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Communications to the Editor

Metallocene-Catalyzed Copolymerization of Ethylene and Isobutylene to Substantially Alternating Copolymers

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The *Encyclopedia of Polymer Science and Engineering* states that "...1,1-disubstituted α-olefins neither homo- nor copolymerize with other monoolefins" using insertion or coordination polymerization conditions.[1] Despite this ominous note, there are a few examples of coordinative copolymerization of 1,1-disubstituted olefins. Kaminsky has reported the copolymerization of isobutylene (IB) with ethylene using bis(indenyl)ethylidenezirconium dichloride activated with methylaluminoxane (MAO).[2] Although copolymers were prepared, no more than 2.8 mol % of IB was incorporated. This low incorporation was despite a very large molar excess of IB to ethylene (4000:1). The presence of IB lowered both the molecular weight of the copolymer and the activity of the catalyst as compared to ethylene alone.

In 1992, Waymouth reported the cyclopolymerization of 2-methyl-1,5-hexadiene (MHD).[3] Cyclopolymerization was reported to dominate even in neat monomer, emphasizing the selectivity for cyclization. This selectivity is remarkable considering that the second insertion, which forms the cyclic repeat unit, is an insertion of a 1,1-disubstituted olefin. Waymouth specifically points out that 2-methyl-1-pentene (2MP) did not polymerize or copolymerize with MHD under similar conditions. He suggests an entropic effect to account for the cyclization of MHD.

Despite these reports, 1,1-disubstituted α-olefins are not considered as viable comonomers because of the inability to incorporate large amounts of the comonomer. We now report the first examples of ethylene/isobutylene copolymers prepared by metallocene catalysis with comonomer contents up to 45 mol %. At this high level of IB incorporation, the copolymer is substantially alternating.

Isobutylene (IB) and ethylene (E) copolymerize using (dimethylsilyl)(tetramethylcyclopentadienyl)(cyclododecylamido)dimethyltitanium (DTCT) activated with one of three different activators: dimethylanilinium tetrakis(pentafluorophenyl)borate (DMAH), triphenylmethyl tetrakis(pentafluorophenyl)borate (TPM), and MAO (30 wt % toluene, Albemarle). The conditions and results of the copolymerizations run at different temperatures and IB/E ratios are found in Table 1. Because metallocene cations and cation/noncoordinating anion salts can initiate carbocationic polymerization,[4−8] the activators and polymerization conditions were chosen to eliminate this possibility. Neither DMAH nor MAO support the carbocationic polymerization of isobutylene under these conditions. DMAH produces *N*,*N*′-dimethylaniline, a strong carbocationic poison, upon activation of DTCT. MAO, although recently used for styrene oligomerization,[9] is a poor catalyst for IB polymerization in nonpolar solvents without added initiators. With TPM, excess DTCT was used to ensure complete consumption of the carbocation salt. Nucleophilic impurities and protic impurities are removed by aging the solvents with triethylaluminum before and after isobutylene addition and prior to contact with the activated catalyst.[10] These precautions were sufficient to avoid isobutylene homopolymerization; i.e., negligble polyisobutylene is formed under these conditions even in the absence of ethylene.

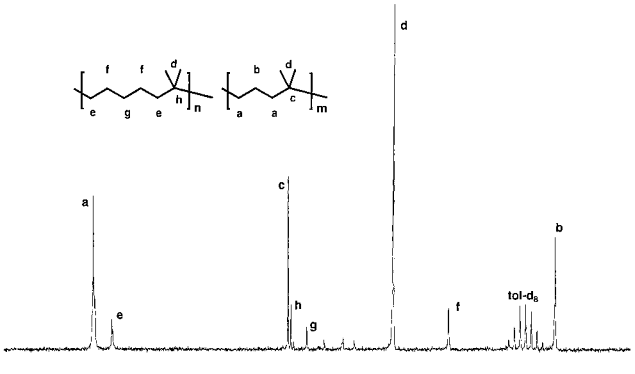

Figure 1. ^{13}C NMR spectrum (toluene-d_8) of IB/E copolymer from run 6 of Table 1.

The catalyst activity in these copolymerizations is comparable to similar catalysts used for ethylene/styrene copolymerization.[11] As expected, these values are lower than that for ethylene homopolymerization.[12−15]

The molecular weight and its distribution, incorporation of isobutylene, and the glass transition temperature of the copolymers were determined. These results are shown in Table 2. The molecular weights of the copolymers are low. The lowering of the copolymer molecular weight with an increase in the IB content would suggest that IB plays an important role in chain transfer. This is further indicated by the polymer chain end functionality discussed below.

Isobutylene incorporation was determined by ^{1}H NMR. The ^{1}H NMR spectrum of the copolymers exhibits an upfield resonance at 0.88 ppm attributed to the methyl protons of the IB repeat unit. Since all the methylene protons from ethylene and isobutylene appear in a complex region around 1.2 ppm, this upfield resonance can be used to calculate IB incorporation.[16] Note that resonances for the homopolymer of IB,

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Table 1. Copolymerization of Isobutylene (B) and Ethylene (E) with (Cp*)(N-c-$C_{12}H_{23}$)($SiMe_2$)$TiMe_2$[a]

run	[catalyst] (mol L^{-1})	activator, [activator] (mol L^{-1})	solvent, volume (mL)	P_E (bar)	temp[b] (°C)	time (min)	yield (g)	activity[c]
1	3.9×10^{-3}	DMAH, 3.9×10^{-3}	toluene, 20	4.4	$21 \rightarrow 40$	5	1.7	1.3×10^5
2	1.8×10^{-3}	DMAH, 1.8×10^{-3}	hexane, 100	4.4	36[d]	10	10.0	1.7×10^5
3	5.7×10^{-4}	DMAH, 5.7×10^{-4}	toluene, 30	4.4	$-20 \rightarrow -17$	60	1.3	3.8×10^4
4	7.7×10^{-4}	TPM, 3.8×10^{-4}	toluene, 30	4.4	$25 \rightarrow 38$	10	2.5	3.2×10^5
5	5.7×10^{-4}	MAO, 5.7×10^{-2}	toluene, 30	1.4	$24 \rightarrow 35$	15	3.3	3.9×10^5
6	5.7×10^{-4}	MAO, 5.7×10^{-2}	toluene, 30	0.34	$28 \rightarrow 34$	135	11.0	1.4×10^5

[a] [IB] = 6.3 mol L^{-1}. Isobutylene collected at −40 °C, $\rho_{\text{isobutylene}}$ (−40 °C) = 0.662 g cm^{-3}. [TEAl] = 1.0×10^{-3} mol L^{-1}. [b] The first number indicates the start temperature, and the second indicates the highest temperature achieved during the run. [c] Activity in units of g of polymer/(mol Ti·h). [d] Temperature maintained at 36 °C by microprocessor control of reactor coolant.

Table 2. Characterization of IB/E Copolymers

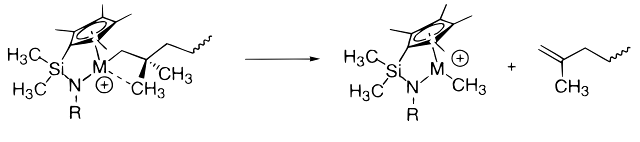
run	M_n	M_w/Mn	isobutylene[a] incorporation (mol %)	T_g[b] (°C)
1	10 300	2.5	33	−36
2	26 500	2.3	24	−37
3	48 500	1.7	31	−36
4	8 910	2.2	33	−36
5	14 500	2.0	38	−31
6	13 200	2.5	45	−25

[a] Calculated from ^{1}H NMR. [b] Determined by DSC.

expected at ~1.1 and 1.4 ppm, are absent, indicating the absence of IB−IB dyads and homopolymer.

Further proof of the structure of this copolymer is given by ^{13}C NMR in Figure 1. The assignments have been made by comparing calculated[17] and published[18] values for chemical shifts of the various microstructures. The *alt*-EIB microstructural unit has been previously observed in the carbocationic isomerization−polymerization of 4-methyl-1-pentene.[18] Isobutylene separated by two ethylenes is the next most dominant structure (EEIB). From the ^{13}C spectrum, we estimate that the *alt*-EIB structure constitutes 85% of this copolymer while the EEIB unit constitutes 14%. The remaining 1% is unidentified larger run lengths of ethylene (E_nIB with $n \geq 3$). No resonances are observed in any copolymer, which indicates the presence of a 2,1 isobutylene insertion following a 1,2 IB−E sequence. Consistent with the ^{1}H NMR, no resonances are observed for IB−IB dyads or homopolyisobutylene. As the content of IB decreases in these copolymers, the amount of *alt*-EIB is reduced and the run length of ethylene is increased.

Because low molecular weight copolymers are prepared, chain end information can be obtained. The ^{1}H NMR spectrum showing the olefin chain end structure of copolymer 1 is given in Figure 2. This figure clearly shows that vinylidene chain ends are the predominant form of olefin termination in copolymers containing more than 10 mol % IB. Vinylidene termination is attributed to β-methyl elimination from the terminal IB unit, as shown below.



As such, this is the primary mechanism of chain transfer. β-methyl elimination has been reported less frequently than β-hydride elimination in ethylene and propylene polymerization. In the cyclopolymerization of MHD, Waymouth reported β-methyl elimination as the exclusive form of chain transfer.[3] With 1,1-disubstituted olefins, β-methyl elimination occurs because of the absence of β-hydrogens. Only in the event of 2,1 insertion is β-hydride elimination possible from the 1,1-disubstituted comonomer. We have found no evidence for 2,1 insertion.

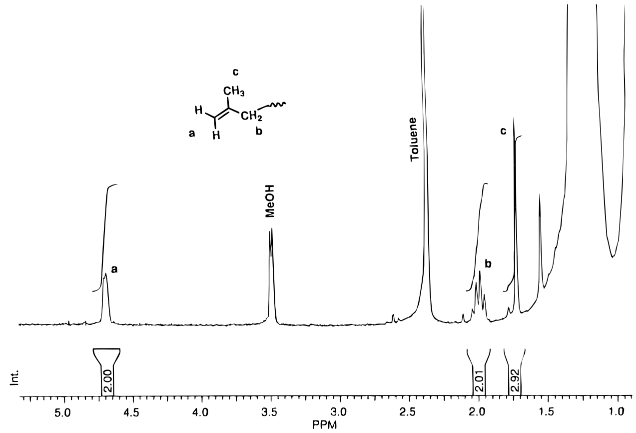


Figure 2. ^{1}H NMR spectrum ($CDCl_3$) of IB/E copolmyer from run 1 of Table 1 showing olefin chain end nature.

A copolymerization of 2MP with ethylene was run to generalize the results obtained with IB.[19] A copolymer was recovered that contained 9.0 mol % 2MP (M_n = 10 780, M_w/M_n = 5.9).

Because the IB/E copolymers are substantially alternating, they are amorphous and exhibit a single glass transition temperature. T_g's are observed between −25 and −37 °C. These values are not expected to correlate well with the parent homopolymers polyethylene (−80 °C) and polyisobutylene (−73 °C), especially at high IB incorporation, because of their alternating nature.[20]

Copolymerizations of isobutylene and propylene with DTCT were unsuccessful. No polymer is obtained in this experiment despite DTCTs ability to catalyze the homopolymerization of propylene.[15] However, admitting small amounts of ethylene to the IB/P experiment causes immediate polymerization and formation of an IB/E/P terpolymer.

In conclusion, we report the first examples of substantially alternating IB/E copolymers prepared by insertion polymerization. The general ability of DTCT type catalysts to incorporate 1,1-disubstituted olefins is demonstrated by the incorporation of 2MP.

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