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Communications to the Editor

Addition Polymerization of Cyclopentene with Nickel and Palladium Catalysts

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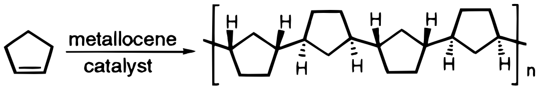
α-Diimine complexes of Ni and Pd catalyze the rapid polymerization of ethylene and α-olefins to high molecular weight polymers.[1,2] We report here that polymerization of cyclopentene with these catalysts gives high molecular weight, semicrystalline addition polymers that are moderately isotactic and have a new crystalline form. They have physical properties unlike any previously reported polycyclopentene.

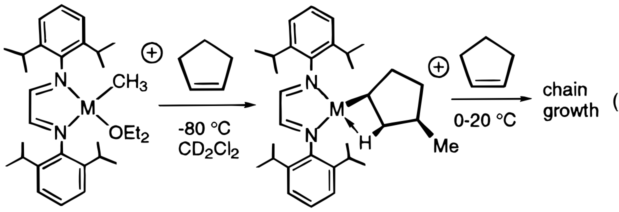
Although ring-opening metathesis polymerization of cyclopentene is facile, there are few reports of addition polymerization of cyclopentene.[3−5] A recent advance that has attracted considerable attention is the polymerization of cyclopentene with a C_2 symmetric zirconium metallocene catalyst by Kaminsky to give a highly crystalline addition polymer with a melting point of 395 °C.[6] Further characterization of this polymer by Collins[7] revealed that it is highly isotactic with cis-1,3-enchainment (eq 1).



(1)

On the basis of comparison of published X-ray data, it appears that the polycyclopentene reported earlier by Boor probably also contained some of the highly isotactic composition.[4,6] Other metallocene catalysts produce a range of structures including atactic *cis*-1,3-polycyclopentene[8,9] and polycyclopentene containing a mixture of cis and trans-1,3-enchainment.[7−9] All polycyclopentenes prepared with metallocene catalysts, including the highly isotactic material reported by Kaminsky, have low molecular weights ($M_n \leq 2000$ by end group analysis of published NMR spectra).

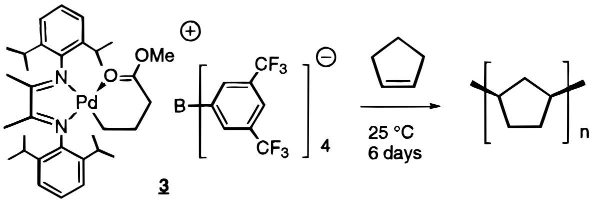
Low-temperature ^{1}H NMR experiments show that cyclopentene reacts rapidly with the metal−methyl bond of cationic Ni and Pd α-diimine complexes **1** and **2** at −80 °C to give insertion products with agostic *β*-hydrogens. The NMR spectra are consistent with the 1,3 isomer shown in eq 2. The presumed initial products of cis-1,2 insertion are not observed; apparently, they rearrange rapidly to the more stable cis-1,3 complexes. When these insertion products are warmed in the presence of excess cyclopentene, chain growth is observed. The complexity of the ^{1}H NMR spectra preclude assignment of the structure of the growing chain. The organic products isolated from polymerization of cyclopentene with **2** at 25 °C are olefin-ended oligomers (^{1}H NMR, ^{13}C NMR, IR, GC−mass spec), suggesting that chain transfer to monomer limits molecular weight growth.



(2)

M = Ni(**1**), Pd(**2**)
anion = $B[3,5-(CF_3)_2C_6H_3]_4^-$

Palladium catalyst **3**,[10] a close relative of catalyst **2**, polymerizes cyclopentene to high molecular weight products (eq 3, Table 1). Polymerizations carried out in neat cyclopentene quickly become heterogeneous as the polymer precipitates from solution. The polymer is insoluble in common organic solvents at room temperature but dissolves readily at 135 °C in both decahydronaphthalene and 1,2,4-trichlorobenzene. DSC of this polymer shows a weak T_g at about 100 °C and a broad melting transition with an onset just above the T_g and an end point of 241 °C. The polymer can be pressed at 290 °C to give clear tough films. A sample of the polymer made with the $[SbF_6]^-$ variant of catalyst **3** was characterized by several ^{13}C NMR solution techniques: comparison of chemical shifts to model compounds,[7] a DEPT spectrum to distinguish methylene and methine carbons, and a 2D INADEQUATE spectrum to establish carbon−carbon connectivity. The NMR results conclusively establish a cis-1,3-enchainment of cyclopentene in the polymer (eq 3).



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(3)

Ni complexes **4**−**6** in combination with $Et_3Al/B(C_6F_5)_3$ cocatalysts[11−13] also polymerize cyclopentene to high molecular weight polymers with cis-1,3-enchainment. The reaction mixtures are initially homogeneous but quickly become hetereogeneous as polymer precipiates. Virtually all of the intense red to purple color of the Ni

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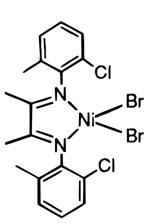
Table 1. Polymerization and Hydrooligomerization of Cyclopentene[a]

cat.	TON[b]	M_w[c]	M_w/M_n	T_m end (°C)	ΔH_f (J/g)	mm (%)	mr (%)	rr (%)
3	3130	251 000	2.49	241	13	26.1	50.7	23.2
4	5580	78 800	2.80	265	16	29.6	49.6	20.7
5	3870	44 800	2.87	285	20	32.6	49.0	18.4
6	3770	*d*	*d*	320	32	40.8	46.0	13.3
6	82[e]	*d*	*d*	330	67	44.1	44.6	11.3

[a] Monomer:cat = 10 000 reactions in neat cyclopentene at room temperature, 7 days. The Ni catalysts were activated by addition of Et_3Al (3 equiv/Ni) to a stirring suspension of (ligand)$NiBr_2$ and $B(C_6F_5)_3$ (3 equiv/Ni) in cyclopentene. Triad analysis is based on GC of the hydropentamers. [b] Turnover number is the molar equivalents of monomer polymerized per molar equivalent of Ni or Pd. [c] GPC in 1,2,4-trichlorobenzene at 135 °C vs polyethylene, infrared detector. [d] Solubility too low for GPC. [e] Reaction conditions: 0 °C, 1 day.



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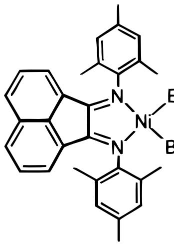

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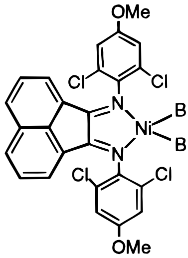

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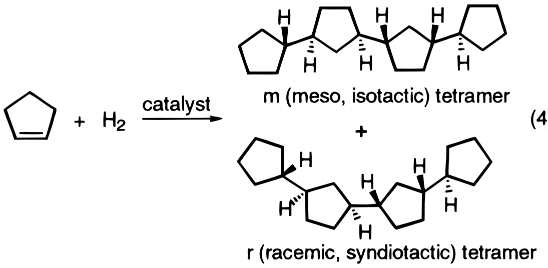
catalyst is contained in the precipitated polymer phase. Alternative cocatalysts $EtAlCl_2$ (50 equiv/Ni) or isobutyl-modified methylaluminoxane (100 equiv/Ni, Akzo Nobel MMAO-3A) give similar results. Polymers made from the Ni catalysts also have broad melting transitions. The end-of-melting point ranges from 265 to 330 °C and varies with the catalyst and the polymerization temperature (Table 1).

We attribute the differences in melting behaviors of these polymers to differences in tacticity. Tacticity was determined by hydrooligomerization reactions. When polymerizations are run in the presence of hydrogen (1−3 atm), the products include low molecular weight saturated oligomers formed by chain transfer to hydrogen. The two possible cis-1,3-enchained tetramers can be resolved and quantified by gas chromatography for diad analysis (eq 4).



(4)

GC separation and quantitation was also achieved for the pentamers (3 isomers), hexamers (5 resolved peaks, mmr and mrm isomers coelute), and heptamers (10 isomers) to give triad, tetrad, and pentad analyses, respectively. The completely isotactic hydrooligomers were assigned by comparison of retention times to authentic samples prepared by hydrooligomerization using a zirconium metallocene catalyst as reported by Collins.[7,14] The remaining oligomer assignments were made by application of the necessary relationships within sets of oligomers and between sets of oligomers.[15]

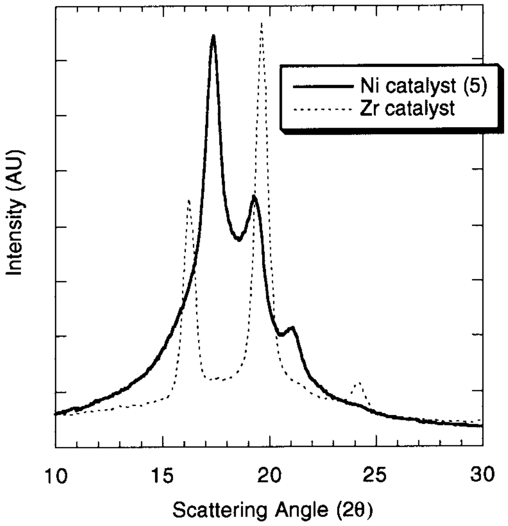


Figure 1. Polycyclopentene X-ray powder diffraction.

All Ni and Pd catalysts give a Bernoullian distribution of hydrooligomers in accord with chain-end control. Diad analyses on the tetramers through heptamers are in good agreement. The tacticity of the hydrooligomers varies with catalyst from essentially atactic (**3**, 51.5% m diads) to moderately isotactic (**6**, 63.7% m diads). When hydrooligomerization with catalyst **6** was performed at 0 °C, the tacticity increased to 66.4% m diads (Table 1). The tacticity determined by hydrooligomerization correlates well with both the end-of-melting point and the heat of fusion of the polymer obtained with the same catalyst (Table 1).

The X-ray powder diffraction pattern of polycyclopentene prepared with Ni catalyst **5** is clearly different from the diffraction pattern of the highly isotactic polycyclopentene made with a Zr metallocene catalyst (Figure 1).[6] The other Pd and Ni catalysts also give polymers with this new diffraction pattern. Thus these polymers, which range from atactic to moderately isotactic, have a new crystalline form.

Up to now, the addition polymerization of cycloolefins by late metal catalysts has been limited to strained monomers that cannot undergo facile β-hydride elimination such as norbornene[16−18] and 3,3-dialkylcyclopropenes.[19] Reaction of cyclopentene with Ni catalysts such as $Ni(acac)_2/Et_3Al/BF_3(OEt_2)$ or $(\pi\text{-}C_4H_7NiCl)_2/AlBr_3$ gives dimers and low molecular weight oligomers.[20,21] The ortho substituents on the *N*-aryl groups of catalysts **3**−**6** are key to the formation of high molecular weight polycyclopentene. They block associative chain transfer in the cationic square-planar olefin hydride intermediate and thereby increase the ratio of propagation to chain transfer.[1]

In summary, α-diimine complexes of Ni and Pd catalyze the addition polymerization of cyclopentene. The polymers are melt processible with end-of-melting points ranging from 241 to 330 °C. They have cis-1,3-enchainment and chain-end control of stereochemistry and range in tacticity from atactic to 66% m diads (i.e., moderately isotactic). They have a new crystalline form that is different from the highly isotactic polymer reported by Kaminsky.

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Supporting Information Available: Details of catalyst synthesis, polymer and hydrooligomer synthesis, and NMR characterization of the polymer and a description of low-temperature NMR experiments (9 pages). See any current masthead page for ordering information and Internet access instructions.

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