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Butadiene 1,4-Polymerization Initiated by Bis[(η^3-allyl)(trifluoroacetato)nickel]: A Perfectly "Living" Coordination System

"Living" chain polymerization reactions have been up to now a nearly exclusive feature of anionic systems,[1] although a few examples of more or less perfectly "living" initiators are known in cationic polymerization[2,3] and long-lived radicals[4] have been studied and used in radical homo- and copolymerization. The importance of these systems has been largely demonstrated by their capability to tailor polymer molecular weight and molecular weight distribution, to lead to end-group functionalization (mono and α,ω) of different backbones, and mainly to allow the synthesis of a variety of block copolymers.[5]

More recently, other examples of such behavior have also been found in anionic-coordination polymerization of lactones[6] and even in coordination polymerization (Ziegler–Natta type) of propene.[7]

That situation prompts us to report now a perfectly "living" coordination initiator, namely, bis[(η^3-allyl)(trifluoroacetato)nickel] or [(A)Ni(TFA)]$_2$, for the selective 1,4-polymerization of butadiene and its further block copolymerization.

(η^3-Allyl)nickel Initiator. [(A)Ni(TFA)]$_2$ is an excellent catalyst for butadiene 1,4-polymerization: it displays a high activity, an excellent regioselectivity (ca. 1% of 1,2 units), and an amazing stereoselectivity controllable from 99% cis to 99% trans units, depending on the choice of proper ligands and kinetic conditions.[8,9] The rate of initiation is high enough to ensure complete initiator conversion in the early stages of polymerization; moreover, irreversible termination with deactivation of propagation centers does not take place.[10] However, hydride-transfer reactions do occur in these η^3-allylic systems (through β-elimination), limiting the chain propagation reaction and the expected molecular weight. We have now found that this [(A)Ni(TFA)]$_2$ complex, when used under well-defined experimental conditions and in the presence of a certain amount of particular ligands, is able to promote a "living" 1,4-polymerization of butadiene, displaying exactly the same attractive kinetic characteristics as a classical anionic "living" system. Two different types of ligands were used: a typical electron donor, i.e., triphenyl phosphite (TPP) and a strongly electron-withdrawing one, i.e., tetrachlorobenzoquinone (or chloranil (CA)); of course, all manipulations were performed under controlled conditions (dry argon atmosphere or vacuum, perfectly dried solvents, and reagents). It is important to stress that under these conditions, polymers obtained have a unimodal molecular weight distribution with a rather narrow polydispersity ($\bar{M}_w/\bar{M}_n$ between 1.2 and 2.0), a good indication for a single type of catalytic sites.

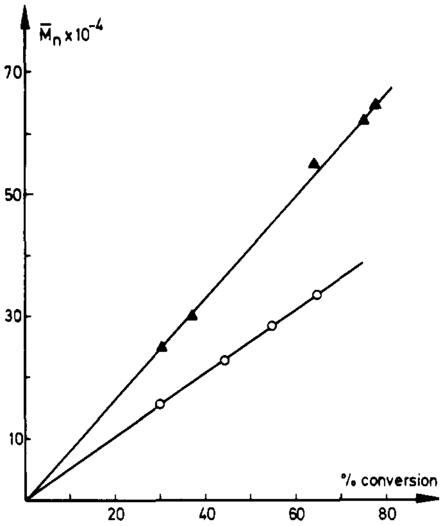

Figure 1. $\bar{M}_n$ as a function of conversion for BD (4.8 mol·L^{-1}) polymerization with [(A) Ni(TFA)]$_2$: (▲) data for polymerization in heptane at 55 °C ([Ni] = 3 × 10^{-3} mol·L^{-1}, [TPP]/[Ni] = 0.18, cis-1,4 ca. 43%); (○) data for polymerization in toluene at 25 °C ([Ni] = 5 × 10^{-3} mol·L^{-1}, [Ca]/[Ni] = 0.35, cis-1,4 ca. 78%); (—) calculated lines.

[(A)Ni(TFA)]$_2$–TPP System in n-Heptane. Experimental data pertaining to this system are gathered in Table I and indicate a satisfactory correlation between experimental and calculated $\overline{DP}$, assuming a "living" process. The fact to be stressed here is obviously that this correlation holds relatively well all over the stereoselectivity scale (i.e., whatever the cis or trans microstructure, leading to very different products). This "living" character has been further ascertained by the linear increase of $\bar{M}_n$ with conversion, the experimental data fitting perfectly the calculated straight line (Figure 1); similar data have been obtained for other [TPP]/[Ni] ratios (0 and 0.8). A final confirmation came from seeding experiments, where after partial consumption of a first crop of monomer ([TPP]/[Ni] = 0.18, 77% conversion, $\bar{M}_n$(calcd) = 66 528, $\bar{M}_n$(exptl) = 65 800), further addition of butadiene ([BD]$_0$ = 3 mol·L^{-1} [Ni] = 2.5 × 10^{-3} mol·L^{-1}) caused resumption of polymerization with the expected increase in $\overline{MW}$ (53% conversion, $\bar{M}_n$(calcd) = 34 344, $\bar{M}_n$(calcd, total) = 100 872, $\bar{M}_n$(exptl total) = 99 900). With all these systems, the possibility exists to obtain high $\bar{M}_n$'s (over 10^5) and quantitative conversions although the catalyst is expectedly somewhat less stable in the absence of monomer.

[(A)Ni(TFA)]$_2$–CA System in Toluene. Exactly the same trends were observed for this system, as illustrated in Table I, which shows furthermore the essential influence of the ligand concentration upon the agreement between experimental and calculated $\bar{M}_n$ values, i.e., on the "living" character, in this toluene medium. Again, $\bar{M}_n$ increases proportionally to conversion at constant microstructure. (See also Figure 1.)

Table I
Butadiene Polymerization with [(A)Ni(TFA)]$_2$, ([BD]$_0$ = 4.8 mol · L^{-1})

[L]/[Ni]	[Ni], mol·L^{-1}	solvent	T, °C	t, h	% conv	$\bar{M}_n$(exptl)[a]	$\bar{M}_n$(calcd)[b]	% cis-1,4[c]
TPP 0.00	3 × 10^{-3}	*n*-heptane	55	24.3	60	46.500	51.840	93.5
TPP 0.18	3 × 10^{-3}	*n*-heptane	55	20.5	65	57.000	56.592	43.5
TPP 0.27	3 × 10^{-3}	*n*-heptane	55	21.3	77	66.500	66.528	30.0
TPP 0.54	3 × 10^{-3}	*n*-heptane	55	22.0	69	60.000	59.616	15.5
TPP 0.80	3 × 10^{-3}	*n*-heptane	55	95.0	52	49.600	44.928	<2.0
CA 0.00	5 × 10^{-3}	toluene	25	13.0	65	16.000	33.696	59.0
CA 0.20	5 × 10^{-3}	toluene	25	3.5	41	22.400	21.254	66.0
CA 0.35	5 × 10^{-3}	toluene	25	2.0	55	28.700	28.512	78.0
CA 0.50	5 × 10^{-3}	toluene	25	0.6	72	37.600	37.325	89.5

[a] Calculated from GPC curves. [b] Calculated as 54 × [BD]$_0$ × % conv × [Ni]$^{-1}$. [c] Calculated from IR spectra.[14]

In conclusion, we have now the ability to prepare "living" 1,4-polybutadiene chains over a broad range of stereostructures. Obviously, this unique behavior paves the way for the synthesis of interesting new block copolymers: suffice it to cite the preparation of a stereodiblock poly(*cis*-1,4-butadiene-*b*-*trans*-1,4-butadiene)[11] and of a poly(1,4-butadiene-*b*-styrene) diblock,[12a] which upon hydrogenation yields an interesting poly(ethylene-*b*-styrene) copolymer useful as an emulsifier for blends of high-density polyethylene and polystyrene.[12b]

One must realize however that one faces here all of the extremely sensitive features of classical coordination catalysis. In particular, the process is critically dependent on temperature and concentrations, on the presence of a given ligand (L) in a particular L/Ni ratio (probably in order to block coordination positions prone to promote β-elimination[13] as will be discussed elsewhere), and very much so on the nature of the solvent.

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