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## Free Ethylene Radical Polymerization under Mild Conditions: The Impact of the Solvent

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Received July 23, 2009

Revised Manuscript Received August 26, 2009

Ethylene is industrially polymerized either by radical polymerization under severe conditions or by catalytic polymerization at lower temperatures and pressures. Free radical polymerization of ethylene is performed under high pressure (1000–4000 bar) and high temperature (200–300 °C) in bulk.<sup>1,2</sup> Under these conditions radical polymerization provides a branched polyethylene due to uncontrolled transfer reactions to polymer. Polymers possess a degree of crystallinity of 45–55% and melting points of 105–115 °C. They contain 15–25 short-chain branches and 2–5 long-chain branches per 1000 carbon atoms. Catalytic polymerizations<sup>3,4</sup> generally occur at low pressure (1–50 bar) and low temperature (near or below 100 °C). Under intermediate conditions (100–200 °C, 100–500 bar) an anionic oligomerization<sup>5,6</sup> of ethylene (“Aufbau” reaction) occurs leading to a linear polyethylene with low molecular weight.

At ethylene pressure below 300 bar and low temperature (<100 °C) radical polymerization has been shown to be inefficient, unless ethylene is activated by strong Lewis acid such as original lithium cations.<sup>7</sup> Clark’s calculations<sup>8,9</sup> of the gas-phase activation energy of methyl radical addition to ethylene predicted a decrease from 60 to 25 kJ/mol when ethylene is complexed with Li<sup>+</sup>.

The development of radical polymerization of ethylene under mild conditions ( $P < 250$  bar and  $50\text{ °C} < T < 90\text{ °C}$ ) is an important challenge since it may open a new field of radical ethylene polymerization allowing the use of solvents, organic additives and classical radical initiators such as diazo compounds. Solvent effects have been observed in radical polymerization with common vinyl monomers,<sup>10,11</sup> although this effect remains tiny except for vinyl acetate. To our knowledge, the influence of the solvent has not been discussed for radical polymerization of ethylene. In the present paper, radical ethylene polymerization is reported using two solvents having different polarities: toluene and THF. The solvent influences on productivity and polyethylene molecular weight are discussed and rationalized.

Radical polymerization of ethylene was performed at 70 °C in the range of 10 to 250 bar using AIBN as initiator in toluene (Figure 1). Toluene was chosen in a first approach as a typical solvent of the slurry catalytic polymerization of ethylene performed using similar conditions.

Under 50 bar of ethylene pressure, no polymer was obtained. From 50 to 250 bar, polymerization occurred but conversion of ethylene remained very low (3% conversion considering a solubility of ethylene<sup>12</sup> of 470 g/L under 100 bar at 70 °C). As expected the radical polymerization of ethylene was inefficient under mild conditions using toluene as solvent.

We investigated ethylene polymerization in THF (typical solvent for radical polymerization), with the aim to improve yield. Surprisingly polymerization in THF occurred down to 10 bar of ethylene, an unusual pressure range for pure radical polymerization of ethylene. At 100 bar 3.9 g of polyethylene were isolated, corresponding to 17% of conversion. Radical polymerization of ethylene was about 6 times more efficient than in toluene. As already mentioned, solvent impact is usually a tiny effect in radical polymerization, but in the case of ethylene polymerization solvent seems to play a major role.

The produced polyethylenes were moderately branched in both solvents (7 branches/1000C in toluene and 9 branches/1000C in THF) as determined by <sup>13</sup>C NMR<sup>13</sup> (see Supporting Information, Figures S1 and S2) and have a melting point between 115 and 119 °C and a crystallinity of 55–70% (see Supporting Information, Table S1). <sup>13</sup>C NMR spectra showed only butyl and longer chain branches and no vinyl chain end. Transfer to solvent provided respectively phenyl-ended and THF-ended polyethylenes which were fully identified by <sup>13</sup>C NMR (see Supporting Information, Figures S1 and S2). In the case of transfer to THF two different structures (1- and 2-polyethylenyl-THF, see Supporting Information, Figure S2) were identified.

Molecular weights were lower in THF than in toluene. As expected molecular weights increased with ethylene concentration: from 950 to 4300 g/mol with toluene and from 440 to 2400 g/mol with THF. At pressure below 100 bar, melting points and molecular weights dropped (runs 3, 8–10, see Supporting Information Table S1) and oligomers were produced.

The number of chains per initiator was about 10 times higher in THF than in toluene. Molecular weights in THF were about 0.6 times lower than in toluene. Assuming AIBN dissociation being similar in both solvents, the rate of polymerization in THF was 6 times higher than in toluene.

To examine the variation of kinetic constants, the kinetic law of the free radical polymerization (eq 1) was checked for both toluene and THF solvents. We plotted  $\ln(1/(1-x))$  versus time (Figure 2)

$$\frac{1}{1-x} \frac{\partial x}{\partial t} = k_p \sqrt{\frac{2fk_d[I]}{k_t}} = k_{tot} \quad (1)$$

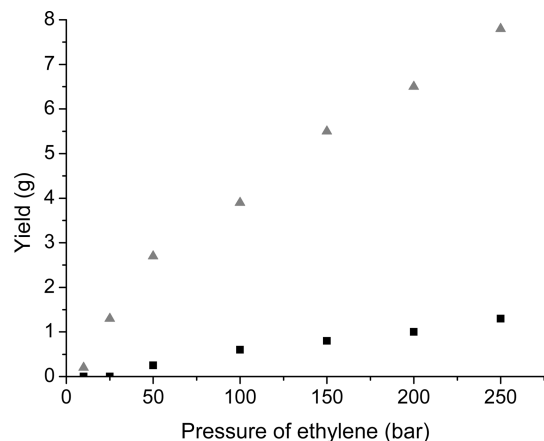
with  $x$  = ethylene conversion,  $[I]$  = AIBN concentration,  $f$  = efficiency factor of the initiator, and  $k$  = kinetic constants of initiator dissociation ( $k_d$ ), propagation ( $k_p$ ), and termination ( $k_t$ ).

A linear relation with a good correlation was observed for polymerization in THF and toluene. The slope  $k_{tot}$  for THF was 6 times higher than the toluene one. After 8 h under 100 bar of ethylene, 7.8 g of polyethylene were produced with THF as solvent (33% of conversion) and only 1.3 g with toluene (5.5% of conversion). A factor of 6 was observed as expected.

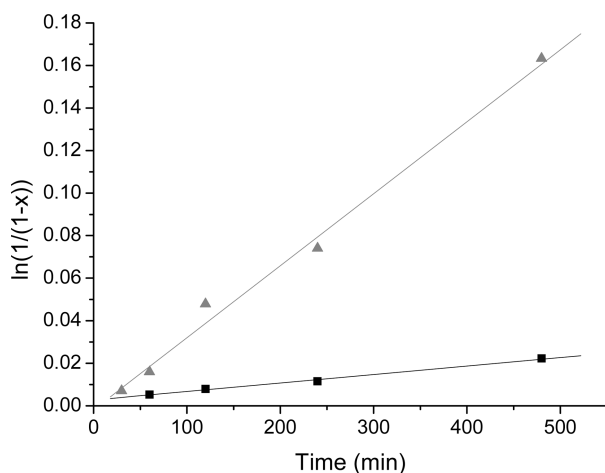
For each solvent, there was neither significant change in the melting point nor in the molecular weight during the polymerization (see Supporting Information, Table S2).

Various concentrations of initiator were evaluated at 100 bar of ethylene pressure and 70 °C (see Supporting Information, Figure S3, Table S3). We plotted  $\ln(1/(1-x))$  versus  $[I]^{1/2}$ . Equation 1 was once again confirmed. As expected molecular weight decreased according to the concentration of initiator, due to an increase of the termination rate. Melting points remained unchanged between 115 and 117 °C.

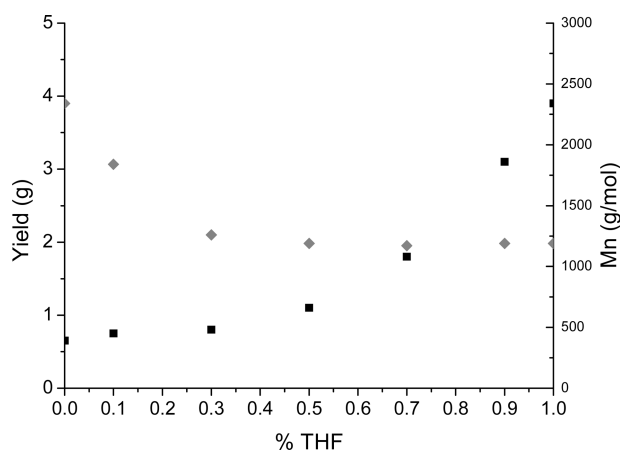
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**Figure 1.** Pressure influence on ethylene radical polymerization: (■) 50 mg of AIBN, 50 mL of toluene, 4 h at 70 °C under ethylene pressure; (▲) 50 mg of AIBN, 50 mL of THF, 4 h at 70 °C under ethylene pressure.



**Figure 2.** Influence of time on radical polymerization of ethylene: (■) 50 mg of AIBN, 50 mL of toluene at 70 °C under 100 bar of ethylene pressure; (▲) 50 mg of AIBN, 50 mL THF at 70 °C under 100 bar of ethylene pressure.



**Figure 3.** Impact of solvent composition in volume on radical polymerization of ethylene: (■) 50 mg of AIBN, 50 mL of solvent, 4 h at 70 °C under 100 bar of ethylene pressure; (◆)  $M_n$  (g/mol) determined using High Temperature SEC.

To further investigate the THF effect, polymerizations of ethylene under 100 bar at 70 °C were performed with different mixtures of THF and toluene as solvent (Figure 3).

**Table 1.** Arrhenius Parameters of Ethylene Polymerization (Assuming the Validity of the Arrhenius Law)

solvent	$E_{tot}$ , global activation energy (kJ/mol)	$\ln(A_{tot})$ , global pre-exponential factor
toluene	27.7	7.6
THF	32.8	10.3

The yield did not increase linearly with the solvent composition. The observed activation was not proportional to the THF amount in the solvent mixture. Below 40% of THF the yield remained even and drastically increased over 40% of THF only. Molecular weights decreased with the addition of THF (see Supporting Information, Table S4) due to transfer to THF.

**How To Explain This Unexpected Effect of Solvent?** The THF activation can be explained by a change of polymerization rate. To go further we aim to calculate the global activation energy and global pre-exponential factor. For this purpose we performed polymerizations at several temperatures (50, 70 and 90 °C) and ethylene pressures (from 50 bar up to 250 bar) in both solvents. One can remark that ethylene conversion seemed not to be linked to ethylene pressure (see Supporting Information, Table S5). At 90 °C ethylene conversion reached 40% after 4 h of polymerization.

From these experiments we plotted  $k_{tot}$  versus  $1/T$  to determine the Arrhenius parameters. Corresponding  $E_{tot}$  and  $\ln(A_{tot})$  are summarized in Table 1.

Ideally, the determination of the Arrhenius parameters for each polymerization step should be performed, but this kind of study is currently incompatible with our conditions of pressure (since stopped flow or pulsed laser polymerizations techniques cannot be used).

$$k_{tot} = k_p \sqrt{\frac{2fk_d[I]}{k_t}}$$

$$= A_{tot} \exp\left(\frac{-E_{tot}}{RT}\right) \left\{ \begin{array}{l} E_{tot} = E_p - \frac{1}{2}E_t + \frac{1}{2}E_d \\ A_{tot} = A_p \sqrt{\frac{2fA_d[I]}{A_t}} \end{array} \right. \quad (2)$$

The global activation energy and the pre-exponential factor (eq 2) are lower in toluene than in THF. Lower global activation energy is usually linked to a more favorable reaction. In both solvents the polymerization mechanism was considered to be the same, so the change in the global activation energy was only due to the relative stabilization of intermediate and activated states, which differ from one solvent to the other.<sup>14</sup> Solubilization by toluene provides a lower energy barrier than in THF.

Despite lower global activation energy, toluene was less efficient than THF. The global pre-exponential factor is higher for THF, which explains, in the range of temperature used, the better efficiency of radical ethylene polymerization in THF. The global pre-exponential factor is proportional to the frequency of efficient shocks. With a higher pre-exponential factor the probability of the mechanism involved is supposed to increase. Differences in geometry of activated states in toluene and in THF could explain the difference of pre-exponential factors. Toluene is less electron donor than THF, more toluene molecules may therefore be necessary to stabilize the radical corresponding to a denser solvation shell. This could explain a higher pre-exponential factor in THF than in toluene.

In summary, this work showed that radical ethylene polymerization can be effective under mild conditions

(50 °C <  $T$  < 90 °C and  $P$  > 10 bar in THF) contrary to what used to be assumed. The polymerization was 6 times more productive in THF than in toluene: conversions of ethylene up to 40% were obtained. Because of transfer to solvent, 1- or 2-polyethylenyl-THF were synthesized. Calculations of Arrhenius parameters have been done to understand THF activation. THF efficiency is not due to a lower global activation energy but to a higher pre-exponential factor corresponding to a higher efficient shock frequency. Further investigations with other solvents of various polarities are under progress in order to discriminate the solvent effect and to increase polyethylene molecular weights by reducing the transfer capacity of solvent.

**Acknowledgment.** E.G. thanks the “Ministère de la Recherche et de l’Enseignement Supérieur” for fellowship.

**Supporting Information Available:** Text giving experimental details, figures showing NMR spectra, influence of initiator concentration on radical polymerization of ethylene, tables showing the influence of ethylene pressure, polymerization time, concentration of initiator, solvent composition, and temperature on the radical polymerization of ethylene. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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