

SHORT COMMUNICATIONS

**Preparation of Novel Magnetic Polyethylene through Polymerization
in Situ Using $\text{Cr}_x\text{Fe}_{3-x}\text{O}_4/\text{AlR}_3/\text{TiCl}_4$ Supported Nanometer
Magnetic Ziegler–Natta Catalyst**

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Audio equipment, office automation equipment and home-use electric appliances are becoming smaller, lighter, more accurate, thinner and longer life span. Much effort, including the exploration of novel magnetic polymer materials, is being done to realize the above features. Novel magnetic polymer materials are a most exciting area in research. Polymer magnetic materials mainly are classed as 'structure type' if magnetic properties arise from polymers themselves and 'filling type' if magnetic properties arise from magnetic fillers. The former is still far from practical industrial production. Polymer magnet of filling type such as plastics magnets in most cases has been used and studied.^{1–3} But it is difficult to compound ferrite powder fillers with polymers, especially with polyethylene due to high special surface of nanometer ferrite powder fillers and differences between nanometer ferrite particle fillers and polyethylene in density and polarity. Therefore, owing to the chemical stability and low water-absorption of polyethylene and easier processing and excellent properties of magnetic polyethylene, magnetic polyethylene with nanometer ferrite particle dispersed well in polymer matrix is attracting attention. Polyethylene containing particles dispersed homogeneously in a matrix can be obtained through polymerization *in situ*.⁴ A new route has been found for preparing magnetic polyethylene with well dispersed nanometer magnetic particle in polymer matrix through coordination polymerization *in situ* on the surface of nanometer magnetic particles used as the support of $\text{Cr}_x\text{Fe}_{3-x}\text{O}_4/\text{AlR}_3/\text{TiCl}_4$ nanometer magnetic Ziegler–Natta catalytic system. The new magnetic polyethylene should find applications in audio equipment, office automation equipment and home-use electric equipment.

EXPERIMENTAL

Polymerization-grade ethylene and propylene (from the Zhen-hai Petroleum Chemical Plant) were purified by passing through four columns with 4A molecular sieve and a hexane solution containing 10 wt% triethylaluminum before polymerization to remove residual traces of moisture. Petroleum ether (bp 90–120°C) of analytical reagent grade was purified before use. Other chemicals (research grade) were commercially obtained.

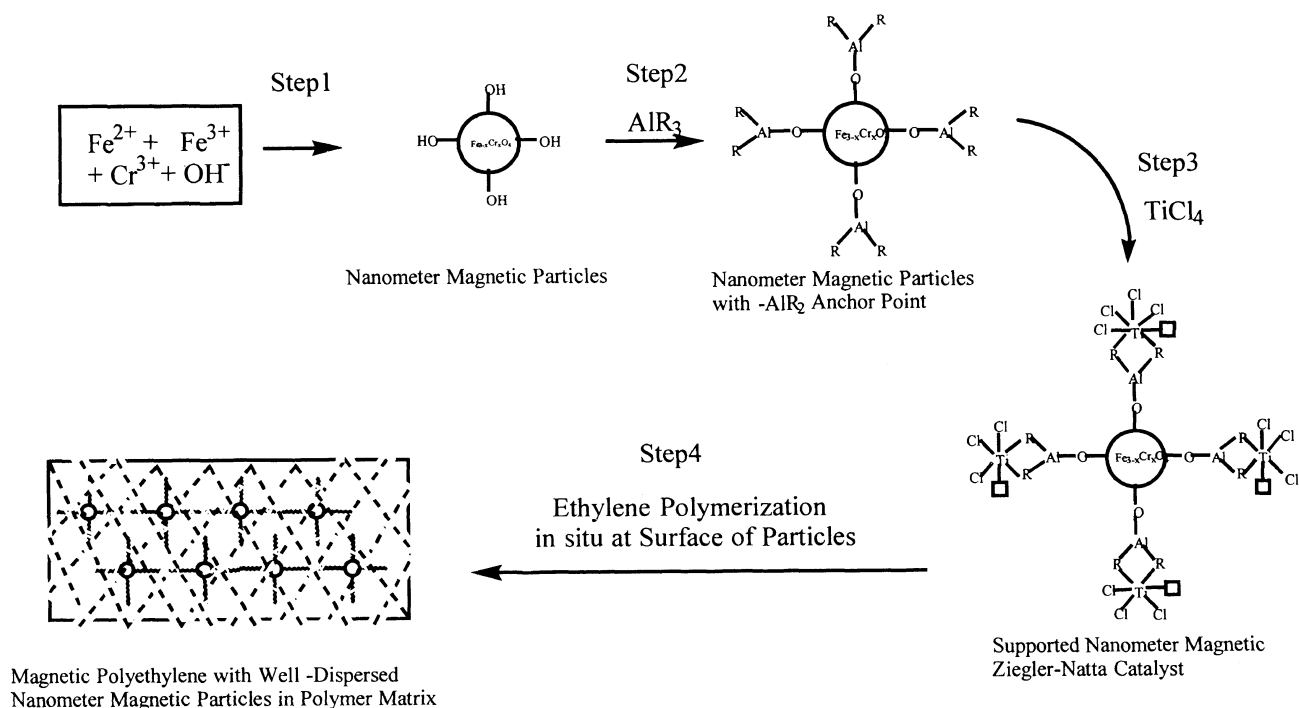
Nanometer particles $\text{Cr}_x\text{Fe}_{3-x}\text{O}_4$ (when $x=0$, Fe_3O_4) have been prepared and studied extensively.^{5–7} Particle diameter and diameter distribution were measured with a Malvern Autosizer 2C instrument.

In a typical preparation of nanometer magnetic catalyst and polymerization, a weighed sample of 12 g nanometer magnetic particle was suspended in 40 mL anhydrous petroleum ether and stirred in a two-neck flask under nitrogen atmosphere. Stoichiometric quantities of organoaluminum compound (for example: AlEt_3) were introduced into the flask and stirred for 0.5 h. The slurry was filtered and the solid washed with anhydrous petroleum ether. 40 mL anhydrous petroleum ether and excess TiCl_4 were introduced into the flask containing nanometer magnetic particles having reacted with organoaluminum compound. The slurry was stirred for another 1 h. The resultant slurry was filtered, washed until no Ti was detected by spectrophotography, dried and used as the supported nanometer magnetic catalyst. Polymerization was carried out at atmospheric pressure in a 200 mL reaction flask provided with a stirrer described elsewhere.^{8–10} 70 mL anhydrous petroleum ether were introduced into the reactor under nitrogen and thermostated at 40°C. Ethylene was rapidly bubbled through the stirred solvent and organoaluminum compound and 1 g supported nanometer magnetic catalyst at an appropriate Al/Ti ratio were added to reactor successively. After the polymerization, the product was washed several times with ethanol and dried in a vacuum oven at 60°C.

RESULTS AND DISCUSSION

The new route of preparing magnetic polyethylene through coordination polymerization *in situ* on the surface of nanometer magnetic particles $\text{Cr}_x\text{Fe}_{3-x}\text{O}_4$ consists of the following four steps (as shown in scheme 1 conceptually): the preparation of nanometer magnetic particles; the reaction between AlR_3 and hydroxyl on the surface of nanometer magnetic particles to form anchor points— AlR_2 for TiCl_4 ; the addition of TiCl_4 and Ti coordination with anchor point on the surface of nanometer magnetic particles to form polymerization active centers; and finally the introduction of ethylene into reaction flask and ethylene polymerizing on the surface of nanometer magnetic particles to produce the magnetic polyethylene with well dispersed nanometer

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Scheme 1. New route for preparing magnetic polyethylene with well dispersed nanometer magnetic particle in a polymer matrix.

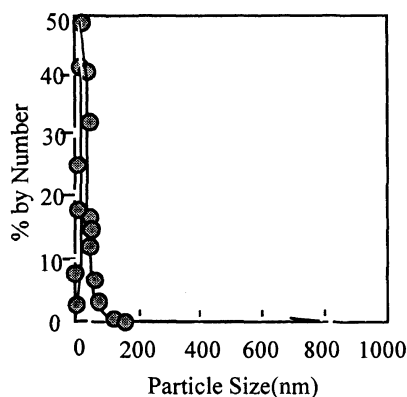


Figure 1. Nanometer magnetic particles with narrow size distribution (reaction temperature $T=80^\circ\text{C}$, reaction time $t=40$ min, and pH 11).

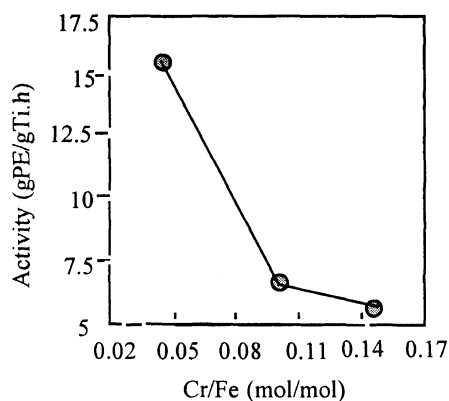


Figure 2. Effects of Cr/Fe in $\text{Cr}_x\text{Fe}_{3-x}\text{O}_4$ on polymerization activity.

magnetic particles in polymer matrix.

Chemical coprecipitation based on the precipitation principle of Fe^{2+} , Fe^{3+} , and Cr^{3+} in basic solution has long been used for obtaining nanometer $\text{Cr}_x\text{Fe}_{3-x}\text{O}_4$ (when $x=0$, Fe_3O_4) particles.^{11,12} Usually, reaction temperature, reaction time and pH are important factors in the manufacture. XRD and particle distribution showed the nanometer magnetic $\text{Cr}_x\text{Fe}_{3-x}\text{O}_4$ particles with narrow particle size distribution (as shown in Figure 1) to be obtained at $T=80^\circ\text{C}$, reaction time $t=40$ min and pH 11. Typical particle mean diameter were ~ 20 nm with saturation magnetization $\sigma_s=52$ eum g^{-1} . Surface OH of magnetic particles, mainly arising from H_2O adsorbed chemically on the surface have been observed.¹³ Reaction between $\text{Cr}_x\text{Fe}_{3-x}\text{O}_4$ and AlR_3 to form anchor point $-\text{OAlR}_2$ of polymerization active center is shown as step 2 in Scheme 1.¹⁴ Many organic aluminum compounds such as $\text{Al}_2\text{Et}_3\text{Cl}_3$, AlEt_2Cl , AlEt_3 , and $\text{Al}(\text{iBu})_3$ can be used for forming anchor point $-\text{OAlR}_2$.

In step 3, Ti content loaded on $\text{Cr}_x\text{Fe}_{3-x}\text{O}_4$ is

Table I. Influence of wt% nanometer magnetic particle on σ_s

Sample	wt% Nanometer magnetic particle	$\sigma_s/\text{eum g}^{-1}$
$\text{Cr}_x\text{Fe}_{3-x}\text{O}_4$	100	52
$\text{Cr}_x\text{Fe}_{3-x}\text{O}_4/\text{PE-1}$	75.3	39
$\text{Cr}_x\text{Fe}_{3-x}\text{O}_4/\text{PE-2}$	72.1	37

$\text{Ti} \approx 2.5\%$. Polymerization of supported $\text{Cr}_x\text{Fe}_{3-x}\text{O}_4/\text{AlEt}_3/\text{TiCl}_4$ nanometer magnetic catalyst roughly was the same as described previously.^{2,3,11} On increasing Cr/Fe in $\text{Cr}_x\text{Fe}_{3-x}\text{O}_4$, polymerization activities decrease as shown in Figure 2. The effect of Cr/Fe on the polymerization activities remains unclear. Decrease in polymerization activities may possibly arise from the electronic structure of Cr. The polymerization was essentially unaffected by Al/Ti at Al/Ti of 2–5.5 (mol/mol) as shown in Figure 3. Al/Ti insensitivity due to supporting of active centers on $\text{Cr}_x\text{Fe}_{3-x}\text{O}_4$ may be expected. Generally, the supported Ziegler–Natta catalyst has less Al/Ti sensitivity when comparing supported

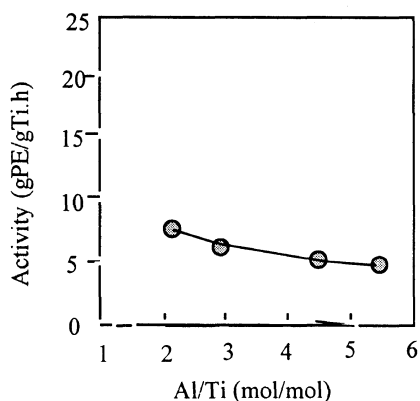


Figure 3. Effects of Al/Ti in $\text{Cr}_x\text{Fe}_{3-x}\text{O}_4/\text{AlEt}_3/\text{TiCl}_4$ on polymerization activity.

and soluble catalysts. Polymerization activities was essentially unaffected by polymerization time of 1 h and ethylene polymerization using supported $\text{Cr}_x\text{Fe}_{3-x}\text{O}_4/\text{AlEt}_3/\text{TiCl}_4$ nanometer magnetic catalyst was much more stable than that using common Ziegler–Natta catalysts.^{8–10} More stable polymerization rate is of benefit in forming dense film covering nanometer magnetic particles. The saturation magnetization σ_s of resultant product virtually depends on the content of nanometer magnetic particle dispersed in polymer matrix. The influence of wt% nanometer magnetic particle on σ_s are summarized in Table I.

The adsorption of H_2O on the surface of magnetic particle decreases σ_s of magnetic particle,¹² especially nanometer particles. H_2O adsorbed on the surface of magnetic particle was completely removed and the surface was covered by a dense polymer layer in this preparation route. Therefore, resultant novel magnetic polyethylene is stable even if exported to air for long period. The advantage of preventing magnet corrosion was evident for these plastic magnet prepared through this route due to the dense polymer cover layer on nanometer magnetic particles. Owing to nanometer lever homogeneity which cannot be obtained by other methods up to now, the product is easier to process.

Rare earth magnetic particle/ $\text{AlEt}_3/\text{TiCl}_4$ and $\text{Fe}_3\text{O}_4/\text{AlEt}_3/\text{TiCl}_4$ catalytic systems instead of $\text{Cr}_x\text{Fe}_{3-x}\text{O}_4/\text{AlEt}_3/\text{TiCl}_4$ catalytic systems were examined to obtain magnetic polyethylene with well dispersed nanometer

magnetic particles in a polymer matrix. On using a mixture of ethylene and propylene as monomer, the magnetic rubber with well dispersed nanometer magnetic particles in the polymer matrix also can be prepared at the same route. The magnetic plastic and rubber may meet the requirements for miniaturization. However, the preparing route provides a step toward initiating a series of new functional polymer materials, such as conductive polymers and optic polymers with well dispersed nanometer conductive and optic particles in a polymer matrix.

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