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Copolymerization Studies of Vinyl Chloride and Vinyl Acetate with Ethylene Using a Transition-Metal Catalyst

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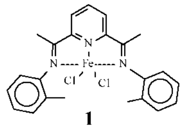
Since the advent of Ziegler−Natta polymerization of ethylene attempts have been made to extend this coordination polymerization to commercially important monomers with polar functionality (such as vinyl acetate (VA), vinyl chloride (VC), and acrylates).[1] Over the past 50 years, there have been many reports of polymerization of polar monomers with transition-metal catalysts.[2] We have reexamined several of these claims and have found that a radical mechanism is involved in the formation of the products.[3] To date, Brookhart's work with acrylate monomers stands as the only polymerization of polar monomers with a mechanism that is unequivocally based on coordination/insertion.[4,5] Recently, Jordan and co-workers have published a study of the chemistry that occurred during the attempted homopolymerization of VC with a Zr(IV) metallocene complex. It was demonstrated that VC inserts into the Zr−methyl bond, followed by rapid β-chloride elimination to produce propylene and a Zr metal chloride.[6] Wolczanski has also recently reported similar chemistry between (^{t}Bu$_3$SiO$_3$)TaH$_2$ and vinyl ethers or vinyl chlorides.[7] The thermodynamic driving force for this process can be calculated from the bond dissociation energies of metal−chlorine (or metal−oxygen) relative to metal−carbon bonds. For group IV metals this difference is quite large (~50 kcals/mol),[8] making elimination chemistry very likely. Late transition-metal catalysts offer more promise as coordination catalysts of polar monomers since this elimination chemistry is not as thermodynamically favorable.[9]

In this report we present evidence for the coordination and migratory insertion of VC and VA into a growing polyethylene chain using the tridentate Fe(II) dichloride **1** first described by both Brookhart and Gibson.[10] The Fe(II) dichloride **1** is well suited for this study: it rapidly oligomerizes ethylene to low-molecular weight linear α-olefins with good selectivity,[11] and the relatively "open" metal center is less demanding sterically, facilitating the incorporation of VC or VA more readily into a growing oligomer chain.



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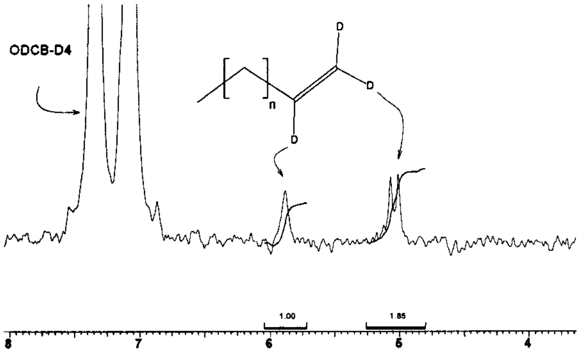

Figure 1. ^{2}H NMR Spectrum of deuterated olefins.

The polymerizations were performed by adding the Fe(II) complex **1**, toluene, and 50 equiv of methylaluminoxane (MAO) to a 45-mL autoclave at 50 °C. The autoclave was charged with perdeuterated VC followed by 150 psig ethylene (molar ratio VC: ethylene was 1:9). Low-molecular weight linear α-olefins were produced having a Schulz−Flory distribution.[12] Under these conditions, the Schulz−Flory constants were identical (0.81) for the ethylene homopolymerizations and the ethylene/vinyl chloride copolymerizations. The olefins were soluble in toluene and could be characterized by GC/MS and deuterium and carbon NMR techniques.[13] To our surprise, the low-molecular weight members of the series of trideuterated olefins were partially resolved from the nondeuterated series by GC/MS. From these data, a ratio of the molecular ion peaks for the two series of each distinct α-olefin fraction, it was determined that the ratio of (trideuterated vs nondeuterated olefins was ca. 1:20. From NMR spectroscopy, comparison of the integrated olefin signals from the deuterium-coupled carbons versus the nondeuterated carbons gave a similar ratio of 1:19. The relative rates at which VC is inserted relative to ethylene can be calculated by multiplying the number average degree of polymerization of the products (8.8) by the above ratios of deuterated versus nondeuterated oligomers. This calculation shows that VC is inserted once for every ~180 ethylene monomers. Given the fact that this catalyst has low reactivity toward α-olefins[11] and the predominance of ethylene in the starting mixture (9:1 vs VC), this incorporation rate is fairly high. The ^{2}H NMR spectrum clearly demonstrated that the deuterium atoms were located exclusively at the olefin terminus, indicating that insertion of VC had occurred, followed by β-Cl elimination. No chlorine-functionalized oligomers were identified in the α-olefin mixture by NMR spectroscopy or GC/MS. The ^{2}H NMR spectrum for the VC/ethylene oligomerization is shown in Figure 1 (D$_4$-ODCB was added as an internal reference).

Much slower ethylene consumption rates were observed when VC was added as a comonomer compared to the ethylene homooligomerizations. One obvious explanation is that the elimination chemistry forms an inactive chloride complex, which must be reactivated by MAO. However, we also noted that the addition of

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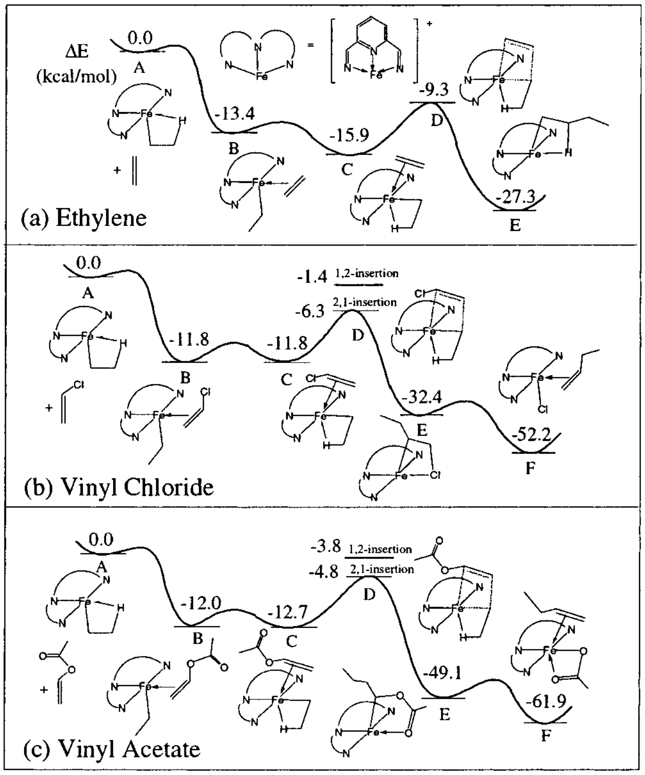

Figure 2. Calculated relative energies (in toluene) of intermediates and insertion transition state for (a) ethylene, (b) VC, and (c) VA.

equivalent quantities of methylene chloride or *o*-dichlorobenzene reduced ethylene consumption rates by the same amount and that may suggest a reversible interaction of the organochlorine with the activated Fe catalyst is also occurring.

A similar study was undertaken with perdeuterated VA, molar ratio of VA to ethylene was 1:7. The ethylene consumption rate was substantially decreased, and the reaction ceased after 10 min, presumably due to conversion of the active Fe catalyst to Fe(II) acetate which is not efficiently reactivated by MAO. The olefins produced had a deuterium:proton ratio of 1:40 (C_8 fraction), indicating that VA is inserted once for every ~350 ethylene monomers. The lower reactivity of VA compared to VC can potentially be ascribed to two factors: the decreased electron density of the olefin and the steric bulk of the acetate functionality. ^{2}H NMR spectroscopy confirmed the deuterium atoms were located only at the olefin terminus. No acetate functionalized α-olefins were identified by NMR spectroscopy or GC/MS. When equivalent amounts of ethyl acetate was added to ethylene homooligomerizations as VA in the copolymerizations, a rate decrease of ca. 50% was observed.

Applying the generally accepted Cosseé mechanism to polar monomer copolymerization satisfactorily explains the observed product mixtures.[14] The propagating Fe center having an attached alkyl chain has two different pathways to follow. The catalyst can either insert another ethylene monomer and continue to propagate until normal β-H elimination occurs, or the Fe catalyst can coordinate and insert the added polar comonomer. Both processes produce a Schulz−Flory distribution of α-olefins. If the latter occurs, then chain growth is terminated by β-Cl elimination to produce an iron chloride and an α-olefin. From our studies with this and other catalysts, coordination and insertion of VC into growing chains occur commonly, but β-Cl elimination terminated further chain growth.[15]

To help understand these results we used first-principles quantum mechanics to calculate structures and energies for key intermediates and insertion transition state of a model catalyst (see Figure 2) polymerizing ethylene, VC, and VA. These calculations use spin-restricted singlet (B3LYP/6-31G*) DFT. Solvation is calculated using the Poisson−Boltzmann model with the molecular surface for the gas-phase structure (toluene: $\epsilon = 2.4$, probe radius = 2.76 Å).

These results (Figure 2) show that VC (or VA) incorporation into the polymer leads to Cl (or acetate) dissociation onto the metal. Our calculations suggest that 2,1-insertion is preferred over 1,2 for both VC and VA.[16] The calculated barrier for VC (or VA) is 3.0 (or 4.5) kcal/mol higher than ethylene. This agrees well with the experimental ratios that (assuming identical A factors) lead to barriers for VC (or VA) 3.3 (or 3.8) kcal/mol higher than ethylene.

In summary, VC and VA behave as comonomers for coordination/insertion polymerizations with ethylene at significant rates. We find that insertion with either monomer leads to termination of the growing chain via β-elimination processes. The two polar monomers studied with catalyst **1** were incorporated at a faster rate than nonpolar α-olefins. For successful coordination polymerizations of these commercially important polar monomers, it will be necessary to find a way to circumvent the elimination process that occurs after insertion.

Supporting Information Available: Detailed experimental procedures, calculations, NMR spectra, and characterization of olefins by GC/MS (PDF). This material is available free of charge via the Internet at http://www.pubs.acs.org.

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(15) Copolymerization of ethylene and VC with 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine iron(II) dichloride/1000 MAO decreased M_n values from 3000 to 1100.

(16) We postulate that the observed products could be the result of either [2,1] or [1,2] insertion modes. We have synthesized HC═CDCl to determine which mode is operational, and these studies are currently ongoing.

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