumably allows the formation of highly active metallocenium cations in the solution phase.

While the Ziegler catalyst $Zr(CH_2C_6H_5)_4$ is itself inactive towards α-olefins, it becomes a highly active ethylene polymerization catalyst when anchored on hydroxyl-terminated oxides such as silica or alumina.[25] In the case of the alumina-supported catalyst, Lewis acid sites on the surface may activate the catalyst by abstracting a benzyl ligand from the anchored active site.[26] When a bright yellow solution of $Zr(CH_2C_6H_5)_4$ was added to a slurry of montmorillonite in toluene, there was an immediate color change. Both the solution and the montmorillonite turned dark green, and the solid phase was inactive for the polymerization of ethylene.

The color change suggests that the organozirconium complex decomposed upon contact with the clay. However, an active catalyst was obtained when the montmorillonite was pretreated with either $(CH_3)_3SiCl$ (TMSCl) or triisobutylaluminium (TIBA). Both pretreatments remove water and cap surface hydroxyl groups. Addition of $Zr(CH_2C_6H_5)_4$ to TMS-capped montmorillonite gave a magenta catalyst with appreciable activity (120 kg PE (mol Zr)$^{-1}$ h$^{-1}$) towards ethylene.

A TEM image of the product shows good dispersion of the clay, Fig. 2a. Higher activity (280 kg PE (mol Zr)$^{-1}$ h$^{-1}$) was observed for $Zr(CH_2C_6H_5)_4$ supported on TIBA-capped montmorillonite, however, a less uniform dispersion of the clay in the polyethylene matrix was achieved, Fig. 2b.

Two other polymerization catalysts that are activated by MAO-treated clay without becoming covalently anchored to the clay surface are bis[2,4-di-*tert*-butyl-6-[phenyl(penta-fluorophenylimino)methyl]phenolato]dichlorotitanium[27] and 6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridineiron(II) chloride.[28] Both generated polyethylene upon exposure to $C_2H_4$, but neither product contained incorporated clay.

Taken together, these results demonstrate that strong bonding between catalyst and clay that persists during *in situ* polymerization is required for effective dispersion of clay into the polyolefin matrix. While such interactions do occur for appropriate early transition metal catalysts, their use to produce clay–polyolefin nanocomposites by *in situ* polymerization may be precluded by the need to protect the catalyst from the clay, *via* chemical passivation of its surface. In contrast, the late transition metal catalysts **1** and **2** can be used without such passivation.

Unlike the clay-activated nickel complexes, the clay-supported $Zr(CH_2C_6H_5)_4$ catalyst also polymerizes propylene, giving polypropylenes with melting points of *ca.* 150 °C. The activity of the supported catalyst is *ca.* five times lower towards $C_3H_6$ compared to $C_2H_4$, and propylene uptake ceases when the clay content reaches *ca.* 30% in our small reactors. Nevertheless, such materials may be of interest as master-batches.

The stability of the clay exfoliation in the absence of compatibilizers is a potential issue during processing or other thermal treatments, when phase separation and reaggregation of the clay may occur. Fig. 3 shows TEM analysis of a 10 wt% clay–PE nanocomposite before and after annealing at 170 °C for 30 min, with little evidence for reaggregation. We suspect

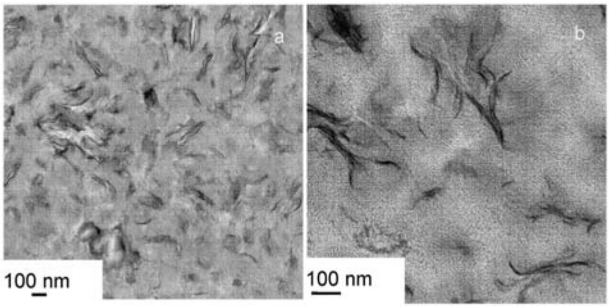

**Fig. 2** TEM images of clay–PE composites generated by *in situ* polymerization with $Zr(CH_2C_6H_5)_4$ supported on (a) TMS–clay (10 wt% clay); and (b) TIBA–clay (5 wt% clay).

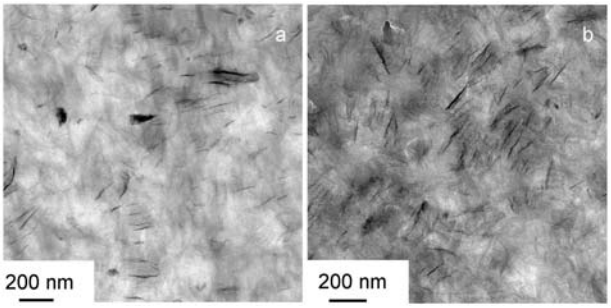

**Fig. 3** TEM of a PE–clay nanocomposite (10 wt% clay) (a) as-prepared, using clay-supported **1**; and (b) after annealing at 170 °C for 30 min.

that the high molecular weight of the PE (*ca.* 500 kg mol$^{-1}$) produced by the clay-supported catalysts **1** and **2**, as well as the high viscosity of the nanocomposites, stabilize the clay dispersion.[29]

The effect of highly-dispersed clay on the mechanical properties of polyolefins is one of the motivations for producing such nanocomposites. At a clay loading of 5 wt%, the polyethylene composite made by clay-supported catalyst **1** under 100 psi $C_2H_4$ has a flexural modulus of 325 MPa (see ESI†). In contrast, the polyethylene produced with $B(C_6F_5)_3$-activated **1** at the same $C_2H_4$ pressure is very soft. When moulded, it deformed so readily that it was impossible to mount in the DMA (dynamic mechanical analysis). The melting point of the composite material is also higher, by 15 °C for the polyethylene produced by clay-supported **1**, compared to $B(C_6F_5)_3$-activated **1**, Fig. 4a. These observations suggest that the clay exerts a significant effect on the mechanical properties of the composite. However, the effect cannot be ascribed entirely to clay reinforcement, because the polymer made by *in situ* polymerization with the heterogeneous catalyst is very different from that produced by the analogous homogeneous catalyst. In particular, the increase in melting point appears to be the consequence of a significantly reduced branching frequency, Fig. 4b. This finding implies that the clay is not behaving simply as a remote Lewis acid activator; it also modifies the relative rates of propagation and chain-walking at the active site during polymerization.

In summary, we have shown that acid-treated montmorillonite activates several kinds of olefin polymerization catalysts without need for organic modification of the clay. However, nanocomposites are formed only with those catalysts that are firmly anchored to the clay surface. Nickel complexes that interact *via* a Lewis basic site on the ligand backbone with a Lewis acid site on the clay surface are particularly effective at causing dispersion of the clay, and require no co-catalysts or scavengers for their activation. The clay dispersion in the polyolefin matrix is stable during annealing. Our on-going investigation focuses on optimizing catalyst activity, controlling polyolefin properties and exploring the properties of these clay-filled polymers.

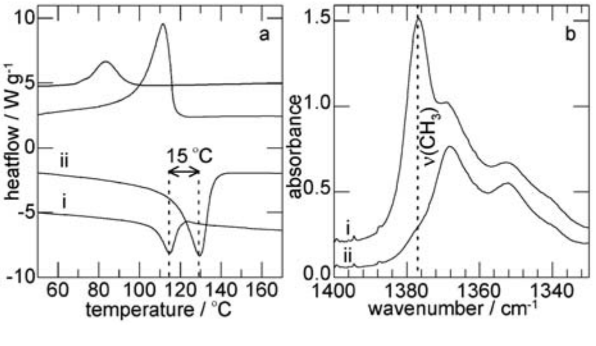

**Fig. 4** Comparison of (a) DSCs; and (b) IR spectra, of PE produced by catalyst **1** activated by (i) $B(C_6F_5)_3$; or (ii) acid-treated montmorillonite.

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