

## Higher Order Polymer Architectures Containing Ethylene and Functionalized Comonomers

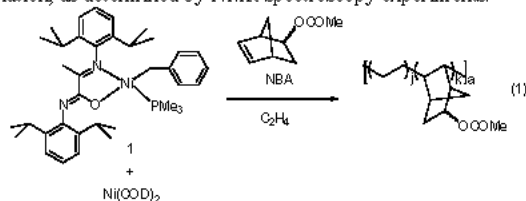
*Guillermo Bazan,\* Steve Diamanti, Robert Coffin, Atsushi Hotta, Vikram Khanna, Glenn Fredrickson and Ed Kramer*

Department of Materials and Institute for Polymers and Organic Solids, University of California, Santa Barbara, California, 93106  
bazan@chem.ucsb.edu

### Introduction

Initiators that provide for the living polymerization[1] of ethylene and 1-alkenes constitute a special area of attention since they allow for accessing macromolecular architectures such as block- and tapered-copolymers,[2] star-shaped structures,[3] end functionalized polymers [4] and grafted backbones.[5],[6] The macromolecular structure impacts the solid state arrangement of the polymer chains and therefore physical and mechanical properties. Living polymerization characteristics are obtained when there is negligible termination or chain transfer within the timescale of the propagation reaction.

We recently disclosed that the activation of [N-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenyl-imino)-propanamide]Ni( $\eta^1$ -CH<sub>2</sub>Ph)(PMe<sub>3</sub>) (1) with Ni(COD)<sub>2</sub> (Ni(COD)<sub>2</sub> = bis(1,5-cyclooctadiene)nickel) generates an active site that is capable of polymerizing ethylene and 5-norbornene-2-yl acetate (NBA) in a quasi-living fashion (Equation 1).[7] The polymerization reaction shows a linear increase in molecular weight with increasing reaction time, however the molecular weight distributions of the products show polydispersities (PDIs) that are larger than the ones expected from a living system. Deviations from a living behavior are likely due to the precipitation of the product as the reaction proceeds and to inefficient initiation, as determined by NMR spectroscopy experiments.



In this presentation we will discuss applications for synthesizing and tapered copolymers and mechanistic work that aims to delineate the active species in these polymerization reactions.

### Experimental

All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk-line techniques. All reagents were used as received from Aldrich unless otherwise specified. Ethylene was purchased from Matheson Tri-Gas (research grade, 99.99% pure) and was further purified by passage through an oxygen/moisture trap (Matheson model 6427-4S). Toluene, THF, hexane, and pentane were distilled from benzophenone ketyl. All polymerization reactions were carried out in a Parr autoclave reactor as described below. Toluene for polymerization was distilled from sodium/potassium alloy. The synthesis of compounds 2, 3, 4, 5 and 6 used procedures similar to the literature procedure for 1 and were purified by recrystallization. NMR spectra were obtained using a Varian Unity 400 or 500 spectrometer. Polymers were dried overnight under vacuum and the polymerization activities were calculated from the mass of product obtained. These values were to within 5% of the calculated mass by looking at the ethylene volume by use of a mass flow controller. The polymers were characterized by GPC analysis at 135 °C in *o*-dichlorobenzene (in a Polymer Laboratories, High Temperature Chromatograph, PI-GPC 200). Polymer melting points were measured on a TA Instruments differential scanning calorimeter (model DSC 2920) at a rate of 10 °C/min for two cycles using a temperature range of 50-200 °C. <sup>1</sup>H NMR spectra of the polymers were obtained in a mixed solvent (C<sub>6</sub>D<sub>6</sub>/1,2,4-trichlorobenzene in a 1:4 volume ratio) at 115 °C. Elemental analysis was performed on a Leeman Labs Inc. CE440 Elemental Analyzer and a Control Equipment Corporation 440 Elemental Analyzer. The CHN analyzer provides a precision of +/- 0.3 weight percent. FTIR spectra were recorded on a Bruker Vector-22 spectrophotometer using KBr pellets and in solution using C<sub>6</sub>D<sub>6</sub> as solvent.

**Typical Tapered Copolymerization of Ethylene and 5-NBA; [1]<sub>0</sub> = 0.15M.** A typical copolymerization is performed as follows. Inside a glove box a metal reactor was loaded with 2 (20 μmol; 31.6 mg), Ni(COD)<sub>2</sub> (50 μmol; 27.6 mg), 1 (4.50 mmol; 0.685 g), and toluene such that the final volume of this solution was 30 mL. The metal reactor was sealed inside the glove box and was attached to a vacuum/nitrogen line manifold. Ethylene was fed continuously into the reactor at 200 psi and the pressurized reaction mixture was stirred at 20 °C. Ethylene was vented after a specific reaction time and acetone was added to quench the polymerization. The precipitated polymer was collected by filtration and dried under high vacuum overnight

### Results and Discussion

#### Synthesis of Tapered Copolymer Structures

It occurred to us that a batch reaction whereby the ethylene pressure is kept constant and the concentration of NBA is allowed to deplete by incorporation into the polymer structure would lead to the desired tapered structure. Under these circumstances, the growing chain is rich in NBA at the start of the reaction. As the reaction proceeds, [NBA] decreases, leading to an increase in the fraction of ethylene incorporated into the chain. The final structure of the polymer was anticipated to have a polar amorphous terminus (rich in NBA) and a non-polar, semicrystalline chain (primarily polyethylene) on the other end. The overall procedure is technically simple. A reactor is initially filled with a solution of the initiator mixture and NBA. Polymerization takes place when ethylene is added and is terminated after a chosen reaction time.

Table 1 summarizes of a set of polymerization reactions where the ethylene pressure was kept constant at 200 psi. Examination of Table 1 shows that there is a progressive increase in average molecular weight with reaction time, even up to 120 minutes. This increase is consistent with the quasi-living characteristics of the polymerization reaction. Ideal living characteristics are not achieved due to reaction variables such as the varying levels of incorporation of NBA into the copolymer chain and the precipitation of the product after 45 minutes of reaction time. Copolymers with larger fractions of NBA are soluble in toluene, whereas the ethylene-rich segments formed at later stages of the reaction have poor solubility in toluene. Table 1 also shows that the overall fraction of NBA in the product decreases with longer reaction times. The chains thus have the highest fraction of NBA at the beginning, when [NBA] is at its maximum

Table 1. Summary of polymerization reactions.

Entry	Reaction Time (min.)	M <sub>n</sub> (kg/mol)	PDI	Mol % NBA
1	4	10 ± 1	1.3	18 ± 1
2	5	18 ± 1	1.2	18 ± 1
3	8	27 ± 2	1.2	14 ± 1
4	10	28 ± 1	1.3	14 ± 1
5	20	37 ± 3	1.4	12 ± 1
6	25	47 ± 3	1.4	11 ± 1
7	35	55 ± 5	1.4	10 ± 1
8	45	63 ± 3	1.3	9 ± 1
9	60	94 ± 10	1.5	6 ± 1
10	80	109 ± 1	1.5	6 ± 1
11	100	136	1.6	5 ± 1
12	120	170	1.5	4 ± 1

The products listed in Table 1 were examined by transmission electron microscopy (TEM). No indication of phase separation was observed for polymers with M<sub>n</sub> < 63 kg/mol (reaction time < 45 minutes). As shown in Figure 1A, a lamellar morphology, where semicrystalline PE layers (light) alternate with amorphous copolymer layers, is observed for a polymer with M<sub>n</sub> = 63 kg/mol (Table 1, Entry 8). For the products obtained after longer reaction times, the morphology changes from alternating lamellar sheets to a less organized phase (Figure 1B), in which the polyethylene-rich segments form the matrix and the NBA rich block forms smaller, cylindrical-like domains. While the tapered structure of the products allows us to create microphase-separated structures whose morphologies are a function of polymer chain length, there are limitations. For example, it is not possible to create short gradient copolymers that order into

microphase separated morphologies. This is due to the finite chain length needed for the polymer to taper from a segment rich in NBA to a sufficiently incompatible polyethylene sequence

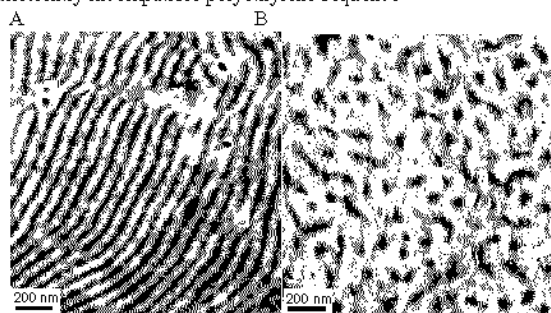


Figure 1. (A) Transmission electron micrograph (TEM) of Table 1, Entry 8 ( $M_n = 63$  kg/mol). The morphology is lamellar, where semicrystalline PE layers (light) alternate with amorphous copolymer layers. The dark spots are caused by stain contamination by  $\text{RuO}_4$ . (B) TEM of Table 1, Entry 12 ( $M_n = 170$  kg/mol). The morphology is a poorly organized hexagonal phase, where amorphous copolymer cylinders are embedded in a semicrystalline PE matrix (light). PE crystals can also be observed in the matrix.

#### Nature of the Initiating Species

A series of nickel complexes containing  $\alpha$ -iminocarboxamide,  $\eta^1$ -benzyl and  $\text{PMe}_3$  ligands were synthesized to identify structural features of neutral Ni complexes that can be employed in ethylene polymerization and ethylene/functionalized norbornene copolymerizations. Variations in steric bulk on aryl substituents in the  $\alpha$ -iminocarboxamide framework were used to probe  $N,N$ - vs.  $N,O$ -binding modes. When the steric bulk is sufficiently large, as in **1**, [ $N$ -(2,6-diethylphenyl)-2-(2,6-diethylphenylimino)propanamidato- $\kappa^2N,O$ ]( $\eta^1$ - $\text{CH}_2\text{Ph}$ )( $\text{PMe}_3$ )nickel (**2**), [ $N$ -(2,6-methyl-isopropylphenyl)-2-(2,6-methyl-isopropylphenylimino)propanamidato- $\kappa^2N,O$ ]( $\eta^1$ - $\text{CH}_2\text{Ph}$ )( $\text{PMe}_3$ )nickel (**3**), one observes  $N,O$ -binding. In the case of [ $N$ -(2,6-dimethylphenyl)-2-(2,6-dimethylphenylimino)propanamidato]( $\eta^1$ - $\text{CH}_2\text{Ph}$ )( $\text{PMe}_3$ )nickel (**4**), both  $N,O$ - and  $N,N$ -bound can be obtained and isolated; the  $N,N$  structure is the thermodynamic product.  $N,N$  products are observed with smaller ligands, as in [ $N$ -phenyl-2-(2,6-diisopropylphenylimino)propanamidato- $\kappa^2N,N$ ]( $\eta^1$ - $\text{CH}_2\text{Ph}$ )( $\text{PMe}_3$ )nickel (**5**) and [ $N$ -(2,6-diisopropylphenyl)-2-(phenylimino)propanamidato- $\kappa^2N,N$ ]( $\eta^1$ - $\text{CH}_2\text{Ph}$ )( $\text{PMe}_3$ )nickel (**6**). Ethylene polymerization, upon activation with  $\text{Ni}(\text{COD})_2$ , is observed only with the  $N,O$ -bound species. NMR spectroscopy shows that addition of  $\text{Ni}(\text{COD})_2$  to **5** and **6** results in removal of the phosphine and the formation of an  $\eta^3$ -benzyl fragment. Furthermore, the phosphine-free complex [ $N$ -(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)propanamidato- $\kappa^2N,N$ ]( $\eta^3$ - $\text{CH}_2\text{Ph}$ )nickel (**7**) is also inactive toward ethylene polymerization. The molecular structure of **7**, as determined by single crystal X-ray diffraction studies is shown in Figure 2.

ORTEP diagram of the molecular structure of **7**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Figure 4. Molecular structure of **7** drawn at 50 % probability. Hydrogen atoms were omitted for clarity.

These observations suggest that ethylene polymerization is preferentially initiated by nickel complexes with  $N,O$ -bound  $\alpha$ -iminocarboxamide ligands.

#### Conclusions

Ni complexes based on  $\alpha$ -iminocarboxamide ligands provide excellent control over the types of polymer structures that can be attained using ethylene and NBA. The polar nature of these polymers makes them potentially interesting in applications such as stabilizers of polymer alloys. Tapered copolymers can be obtained via a very simple single batch mode.

The nature of the initiating species in Equation is now better understood. This mechanistic information is now being used to develop single site initiators that should offer more control over the polymerization reactions.

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