Stereoregular, alternating ethylene–norbornene copolymers from monocyclopentadienyl catalysts activated with non-coordinating discrete anions

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Abstract

Cyclic olefins copolymerize efficiently with ethylene using metallocene catalysts to make rigid engineering polyolefins with high chemical homogeneity. Materials with a high chemical homogeneity have value because they show reduced light scattering resulting in excellent clarity. The ultimate chemical homogeneity in a two component copolymer occurs when an alternating sequence distribution is achieved. Low symmetry bis-metallocenes have been shown to make alternating, stereoregular cyclic olefin copolymers under the right process conditions. These copolymers are semicrystalline and have high melt temperatures. Herein we report two group 4 monocyclopentadienyl catalyst systems that yield semicrystalline ethylene/norbornene copolymers over a range of reactor conditions. The clear copolymers have glass transition temperatures over 110°C and melt temperatures over 240°C. Further characterization data is presented and a short discussion of a plausible polymerization mechanism is given. © 1998 Elsevier Science B.V.

Keywords: Cyclic olefin copolymer; Alternating; Stereoregular; Ethylene; Norbornene; Hemi-isotactic; Metallocene

1. Introduction

A recent US patent that teaches a process for making cyclic olefin copolymers with high chemical homogeneity from metallocene catalysts has been issued to Hoechst AG [1]. Materials with a high chemical homogeneity are of value because they exhibit reduced light scattering resulting in excellent clarity. The ultimate chemical homogeneity in a two component copolymer occurs when an alternating sequence distribution is achieved. Disclosed was $R_2C(Flu)(3\text{-}MeCp)ZrCl_2$ [R = Me or Ph] (**1a**), a C_1-symmetric, bridged, metallocene that yielded

alternating copolymers over a range of reactor conditions and resulted in semi-crystalline ethylene/norbornene copolymers with melt temperatures between 235 and 285°C. Evidence for the alternating sequence distribution and the conformational regularity were suggested by a unique and simpler chemical shift pattern in the ^{13}C NMR [2]. The stereoregular, alternating architecture of these semicrystalline copolymers is due to stereospecific polymerization by the metallocene. **1a** was first synthesized at Hoechst [3] and reported to make a new polypropylene microstructure labeled 'syndio-isoblock' and later studied by Ewen as a hemi-isospecific propylene catalyst [4]. Under proper process conditions (excess norbornene) complex **1a** yields

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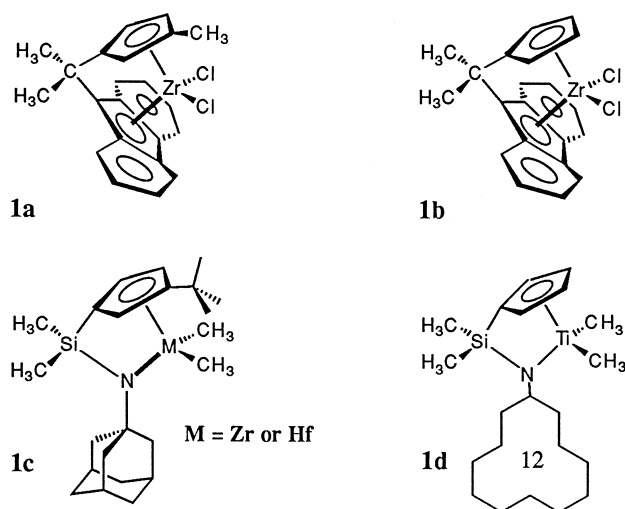[*] Corresponding author. Fax: +1-7137-4251387.

Fig. 1. Metallocene structures.

crystalline ethylene/norbornene copolymers whereas complex **1b**, which does not contain the methyl substituent, yields amorphous ethylene/norbornene copolymers (Fig. 1). To date **1a** is one of only a few metallocenes reported to yield either hemi-isotactic polypropylene or stereoregular alternating copolymers.

Herein we report two group 4 monocyclopentadienyl catalyst systems (**1c**) that yield semicrystalline ethylene/norbornene copolymers over a range of reactor conditions. The clear copolymers have T_g over 110°C and melt temperatures over 240°C. Further characterization data is presented and a short discussion of a plausible polymerization mechanism is given.

2. Experimental

2.1. Catalyst preparation

Synthesis of the Hf and Zr analogs of **1c** were made by methods previously disclosed [5].

2.2. Catalyst activation

μ-Me$_2$Si(3-*tert*-butyl cyclopentadienyl) (adamantylamido)HfMe$_2$ (**Hf 1c**, 40 mg, 0.075 mmol) was preactivated with dimethylanilinium-tetrakis(pentafluorophenyl)borate [DMAH$^+$ B(pfp)$_4^-$] (55 mg, 0.069 mmol) in toluene (3 ml) under an inert atmosphere. This mixture was allowed to activate until the evolution of methane stopped (5–10 min) and then sealed for transfer to the reactor.

2.3. Copolymer synthesis

Toluene (775 ml) was transferred to a 2 l reactor and stirred under N$_2$ purge while the temperature was equilibrated at 60°C. Norbornene (242 g) was added to the reactor as an 85 wt% solution in toluene by cannula. Tri-isobutyl aluminum in toluene (1.0 ml, 0.4 mmol) was added by cannula as scavenger. The reactor was sealed and the solution saturated with ethylene at 21 psi (gauge). The activated catalyst was added by quickly venting the ethylene and transferred by cannula into the liquid phase under an ethylene purge. The reactor was then sealed and quickly repressured with ethylene. This mixture was stirred (0.4 h) at constant temperature and ethylene pressure. The reaction was monitored by ethylene uptake. When ethylene consumption diminished or ceased, the

reactor was vented and the contents poured into isopropanol/acetone to precipitate the polymer. The product was filtered, washed and dried at 80°C in a vacuum oven for 16 h. The resulting white solid (33.1 g) showed a melting endotherm by DSC of 258°C, a glass transition of 115°C and 48.2 mol% norbornene by ^{13}C NMR.

Similarly, μ-Me$_2$Si(3-*tert*-butyl cyclopentadienyl)(adamantylamido)ZrMe$_2$ (**Zr 1c**, 30 mg, 0.069 mmol) was preactivated with DMAH$^+$ B(pfp)$_4^-$ (52 mg, 0.065 mmol) in toluene (3 ml) under an inert atmosphere. Reaction conditions were identical to above with the following modifications: 600 ml toluene, 107 g norbornene and 15 psi (gauge) ethylene. After workup the resulting white solid (30.4 g) showed a melting endotherm by DSC of 250°C, a glass transition

of 118°C (see Fig. 3) and 48.9 mol% norbornene by ^{13}C NMR.

3. Characterization

3.1. ^{13}C NMR

Five resonances would be expected in the carbon spectrum of a perfectly alternating stereoregular ethylene/norbornene copolymer. The spectrum of the product from **Hf 1c**, Fig. 2, approaches this simplicity with only five major resonances assigned to the four norbornene carbons and one ethylene carbon in alternating NENEN sequences [6,7]. The resonances known to be associated with isolated norbornene units (EENEE) are also seen (labeled ISO) as minor
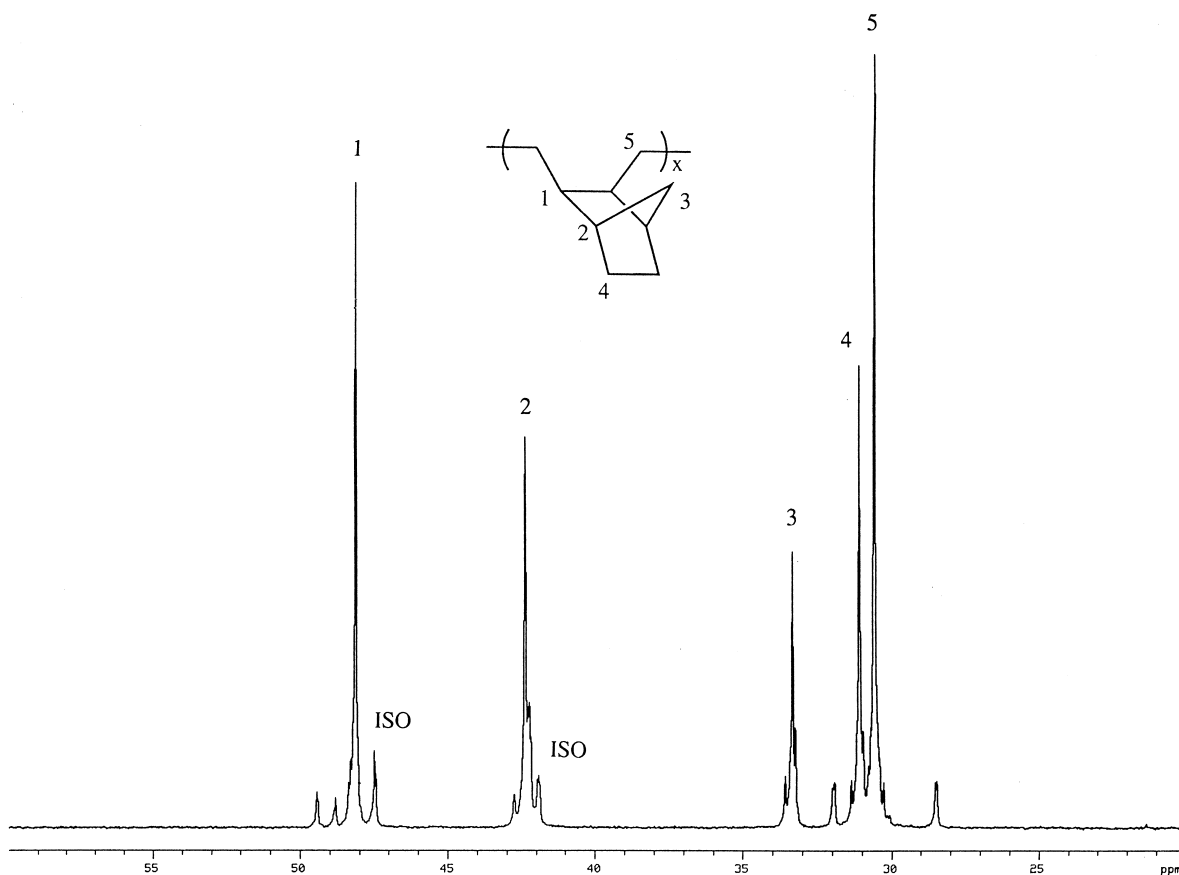

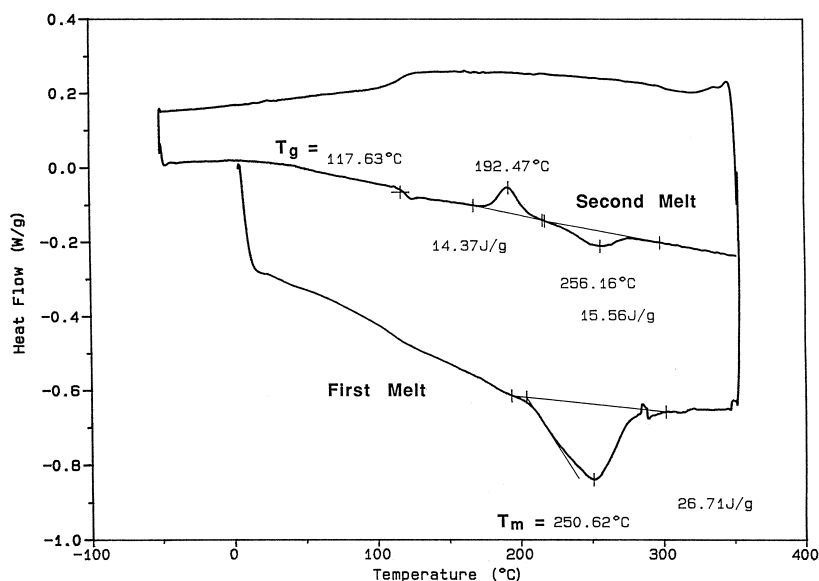Fig. 2. C NMR of the product from Hf **1c**.

Fig. 3. DSC profile of the product from Zr **1c**.

resonances suggesting occasional ethylene–ethylene diads [1]. Copolymers with occasional ethylene diads are required to give the solubility needed to obtain a spectrum. Down field from the alternating resonances are found minor resonances thought to be associated with occasional orientation mistakes. The simplicity of this spectrum is significant because it confirms that the majority of the norbornenes are alternating and that the majority of norbornene orientations are stereoregular. The product from **Zr 1c** gave a virtually identical ^{13}C NMR spectrum.

3.2. DSC

The scanning calorimetry profiles of the products made from **1c** show evidence for a melting endotherm around 250°C on the first melt. Generally there is less of an endotherm evident on the second melt. It is thought that copolymer chains can crystallize on precipita-

tion from dilute solution, but cannot recrystallize from the amorphous melt due to restricted chain mobility. Fig. 3 is the first and second melt DSC profile for a semicrystalline copolymer made from **Zr 1c.** The first melt profile for a copolymer made from **1d**, a higher symmetry catalyst with a bulky amido group and a unsubstituted symmetrical Cp ring, shows no melting endotherm. The product from **Hf 1c** gave a virtually identical DSC trace.

3.3. DMTA

Further evidence for the crystallinity of the products from **1c** is seen in the plot of the elastic modulus versus temperature, Fig. 4. At similar norbornene content and molecular weight, the copolymer from **Hf 1c** is dramatically different than that of a copolymer made from a higher symmetry catalyst. The alternating stereoregular copolymer has a lower T_g than its statistical equivalent, a phenomena associated with symmetrical chains [8] and references therein. Also, the decay of the elastic moduli in the stereoregular copolymer has a shallow slope above its T_g compared to the random copoly-

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[1] Isolated norbornene resonances were assigned from the spectrum of EN copolymers with less than 2 mol% norbornene content.
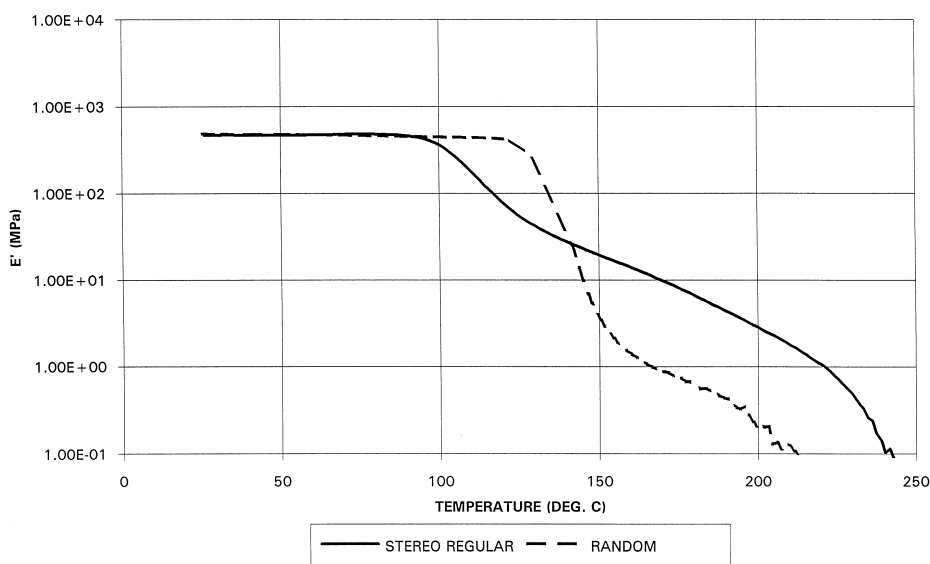
Fig. 4. DMTA scan of the product from Hf **1c**.

mer. This slow decay of the elastic modulus is typical of semi-crystalline copolymers where the crystallites form a network and thereby provide some structural integrity up to their melting point. Further evidence for a crystalline network can be found in the oscillatory shear viscoelastic behavior of the two copolymers. For example, at 190°C, the storage modulus (G') is much greater than the loss modulus (G'') at all frequencies for the alternating stereoregular copolymer, indicating that it is a more rubbery viscoelastic material than the randomly oriented material. DMTA of the product of **Zr 1c** was not measured.

4. Results and discussion

These monocyclopentadienyl catalysts are ideal candidates for the stereospecific copolymerization of ethylene and norbornene since the dissimilar ligands provide ample routes to low symmetry structures and because they are known to incorporate comonomers efficiently [5,9]. **1c** was chosen because of the blocking effect the bulky adamantyl group would provide and the directing influence the *tert*-butyl group would provide. A plausible mechanism for the formation of alternating stereoregular ethylene/ norbornene copolymer may be one that is similar to that proposed for **1a** in hemi-isospecific propylene polymerizations [4], where every other propylene has the same orientation and the propylene's between these have random orientation (additional lead references include Refs. [10,11]).

If one considers that norbornene is directed in the same manner as the oriented propylenes and that the ethylene insertions are directed as the random propylenes then a straight forward explanation can be proposed.

To begin, the catalysts generated from **1c** have a ligand structure that sterically prevents adjacent norbornene insertions. This is proved by the lack of norbornene diad signals in the ^{13}C NMR [6] Second, the large excess of norbornene limits the number of ethylene–ethylene insertions. The polymerization results are best explained by an alternating or migratory insertion step in which the growing chain migrates from side to side after monomer insertion (Refs. [12,13] and references therein). However, a mechanism in which the polymer chain resided in the metal's center orbital and ethylene coor-

dinated at either side, but norbornene only at the least crowded side, would also be consistent. The actual mechanism of polymer chain growth is still under debate.

5. Conclusions

Stereoregular, alternating ethylene–norbornene copolymers can be made with high comonomer conversion and catalyst activity using the C_1-symmetric monocyclopentadienyl complexes. These high performance polyolefins have high melt temperatures and excellent clarity making them potential candidates in engineering applications.

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