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Synthesis and Characterization of Macroalkoxyamines Based on Polyethylene

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The excellent combination of chemical and physical properties of polyolefins[1−3] along with low cost, superior processability, and recyclability has positioned these polymers as the most preferred commercial ones. Despite the great successes, there are some inherent shortfalls in polyolefin materials that prevent their wider usage in many areas currently occupied by other polymers that are much more expensive and less environmentally friendly materials. Among the major drawbacks of polyolefins are their poor adhesion and incompatibility with other materials and most polymers. The incorporation of end-functional groups offers an opportunity to serve as a building block for constructing multisegmented polymers. The resulting materials would then be for instance more effective compatibilizer for improving the interfacial interaction between two polymers.

In chemistry, the general method of preparing end-functionalized polyolefins has been based on living polymerizations with a chemical reaction to convert the reactive chain end into a functional group. The chemical reaction concerns the transformation of a carbon−metal bond. One of the best known transformations of a carbon−metal bond in organic chemistry is probably the Grignard reaction where, for example, carbon−carbon bonds (R−R′) are generated from the reaction of organomagnesium compounds (RMgX) with halides (R′X)[4] or stable radicals (R′•).[5,6]

A large range of compounds are synthesized via this reaction type and among them alkoxyamines, which are of great importance as initiators and controlling agent in the field of "living"/controlled radical processes via stable free radical polymerization (SFRP). In the latter case, the organometallic compound is reacted with 2 equiv of a stable nitroxide radical (R′ = O−N(R^{1}R^2)). For example, alkyl(C$_6$)-TEMPO (TEMPO = 2,2,6,6-tetramethylpiperidinyl-1-oxy) alkoxyamine has been synthesized according to this strategy.[5] With a view of introducing free radical initiator at the chain end of polyolefins, we plan to investigate a strategy based on the above-mentioned Grignard-type chemistry. Indeed, dialkylmagnesium compounds can be used as chain transfer agents (CTA) in ethylene polymerization. It has been shown that a pseudo-living ethylene polymerization via chain transfer reaction between dialkylmagnesium derivatives and the lanthanidocene complex ($(C_5Me_5)_2LnCl_2Li(OEt_2)_2$) could be achieved (Ln = Nd,[7] Sm[8]). As chains are generated onto the catalyst, a constant and reversible transfer is operating onto the CTA where the chains are stored during the growth of other chains at the lanthanide center. As a result, the obtained long-chain dialkylmagnesium compounds, Mg(PE)$_2$ (PE = polyethylene), of narrow molar mass distribution are excellent candidates for an end-functionalization with nitroxide derivatives.

Table 1. Ethylene BOMg/$(C_5Me_5)_2NdCl_2Li(OEt_2)_2$-Mediated Polymerizations and Functionalization with TEMPO[a]

entry	yield (g)	M_n[b] (g mol^{-1})	M_w/M_n[b]	$M_{n,NMR}$ (g mol^{-1})	Me/ 1000C	vinyl/ 1000C	TEMPO/ 1000C	% funct[c]
1	0.59	790	1.12	851	31.7	1.21		
2	0.60	770	1.36	1072	16.16	1.76	8.21	62.7
3	1.00	1200	1.21	1358	19.25	1.35		
4	1.20	1340	1.27	1682	10.14	1.77	4.70	56.5
5	2.06	1780	1.3	1926	13.15	1.39		
6	1.96	1700	1.31	1921	9.59	1.33	3.71	51.0

[a] Reaction conditions: number of moles of $(C_5Me_5)_2NdCl_2Li(OEt_2)_2$ = 5.46 × 10^{-2} mmol, BOMg = 0.5 mmol; ethylene pressure = 1.3 atm; toluene = 100 mL; molar ratio TEMPO/Mg = 4; temperature = 80 °C. [b] Determined by high temperature (150 °C) SEC with trichlorobenzene as eluent (1 mL min^{-1}). [c] TEMPO functionalization rate determined by ^{1}H NMR at 363 K in TCE/C$_6$D$_6$ (2/1 v/v).

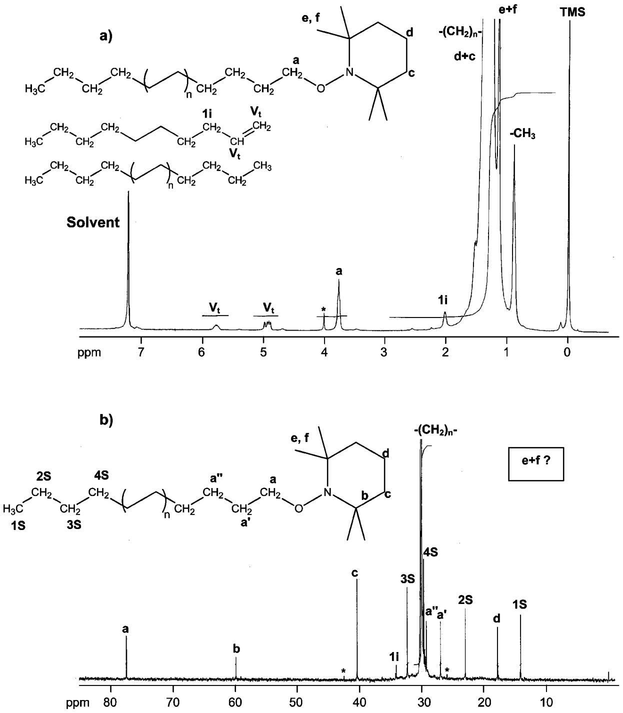

Figure 1. PE-TEMPO NMR analyses performed in a mixture of C$_6$D$_6$/TCE (1/2 v/v) at 363 K: (a) ^{1}H NMR (NS = 128) and (b) ^{13}C NMR (NS = 10 240). Stared resonances correspond to solvent impurities.

In this study, ethylene $(C_5Me_5)_2NdCl_2Li(OEt_2)_2$-mediated polymerization was performed in conjunction with butyloctylmagnesium (BOMg) at 80 °C in toluene. A prerequisite to use the strategy mentioned in the introduction part to functionalize polyethylene chains

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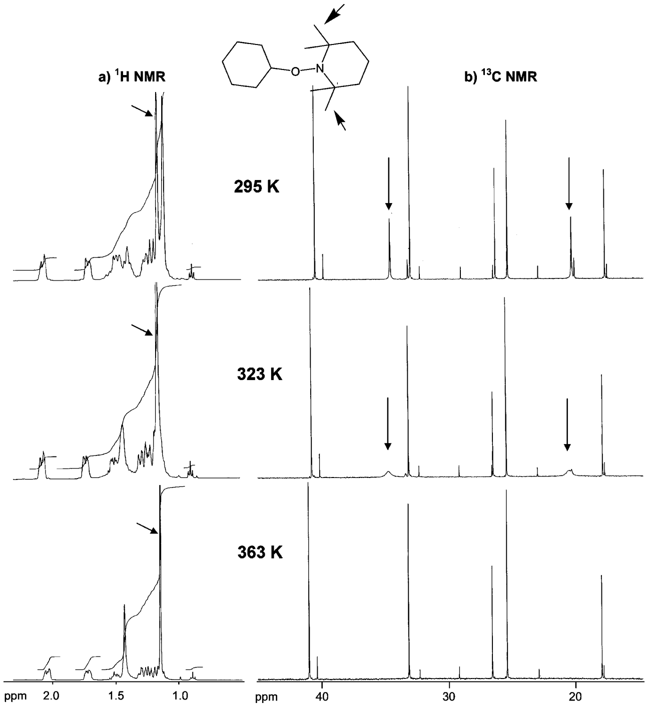
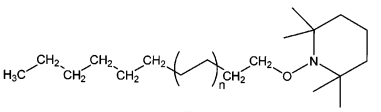


Figure 2. Evolution of the *gem*-dimethyl resonances in (a) ^{1}H NMR (NS = 128) and (b) ^{13}C NMR (NS = 1024) analyses of cyclohexyl-TEMPO vs temperature; solvent = C_6D_6/TCE (1/2 v/v).

with a nitroxide was first to check that the process is operating according to a controlled mechanism. For that purpose, three experiments were conducted up to different yields (entries 1, 3, and 5, Table 1), and the molar ratios of ethylene to BOMg were controlled from the observed drop of ethylene pressure in a reservoir connected to the reactor (see polymerization procedure in the Supporting Information). As shown by SEC analyses, for the three experiments, narrowly distributed molecular weights (MW) are obtained (PDI < 1.3). Molecular weights (MW) were determined by both high-temperature SEC and ^{1}H NMR (by comparison of the integral of the CH_2 of the main chain and the integrals corresponding to saturated and unsaturated chain ends). ^{1}H NMR analysis shows that the oligomers formed in the presence of BOMg are highly saturated, assuming a fast interchange between the growing chain at the Nd center and alkyl chains at the Mg center (Table 1) in agreement with previous studies.

As the controlled characteristics of the system were evidenced, the functionalization of the polyethylene chains by a stable nitroxide; namely, the 2,2,6,6-tetramethylpiperidinyl-1-oxy radical (TEMPO) was investigated. In that respect, at the end of the polymerization, a solution of TEMPO in toluene was simply added to the medium at 80 °C (molar ratio TEMPO/Mg = 4/1), and the resulting mixture was stirred for 2 h (entries 2, 4, and 6, Table 1). The recovery of the polymer by precipitation in methanol gave a white powder which was analyzed by ^{1}H and ^{13}C NMR. The obtained spectra corresponding to entry 4 (Figure 1a,b) are typically those of a polyethylene that is usually prepared with the used catalytic system, except for the presence of resonances that are attributable to end groups derived from TEMPO. Because of a conformational interconversion involving ring inversion,[9] the *gem*-dimethyl groups on TEMPO-based organic molecules are usually observed under



P₁

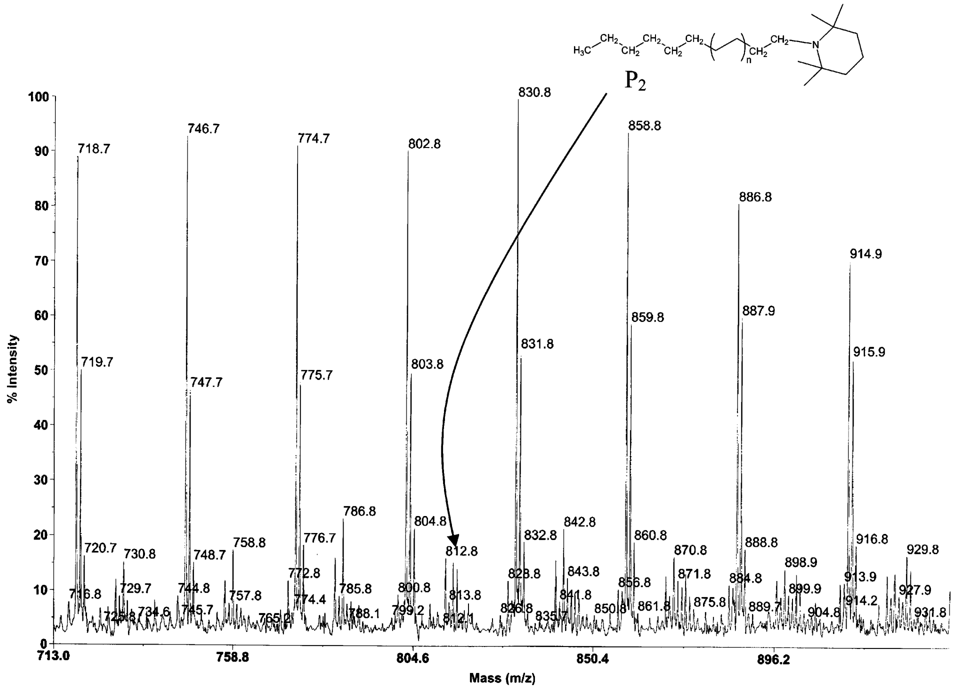


Figure 3. MALDI−TOF mass spectrometry of PE-TEMPO (entry 4, Table 1) using a tetrahydroxyacetophenone matrix (accelerating potential of 20 kV; laser: 337 nm nitrogen laser).

several resonances between 1.10 and 1.30 ppm for ^{1}H NMR and around 20.0 and 33.0 ppm for ^{13}C NMR performed in $CDCl_3$. The authors showed that, as for any dynamic process of exchange, the ring conversion gives rise to temperature-dependent NMR *gem*-dimethyl resonances. In our case, for solubility purposes, the obtained polyethylenes are analyzed in a mixture of C_6D_6 and tetrachloroethylene (1/2 v/v) at 363 K. Thus, to investigate the effect of the temperature on the *gem*-dimethyl resonances, ^{1}H and ^{13}C NMR spectra of a model compound, namely the 2,2,6,6-tetramethyl-1-(cyclohexyloxy)piperidine (cyclohexyl-TEMPO),[10] were recorded at 295, 323, and 363 K (Figure 2a,b). Indeed, at 363 K, *gem*-dimethyl groups give a unique sharp ^{1}H NMR (400 MHz) resonance located at 1.14 ppm, indicating that the coalescence temperature is overtaken and give nondetectable ^{13}C NMR (100.6 MHz) resonances due to a very important broadening typically observed near the coalescence temperature. All these observations confirmed the assignments proposed in Figure 1 (protons e + f at 1.14 ppm) and the successful synthesis of TEMPO end-functionalized polyethylene chains. The comparison of the integrals of the methylene adjacent to the oxygen atom and the integrals relative to saturated and unsaturated chain ends was used to assess the functionalization rate which is reported in Table 1. Without any optimization (temperature, stoichiometry, reaction time), more than 50% of the chains can be functionalized by this very simple and direct method.

The introduction of this polar end group drove us to tentatively analyze the obtained polyethylene chains by MALDI−TOF mass spectrometry, a technique usually hardly used for this kind of polymer lacking of cationizable groups.

As expected, polyethylene obtained in entry 3, Table 1, did not give any signal when analyzed by MALDI−TOF. Different MALDI−TOF analysis conditions were screened for our model compound cyclohexyl-TEMPO. The trihydroxyacetophenone matrix gave the best results with one peak of 240.2 g mol^{-1}, in agreement with the expected molecular weight (MH^+). PE-TEMPO chains were then analyzed under the same conditions (Figure 3). A very clean spectrum was obtained, and the main population (P_1) corresponds to the expected PE-TEMPO population (as in the case of cyclohexyl-TEMPO, PE-TEMPO-H^+ is observed). The side population P_2 may be attributed to the structure given in Figure 3. (A definitive assignment will be given in a forthcoming publication.)

In conclusion, alkoxyamine-terminated polyethylene chains (PE-TEMPO in the present study) can easily be prepared, and we are presently investigating the use of a large range of nitroxides for the same purpose. The functionalization technique is easy to handle, and the obtained polyolefins are easily analyzed by MALDI−TOF mass spectrometry. The efficiency of these new macroinitiators is currently assessed in conventional and controlled radical polymerizations.

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Supporting Information Available: Polymerization procedure, polyethylene functionalization, and characterization methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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