Preparation and Reactivity Studies of Highly Versatile, Nickel-Based Polymerization Catalyst Systems

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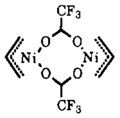
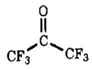
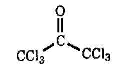
The utilization of transition metals as polymerization catalysts has led to many vast improvements in the industrial synthesis of polymeric materials.[1] Some examples of these improvements are higher rates of monomer consumption, polymer molecular weight control, and stereochemical control over polymer microstructure.[1,2] Current goals in polymer syntheses using metal initiators include increasing conversion rates and stereochemical control, as well as the polymerization of monomers containing polar functional groups.[3] Toward these goals, we describe our results concerning the promotion of a mildly active initiator with limited monomer variability (π-allylnickel trifluoroacetate, **I**),[4] to very highly active initiators with a very broad scope of applicability through addition of controlled amounts of either hexafluoroacetone (HFA) or hexachloroacetone (HCA).



I

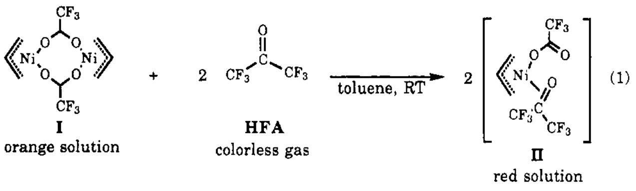


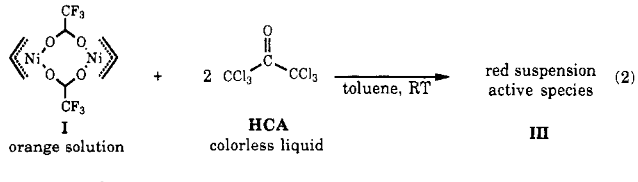
HFA



HCA

We have prepared two-component mixtures consisting of **I** and either HFA or HCA and found these to be highly active initiators for polymerization of a wide variety of unsaturated substrates. Simple addition of one or greater equivalent(s) of either HFA or HCA per nickel atom to a toluene solution of **I** (under a rigorously oxygen- and water-free environment at room temperature) results in formation of mixtures (**II** and **III**, respectively) which can be used directly for polymerization reactions (eqs 1 and 2).





The product **II** exists as a red homogeneous solution in toluene directly upon preparation and can be isolated by removal of the solvent. This material is soluble in ethereal and aromatic solvents and retains its catalytic activity indefinitely when stored without solvent. The product **III** exists as a cream/red suspension in toluene directly upon preparation, and the active part of the mixture is only a small fraction (*ca.* <10%) of the total added components. Analysis of the solid residue from **III** indicated it to be chloronickel trifluoroacetate (**IVa**), and the main constituent of the supernatant proved to be 1,1,1-trichloro-3,3-dichlorohex-5-en-2-one (**IVb**; see the supplementary material).

Complex **I** (both with and without other coinitiators) has been demonstrated to be a fairly active initiator for the polymerization of 1,3-butadiene[4] as well as a few other monomers (cycloolefins,[5] isoprene,[6] styrene,[7] and isocyanides[8]). As a source of comparison, a butadiene polymerization initiated by **I** was found to have a half-life of *ca.* 24 h at 298 K.[4] When **II** was used as initiator (equal starting concentrations of both butadiene and **I**), this half-life was reduced to *ca.* 0.5 h. For the same reaction with **III**, the half-life was shortened even more to *ca.* 2 min. Furthermore, the stereoregularity of the polymer was increased in going from **I** to **II** to **III**: the ratio of *cis*-1,4 to *trans*-1,4 units along the backbone was found to increase from 3:1 to 9:1 to 98:1, respectively, as determined by NMR spectroscopy. In addition, the related monomer, isoprene, which under given conditions (60 °C, 20 h) gave only 25% polymer (42% *cis*, 50% *trans*, and 8% 3,4-addition) with **I**,[6] gave 53% of a much higher quality polymer (>98% *cis*-1,4 addition) under milder conditions (50 °C, 15 h) using **III**.

Cyclic and electron-deficient monomers were also examined. Norbornene is not polymerized by **I** at room temperature.[5,9] However, when **III** is used as initiator, high (70%) yields of addition polymer can be obtained in short time periods (24 h). Using **III** as initiator, we were able to polymerize styrene ($\bar{M}_n$ = 2000) at ambient temperature. **I** has previously been reported to polymerize styrene at low temperature (−10 °C), but no further data were given.[7]

Functionalized monomers were also polymerized, namely, vinyl ethers (2-chloroethyl vinyl ether and (trimethylsilyl)oxy vinyl ether). As with cyclic olefins, vinyl ethers are not polymerized by **I** alone.[9] When **III** is used as initiator, nearly quantitative yields of addition polymer poly(2-chloroethyl vinyl ether) can be isolated with reasonably high molecular weight ($\bar{M}_n$ = 50 000). When (trimethylsilyl)oxy vinyl ether is polymerized, the polymeric product isolated is poly(vinyl alcohol) (37%) after hydrolysis of the oxygen–silicon bond. Thus, **III** represents a convenient route into alkoxy- and hydroxyl-functionalized polymers. The results of these polymerization studies are summarized in Table I.

The exact structures of the catalysts/initiators **II** and **III** are not currently known, yet we have been able to gain some insights into their nature. The structure of **II** can be thought to be similar to other known complexes of nickel with carbonyl functionalities and with quinone type molecules. There are a few literature examples where allylnickel compounds, analogous to **I**, have been promoted to active initiators by addition of electron-deficient additives (e.g., $TiCl_4$, $AlCl_3$, chloranil, and bromanil).[10,11] The metal salts were believed to generate cationic complexes by abstraction of halide ions (eq 3), and the quinones were believed to oxidize the nickel center by removal of an electron (eq 4); it must be stressed, however, that neither of these mechanisms has been verified experimentally (however, a cationic allylnickel(II) complex has been shown to be an active polymerization catalyst).[12] Since HFA is electronically similar to quinones, the complex **II** can be hypothesized to lie somewhere between a coordination

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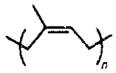
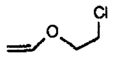
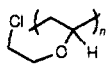
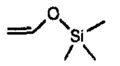
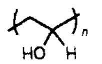
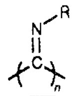
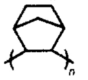
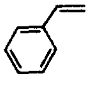
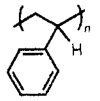
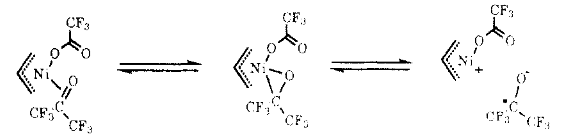
Table I. Summary of the Results of Polymerization Studies

monomer	polymer	catalyst	activity	yield (%)
		I	low	100
		II	high	100
		III	very high	100
		I	very low	25
		II	low	31
		III	mild	53
		I	inactive	0
		II	high	100
		III	very high	100
		I	inactive	0
		II	low	ND
		III	mild	37
		I	inactive	0
		II	high	60
		III	very high	70
R—N≡C		I	high	100
		II	high	100
		III	high	100
		I	low	55
		II	high	89
		III	high	96

complex and an electron-transfer complex of the metal center and the electron-poor ligand (HFA) (eq 5).[13]

(3)

(4)



(5)

The complex **III** was found to undergo a series of decomposition reactions which generated side products which were not active initiator species. When **I** and HCA are mixed, the reaction mixture immediately turns very dark. Within a few minutes the color bleaches and a pale yellow sediment is observed to fall out of solution. This precipitate, which is soluble in acetonitrile (green solution), was subsequently characterized as chloronickel trifluoroacetate, $[ClNiO_2CCF_3]_n$ (**IVa**), by elemental analysis, IR, and ^{19}F NMR. It was also characterized by single-crystal X-ray diffraction studies as the THF solvate: $Cl_4Ni_4(O_2CCF_3)_4 \cdot (THF)_6$ (Figure 1). **IVa** was found not to be an active polymerization initiator for any of the monomers listed above. The supernatant solution remaining from the complex **III** preparation was also analyzed. It was found to contain a colorless high boiling oil which was characterized by IR and ^1H and ^{13}C NMR as 1,1,1-trichloro-3,3-dichlorohex-5-en-2-one (**IVb**). Likewise, this product was found not to be an active polymerization catalyst. Therefore, since both these products were isolated in high yield (*ca.* 90%), the active initiator species in **III** must be present in very small amounts and are highly unstable relative to the end products characterized above. A hypothetical scheme for the formation of these products and possible intermediates is given in Scheme I. We are currently working on elucidating the true structures of both **II** and **III**.

To determine whether or not these polymerizations are catalyzed by the nickel center or are simply cationic, we conducted an experiment with a different, yet related, nickel complex to see how catalyst reactivity was affected. Instead of **I**, we used π-allylnickel acetate in conjunction with HCA. With butadiene, the propagation rate for polymerization is *ca.* 15 times slower when π-allylnickel acetate is used as catalyst instead of **I**.[9] Therefore, if nickel is involved in the propagation reaction, the rate for polymerization should decrease as well when π-allylnickel acetate is used with HCA. A mixture of π-allylnickel acetate and HCA gives a yellow precipitate which dissolves in butadiene and forms polymer with a half-life of *ca.* 15 h at 298 K, showing that, although this catalyst mixture is much more active than π-allyl nickel acetate, it is much slower than our system **III**. Further evidence against a cationic process is the microstructure of the polymers that are produced. The very high *cis* content of the polybutadiene argues strongly against a cationic process. These results seem to indicate that the nickel center and the ligands in its coordination sphere are an integral part of the polymerization mechanism.

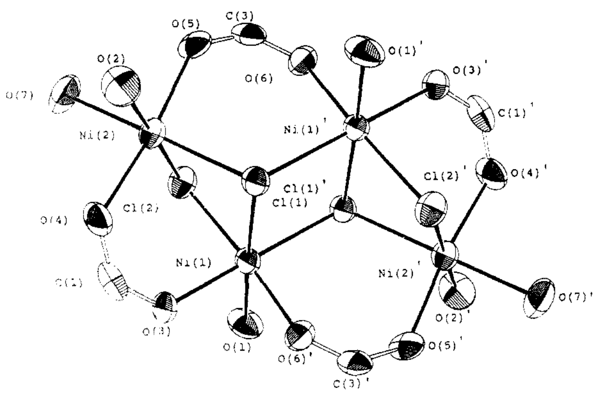
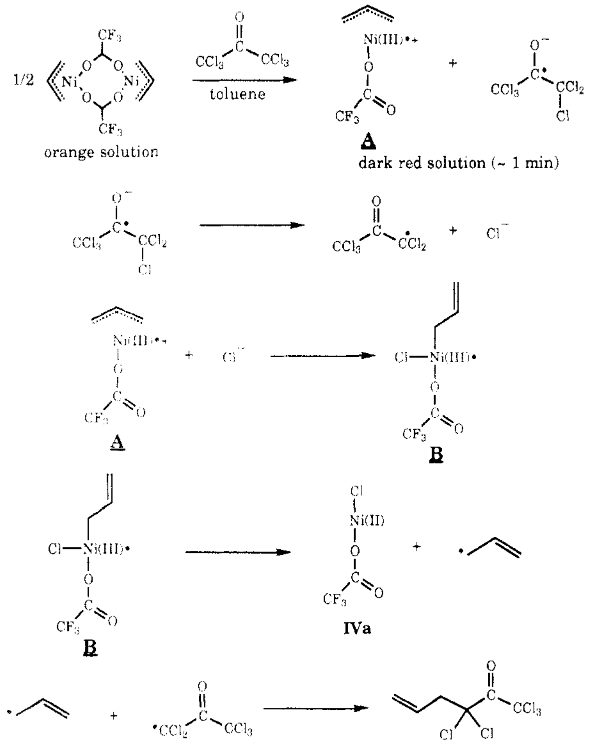


Figure 1. ORTEP view of $(IVa)_4 \cdot (THF)_6$; The CF_3 groups have been omitted from the trifluoroacetate groups (C(1), C(3), C(1)′, C(3)′), and $-(CH2)_4-$ rings have been omitted from THF oxygens (O(1), O(2), O(7),O(1)′,O(2)′,O(7)′) for clarity.

Scheme I.[a] Possible Reactions in the Preparation of III



[a] A and B are potential active species.

As stated above, there have been a few reported examples whether other allylnickel complexes have been activated toward polymerization (mostly of diene monomers) by addition of electron-poor additives. The closest examples perhaps are the reported addition of ${}^1/_2$ equiv of chloranil to **I** which was stated to enhance the rate of polymerization of butadiene (half-life *ca.* 0.5 h) as well as increase the *cis* content of the polymer (*cis*-1,4 to *trans*-1,4 ratio of 9:1)[11] and some reports where chloral, trichloroacetic acid, and HCA were added to some allylnickel halides to prepare polybutadiene.[14] Compared to our data, the chloranil system is roughly equivalent to our system **II** and yet is much less active than our system **III**. The mixture of HCA and allylnickel halides prepared polybutadiene but at lower conversions and at slower rates than the mixture with **I**. Furthermore, we have been able to find no mention of where any of these catalyst preparations have been able to polymerize the variety of monomers described here (Table I). In conclusion, we hope to have demonstrated the utility of electron-deficient carbonyl compounds as highly powerful activators for the polymerization catalyst **I**.

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Supplementary Material Available: Experimental procedures for the preparation of **II** and **III** and for all of the polymerization reactions and tables of thermal and positional parameters and of selected intramolecular bond lengths and angles for compound **IVa** (11 pages). Ordering information is given on any current masthead page.

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