Macromolecules

ARTICLE

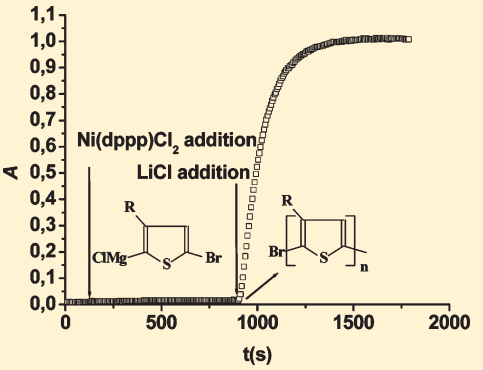
pubs.acs.org/Macromolecules

Kinetic Study, by UV−Vis Spectroscopy, on the Strong Effect of LiCl on the Controlled Polymerization of 2-Bromo-3-hexyl-5-iodothiophene and 2-Iodo-3-hexyl-5-bromothiophene: Determination of the Propagation Rate Constants, Application to the Synthesis of High Molecular Weight Polydodecylthiophene

J.-P. Lamps and J.-M. Catala*

Institut Charles Sadron, CNRS, UdS, 23 rue du Loess, 67034 Strasbourg, France

ABSTRACT: The controlled polymerization of the 2-bromo-3-hexyl-5-iodothiophene (**5**) and 2-iodo-3-hexyl-5-bromothiophene (**2**), using Ni(dppp)Cl_2 as a catalyst and LiCl as an additive, was followed in real time by UV−vis spectroscopy. It was shown that the propagation rate constant depends strongly on the ratio R = [LiCl]/[M]. For R = 4 the polymerization rate constant for the regular monomer **5** achieves a constant value 20 times higher than the one obtained without LiCl: $k_p = 44 \pm 5\ mol^{-1}L\ s^{-1}$. For the reverse monomer **2**, the addition of LiCl (R = 4) leads to a polymerization reaction with a similar propagation rate constant. The slow initiation reaction of monomer **2**, with and without LiCl, has been analyzed by ^{31}P NMR, UV−vis spectroscopy, SEC. It was shown that the addition of LiCl increases the reactivity of the activated monomers under their Grignard forms but also modifies the active center by exchanging the bromine atom by a chlorine atom. This new process was extended to the synthesis of well-defined poly(dodecylthiophene) of high molecular weight.



INTRODUCTION

The number of studies on the synthesis of regioregular polythiophenes, by the Kumada coupling reaction, has grown significantly last years since the discovery by Yokozawa[1] and McCullough[2] that this process proceeds via a chain-growth polymerization. Several works were devoted to the mechanism itself and in particular to the location of the catalyst. It was evidenced that the nickel catalyst mainly undergoes selective "ring walking" along the conjugated chain comprising two or even three thiophene rings.[3a] This conclusion was completed recently, by the same authors, who suggest that catalytic Ni(0) species are able to walk along the chain up to the opposite end and can initiate polymerization there.[3b] Nevertheless, an alternative mechanism has been also proposed, based on the interchain diffusion of the catalyst and dependent on the initial monomer concentration.[4] The role of the substituent and in particular its position with respect to the active center has also been studied. It was demonstrated that Grignard-activated monomer from 5-bromo-3-hexyl-2-iodothiophene (reverse monomer) in the presence of Ni(dppp)Cl_2 is unable to the form the head to head dimer.[5a] This was related to the steric hindrance occurring during the dimerization. Moreover, by using an external functionalized aryl halide initiator it was shown that the initiation reaction was performed but not the propagation step. It was suggested that a lack of *ortho*-stabilization, by the alkyl chain, of the nickel complex prevents the oxidative addition of the nickel into the Ar−Br bond. However, another explanation was given from a study done with the same monomers and 3,4-dihexylthiophene.[5b] The authors proposed that the second transmetalation step was in fact the key step of the polymerization of alkyl thiophene and that the *ortho*-stabilization of the propagating Ni species by the substituent is not important. They suggested that the alkyl substituent *ortho* to the magnesium center impede the transmetalation stronger than the nickel center. Recently, we observed that this lack of initiation and propagation for the reverse monomer could be modified by adding a salt like LiCl. The effect of this additive has already been described in particular in the increased activity of the isopropyl magnesium chloride[6a] in the Br/Mg exchange reaction, but also to an acceleration of the polymerization rate during the synthesis of poly(2,5-bi(hexyloxy) phenylene).[6b] However, similar studies have shown than this effect depends on the ligand catalyst (Ni(dppe)Cl_2 or Ni(dppp)Cl_2).[6c,d]This additive was also used to prepare well-defined functionalized polyhexylthiophene; the authors have observed an improvement of the yield and of reproducibility of the process.[7] Very recently it was shown that, during the polymerization of 2,5-dibromo-3-hexylthiophene, LiCl accelerates the rate of polymerization (17%), increases the

Received: July 19, 2011
Revised: September 15, 2011
Published: September 29, 2011

dx.doi.org/10.1021/ma201654f | *Macromolecules* 2011, 44, 7962–7968

yield, and favors to a small extent the incorporation of the reverse monomer with a small effect on the regioregularity.[8] To quantify the effects of LiCl observed in our experiments by the corresponding propagation rate constant, we undertook a kinetic study involving a spectroscopic technique developed in our laboratory.[9] This technique, based on a UV−vis probe immersed in the reaction medium, allows us to follow the different stages of the polymerization reaction. Indeed, as the monomer is consumed, a conjugated polymer is formed in the medium characterized by a UV−vis spectrum. The monitoring of the evolution of the polymer absorbance with time permits to quantify the monomer consumption during the propagation step.

The theoretical eq 1, associated with the graph $A = f(t)$, was established as follows:

$$d[P]/dt = -d[M^*]/dt = k_p[M^*][Ni]_0$$

$$[M^*] = [M^*]_0 \exp(-k_p t[Ni]_0)$$

$$[P] = [M^*]_0 - [M^*] = [M^*]_0(1 - \exp(-k_p t[Ni]_0))$$

$$A_p = [M^*]_0(1 - \exp(-k_p t[Ni]_0)\varepsilon_p l)$$

$$A_p = A_{fp}(1 - \exp(-k_p t[Ni]_0)) \quad (1)$$

or

$$\ln((A_{fp}/(A_{fp} - A_p))/[Ni]_0 = k_p t \quad (2)$$

A_{fp}: final absorbance of the polymer when all the monomer is consumed.

This procedure applied to the polymerization of halogenoalkylthiophene has proved its potential and its accuracy by showing that two rate constants of propagation are needed to characterize the process. In this contribution, the effect of LiCl on the reactivity of the monomers activated on carbon 2 and 5 and therefore one the kinetic parameters are presented. To enable a better understanding of the text, the 2-bromo-3-hexyl-5-iodothiophene and the 2-iodo-3-hexyl-5-bromothiophene having a iodine atom on the carbon 5 or 2 of the thiophene ring have been designated by **5** and **2**, where **5*** and **2*** correspond to their Grignard forms.

EXPERIMENTAL SECTION

Materials. 3-Hexylthiophene (Aldrich, 97%), *N*-bromosuccinimide (Aldrich, 99%), iodine (Aldrich, 99.8%), iodobenzene diacetate (Acros, 98%), 2-bromo-3-hexylthiophene (Aldrich, 97%), Ni(dppp)Cl_2 (Acros, 99%), 3-dodecylthiophene (Aldrich 97%), *i*-PrMgCl ((2 M solution in THF, Acros), and heptane (Carlo Erba) were used without further purification. THF (Erba, 99.9%) was distilled twice under argon, and on benzophenone-sodium radical anion. For flash chromatography, silica gel (Marck Geduran Si 60 40−63 μm) was used.

Synthesis of 5-bromo-3-hexylthiophene (1). Into a three-necked flask placed under argon was introduced 1 g of 3-hexylthiophene (0.4×10^{-2} mole) and 10 mL of anhydrous THF. After cooling down to −78 °C, *n*-BuLi was added dropwise (0.4×10^{-2} mole) under stirring. Two hours later, tetrabromomethane was added (1 equiv) and the resulting solution was maintained at −78 °C during 2 h. The reaction was ended at this temperature by adding a mixture of methanol and water containing $Na_2S_2O_3$. The organic layer was extracted twice with hexane, washed with water and dried over $MgSO_4$ before filtration and evaporation. The crude product contains 75% of 5-bromo-3-hexylthiophene, 10% of 2-bromo-3-hexylthiophene and 15% of hexylthiophene. The purification was done by several flash-chromatographies on silica gel, using heptane as elution solvent. (Yield: 40%.)

^{1}H NMR in $CDCl_3$: δ= 0.89 ppm (t, J = 6,8 Hz, 3 H), 1.30 ppm (m, 6 H), 1.56 ppm (qn, 2 H), 2.55 ppm (t, J = 7.46 Hz, 2H), 6.80 ppm (d, J = 1.77 Hz, 1 H), 6.88 ppm (d, J = 1.77 Hz, 1 H).

Synthesis of 5-Bromo-3-hexyl-2-iodothiophene (2). This monomer was synthesized according to the literature procedure.[5a] 1H NMR in $CDCl_3$: δ 0.89 ppm (t, 3 H), 1.29 ppm (m, 6 H), 1.58 ppm (m, 2 H), 2.53 ppm (t, 2H), 6.97 ppm (s, 1 H).

Synthesis of 2-Iodo-3-hexylthiophene (3). According to ref 5a, ^{1}H NMR in $CDCl_3$: δ = 0.89 ppm (t, 3 H), 1.31 ppm (m, 6 H), 1.54 ppm (qn, 2 H), 2.55 ppm (t, 2H), 6.76 ppm (d, 1 H), 7.38 ppm (d, 1 H).

Synthesis of 2-Bromo-3-dodecylthiophene (4). A 1 g (3.96×10^{-3} mol) sample of 3-dodecylthiophene was dissolved in 10 mL of anhydrous THF under argon. After cooling down to 0 °C, 1 equiv of *N*-bromosuccinimide (0.70 g, Acros, 99%) was added while stirring. After 2 h, the solution was allowed to warm up to room temperature overnight. After solvent evaporation, the residue was mixed with 50 mL of pentane leading to precipitation of succinimide that was removed by filtration. After solvent evaporation, light yellow oil was recovered and purified by flash-chromatography using heptane as elution solvent. Yield: 66%.

^{1}H NMR ($CDCl_3$): δ = 0.89 ppm (t, J = 7 Hz, C**H**$_3$), 1.27 ppm (m, −(C**H**$_2$)$_7$−CH$_3$), 1.56 ppm (m, C−CH$_2$C**H**$_2$), 2.57 ppm (t, J = 8 Hz, C−C**H**$_2$), 6.80 ppm (d, J = 5.6 Hz, −C$_4$**H**), 7.19 ppm (d, J = 5,6 Hz, −C$_5$**H**).

Synthesis of 2-Bromo-3-hexyl-5-iodothiophene (5). This monomer was synthesized as described in ref 1a. ^{1}H NMR in $CDCl_3$: δ = 0.89 ppm (t, 3 H), 1.29 ppm (m, 6 H), 1.58 ppm (m, 2 H), 2.53 ppm (t, 2H), 6.97 ppm (s, 1 H).

Synthesis of 2-Bromo-3-dodecyl-5-iodothiophene (6). A 0.7816 g (2.63×10^{-3} mol) sample of 2-bromo-3-dodecylthiophene was dissolved in 2 mL of dichloromethane at 0 °C. Then 0.17 g of iodine (6.7×10^{-4} mol) and 0.383 g of iodosobenzene diacetate (1.18×10^{-3} mol) were then added. After 10 min, the solution was brought to ambient temperature. As soon as the iodine had been consumed, 0.16 g of iodine (6.3×10^{-4} mol) was added. Three hours later the solution was diluted with a few milliliters of dichloromethane and washed with a aqueous solution of sodium thiosuphate. The organic layer was then dried over magnesium sulfate. After removing the solvent, 0.83 g of crude product was recovered. Purification by flash-chromatography (heptane as eluent) led to 0.65 g of pure product. ^{1}H NMR in $CDCl_3$: δ = 0.88 ppm (t, 3 H), 1.29 ppm (m, 18 H), 1.53 ppm (m, 2 H), 2.53 ppm (t, 2H), 6.97 ppm (s, 1 H).

General Procedure for Kinetic Experiment. In a 50 mL reactor equipped with a UV−vis probe (l = 0.0120 ± 0.0005 cm) and placed under argon, 20 mL of purified THF was added at 20 °C, under stirring. A first UV−vis baseline was done between 600 and 250 nm. The reaction medium was cooled at 0 °C and a second baseline was done between 600 and 250 nm. The recording of the UV−vis spectra between 600 and 250 nm (10 scans/min) was started and small drops of *i*-PrMgCl was introduced until the observation of a small absorbance at 250 nm. The exact amount of *i*-PrMgCl (2 M solution in THF, 0.125 mL, 0.250 mmol) was then added. The 2-bromo-3-hexyl-5-iodothiophene was introduced (0.0955 g, 0.256 mmol) and the evolution of spectra was followed until the stabilization of the absorbance. 44 mg of LiCl (1 mmol) in a small cup and dried just before the experiment (1 h at 140 °C) was place under argon in a lateral compartment of the reactor. The small cup was then pushed in the solution maintained at 0 °C under stirring. After the salt dissolution, the exact amount of activated monomer was checked from a small withdrawal deactivated on CH_3OD. The reaction mixture was then warmed to 20 °C and the recording of the UV−vis spectra, between 600and 250 nm, was then started. According to the procedure described previously, the Ni catalyst (2.17 mg, 0.004 mmol), placed in a small cup under argon, was introduced in the medium. The polymerization reaction was followed

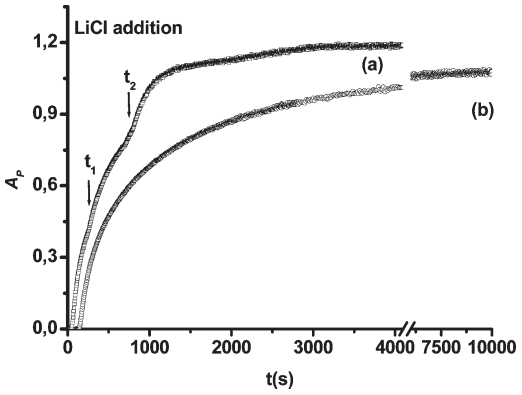


Figure 1. Evolution of the absorbance A_p (λ = 448 nm) vs time during the polymerization of the 2,5-dibromo-3-hexylthiophene, with (a) and without LiCl addition (b); (a) [M] = 0.87 × 10^{-2} mol·L^{-1} [Ni] = 4.52 × 10^{-4} mol·L^{-1}; (b) [M] = 0.85 × 10^{-2} mol·L^{-1}, [Ni] = 4.45 × 10^{-4} mol·L^{-1}, t_0 = 100 s; T = 20 °C.

until a stabilization of the absorbance at 448 nm. The reaction medium was then deactivated by addition of a few drops of concentrated hydrochloric acid. The polymer was precipitated in methanol.

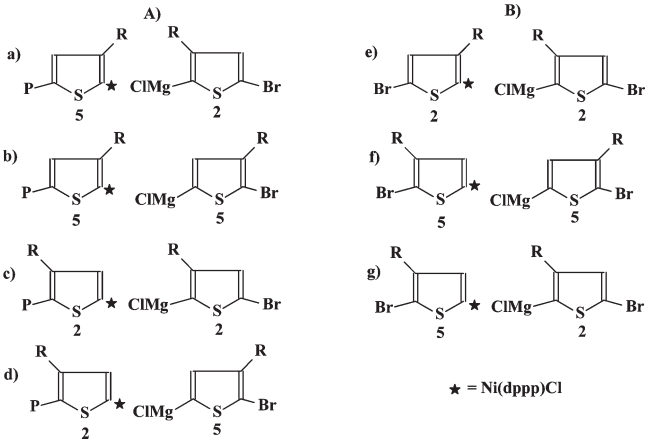
Characterizations. ^{1}H, ^{13}C, and ^{31}P NMR measurements were performed on a Bruker AC 400 spectrometer. For ^{1}H and ^{13}C NMR, $CDCl_3$ was used as a solvent. For ^{31}P NMR done on the reaction medium, a capillary containing a solution of H_3PO_4 in D_2O (0.36 M) was placed inside a special NMR tube bearing a stopcock. Molecular weight was determined at room temperature, with two size exclusion chromatography (SEC) apparatus using THF as eluent (flow rate: 1 mL/min): for high molecular weight the apparatus is equipped with a refractometer detector (ShimadzuRID10A), five columns PL GEL-(10 μm particles) (3 mixed B, 10^3 Å, 10^5 Å), a light scattering detector MALS TREOS (Wyatt) a UV−vis detector (Shimadzu SPD M20); for low molecular weight the apparatus is equipped with a refractometer detector (ShimadzuRID10A), four columns PL GEL(5 μm particles) (50 Å, 100 Å, 500 Å, 1000 Å), a UV−vis detector (Shimadzu SPD10VP). The UV−vis spectra were obtained with a UV−vis spectrophotometer (Varian Cary 50).

RESULTS AND DISCUSSION

To show the global effect of LiCl on the polymerization rate of the 2,5-dibromo-3-hexyllthiophene, the monomer was activated with *i*-PrMgCl and the evolution of the absorbance versus time was followed during the successive addition of the salt, according to the following procedure: at t = 0 s the catalyst was added on the solution of the activated monomer without any salt. At t_1 = 260 s, the first addition of LiCl was done in the ratio [LiCl]/[M*] = 0.26; the second one was carried out at t_2 = 720 s ([LiCl]/[M*] = 0.56).

In Figure 1 are represented the variation of the absorbance versus time for the same reactions carried out with salt (graph a) and without salt (graph b). As expected at the beginning of the process, the experimental conditions being identical, the absorbances observed on the two graphs are similar: the polymerization starts quickly and then slows over time. The addition of LiCl in experiment **a** (graph a), at $t = t_1$, causes an immediate increase in the rate of polymerization. At t_2 = 720 s, the rate slows done and the second addition of salt can then take place. This new addition leads to a similar behavior: an increase of the monomer consumption and then a slowing. However, while a plateau seems to be reached (t = 1200 s, A_p = 1.1), suggesting the end of the

Scheme 1. Schematic Representation of the Intermediate State during Polymerization (A) and Initiation (B) Reactions of Activated Monomers 2* and 5*.



polymerization, the kinetics restarts before to stop definitively (t = 3200 s, A_p = 1.23). For the reaction done without salt (Figure 1b), only one plateau is reached at t = 7000 s with A_p= 1.1.

This difference in behavior, at the end of the process, was quite unexpected but the examination of the NMR spectra obtained from withdrawals deactivated on CH_3OD gives us the explanation. Indeed, the activation reaction of 2,5-dibromo-3-hexylthiophene leads to two reactive species, **5***and **2*** (Scheme 1), corresponding to the active site on carbons 5 or 2 of the monomer ring, in the ratio 80:20. The ^{1}H NMR chemical shifts of these compounds deactivated on CH_3OD, in the aromatic region, are two singlets at 6.89 and 6.80 ppm, respectively. Integrations of these peaks permit to follow the consumption of these two species. Examination of all spectra reveals that, for the reaction done with salt addition (Figure 1a), only the activated monomer **5*** is totally consumed between t = 0 and t = 1200 s. During the same period the concentration of the activated monomer **2*** remains constant but, for t > 1200 s, this latter starts to decrease. The total consumption of **2*** occurs at t = 3200 s and leads to a stabilization of the absorbance whose value is obviously higher than the one obtained with the polymerization of **5*** alone (Figure 1b).

All these observations suggest that LiCl interacts with the monomers under their Grignard form by increasing their reactivity whatever the position of the active site, on carbons 5 or 2 of the thiophene ring. However, the formation of successive blocks and in particular the polymerization of **2*** after the consumption of **5*** shows that the addition of **2*** on the growing chains of **5** monomer, k_{52}, is close to zero. Moreover, the evolution of the polymerization rate suggests that after addition of the monomer-(LiCl) species on the growing chain, the LiCl salt is not completely generated "free" in the medium (eq 3) because otherwise it would have interacted with another monomer molecule and have thus maintained a high rate of polymerization.

$$\text{P}-\text{Ni(dppp)Br} + \text{Br}-\text{M}-\text{MgCl(LiCl)}_n \rightarrow \text{MgClBr} + n\text{LiCl} + \text{P}-\text{M}-\text{Ni(dppp)Br} \quad (3)$$

All these observations have to be clarified but first we investigated the effect of the ratio R = [LiCl]/[monomer] on the polymerization rate constant.

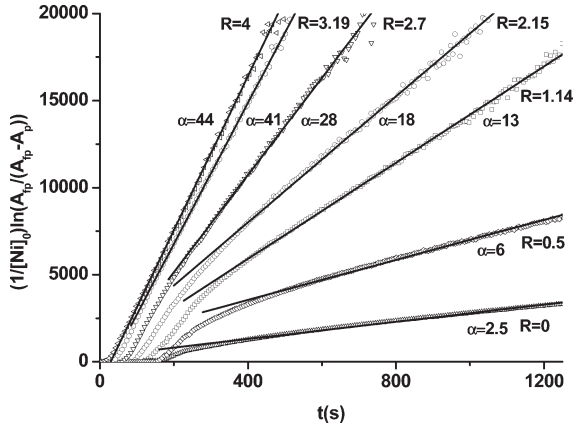


Figure 2. Evolution of $\ln((A_{fp}/(A_{fp} - A_p))/[Ni]_0$ versus time (for [M] and [Ni] see Table 1).

Table 1. Evolution of the Propagation Rate Constants with *R* ($\Delta k_p/k_p$ = 10%)

R	[M] × 10^2 mol L^{-1}	[Cat] × 10^4 mol L^{-1}	k_{p1}, mol^{-1} L s^{-1}	k_{p2}, mol^{-1} L s^{-1}
0	0.86	2.95	6	2.5
0.5	1.3	2.6	20	6
1.14	1.14	2.0	24	13
2.15	1.10	2.15	31	18
2.7	1.07	2.0	37	28
3.19	1.03	2.0	41	
4	1.11	2.10	44	

EFFECT OF LICL CONCENTRATION

For this study, the 2-bromo-3-hexyl-5-iodothiophene (**5**) was used because this monomer leads to single active species **5*** during the reaction with *i*-PrMgCl and not to a mixture as observed for the 2,5 dibromo-3-hexyl thiophene. As a consequence, the end of its polymerization is highlighted by a well-defined plateau on the curve A_p = f(t) and this leads to a better accuracy of A_{fp} and k_p. In the case of the 2,5 dibromohexyl thiophene, the evaluation of A_{fp} corresponding to the total consumption of M_5* is less accurate because, at the same time, the polymerization of **2*** starts (Figure 1a).

In all experiments, LiCl was added at 0 °C after the activation step. The reaction medium was then kept at 20 °C before addition of the Ni(dppp)Cl_2 catalyst. The polymer formation versus time was followed by UV−visible spectroscopy.

On Figure 2 are represented the different graphs obtained from the relations 2 and A_p= f(t) for different *R* values.

Figure 2 shows two types of behavior depending on the ratio *R*. For *R* greater than 3, a single rate constant of propagation is observed. Its value (k_{p1}= α= 44 mol^{-1} L s^{-1}) is 20 times greater than that the one determined for a polymerization carried out without addition of salt (k_{p2} = α= 2.5 mol^{-1} L s^{-1}, Table 1). For intermediate values of *R*, a clear change in slope appears, indicating the presence of less reactive species in the reaction medium. Depending on their concentration and their respective propagation constant, the overall rate of monomer consumption is modified. Therefore, the propagation rate constants collected in Table 1 are only apparent rate constants. The values of these

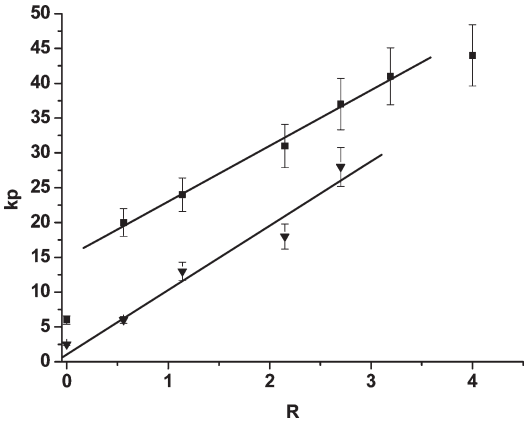


Figure 3. Variation of k_{p1} (■) and k_{p2} (▼) with the ratio *R*.

ones increase regularly with the R ratio (Figure 3) and reach a constant value for *R* > 3.

Our attempt to rationalize this trend, by establishing a kinetic equation based on equilibrium between different active species, was unsuccessful. It should be noted that if different active species are in equilibrium with LiCl, without any change of the concentration of the latter during the process, it should not be observed a decrease of the propagation rate constant. Indeed, the presence of LiCl released by the monomer after its addition on the growing chain would logically shift this equilibrium to the most active species. This is not observed and implies that LiCl is involved in another reaction as it was suggested during the first experiment on the sequential addition of this salt.

POLYMERIZATION OF THE REVERSE MONOMER 2

As shown in Figure 1, the initiation of **2*** by the active center of a growing chain bearing the monomer **5** (a, Scheme 1) is possible when a salt like LiCl is added. However, this initiation reaction takes place almost after the consumption of **5***. The steric hindrance involves in the formation of the diadduct on the Nickel center is probably at the origin of this observation. Scheme 1 shows also that during the propagation reaction of **2*** (c, Scheme 1) or **5*** (b, Sheme 1) species, the steric hindrance of the Ni adduct intermediate should be of the same magnitude. This should lead to similar propagation rate constants. On the contrary, a major difference should be observed between the addition of **5*** on the active center of a growing chain of **2**-(d, Scheme 1) and the reverse reaction, addition of **2*** on the growing chain of **5** (a, Scheme 1). This last reaction is similar to the initiation reaction of **2***which implies, in a first step, the formation of a diadduct on the Ni(dppp)Cl_2 . This latter presents (e, Scheme 1) a higher steric hindrance that is usually mentioned as being at the origin of the lack of polymerization observed after the addition of the catalyst.[5a,b]

Therfore, it was interesting to check the following suggestions, first that the activated monomer **2*** alone, in the presence of Ni(dppp)Cl_2 and LiCl, could be added on the Ni catalyst and could be polymerized and second that the propagation rate constants of both monomers (**2** and **5**) are similar.

To achieve this goal, the 2-iodo-3-hexyl-5-bromothiophene (**2**) was synthesized according to a method described in the literature.[5a] A modification of the bromination step was done to get the 2-bromo-3-hexylthiophene without its isomer **5** before the iodination step.

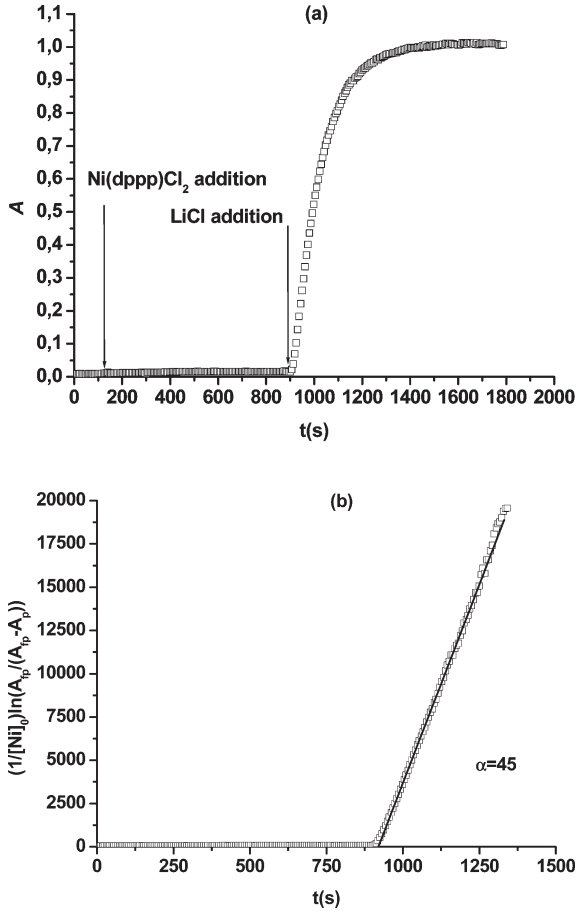


Figure 4. Polymerization of the 2-iodo-3-hexyl-5-bromothiophene ([**2**] = 1.11 × 10^{-2} mol L^{-1}) with Ni(dppp)Cl_2 ([Ni] = 2.06 × 10^{-4} mol L^{-1}) and LiCl (R = 4) (a) Variation of the absorbance (λ = 448 nm) versus time. (b) Evolution of ln $((A_{fp}/(A_{fp} - A_p))/[Ni]_0$ versus time; T = 20 °C.

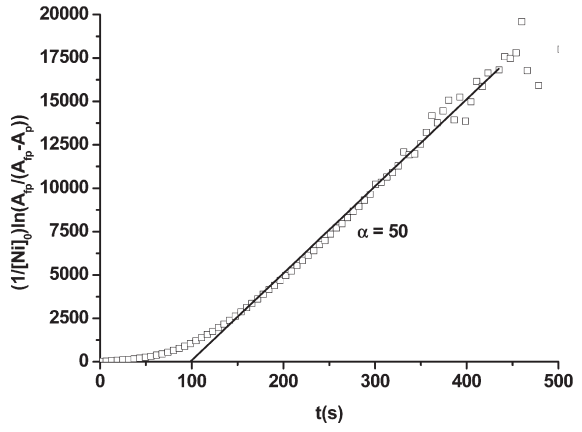


Figure 5. Evolution of ln $((A_{fp}/(A_{fp} - A_p))/[Ni]_0$ versus time (relation 4 for the polymerization of the 2-iodo-3-hexyl-5-bromothiophene ([**2**] = 1.0 × 10^{-2} mol. L^{-1}) in the presence of Ni(dppp)Cl_2 ([Cat] = 3.15 × 10^{-4} mol L^{-1}) and LiCl (R = 4); T = 20 °C.

To show clearly the effect of LiCl on the process, the propagation reaction was carried out in two steps illustrated in Figure 4. At t = 0 s, the Ni(dppp)Cl_2 was added on the

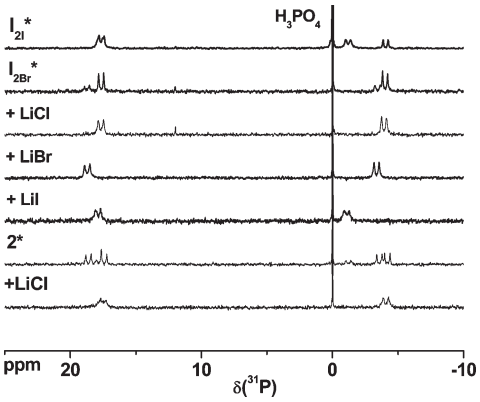


Figure 6. ^{31}P NMR spectra of the solution obtained after addition of two equivalents of Grignard compounds on Ni(dppp)Cl_2: effect of salt addition. [I_{2I}*] = [I_{2Br}*] = 3 × 10^{-2} mol L^{-1} [Ni] = 1.5 × 10^{-2} M; [**2***] = 2.4 × 10^{-2} mol L^{-1} [Ni] = 1.2 × 10^{-2} mol L^{-1}.

activated monomer **2***. During a period of 900 s, the UV−visible absorption spectrum remains unchanged implying the absence of any polymerization reaction during this step. The addition of LiCl in the reaction medium quickly leads to the appearance of a peak at 448 nm and to an increase of the absorbance over time. The propagation rate constant was evaluated by using relation (2) and by considering that all the catalyst molecules were involved in the initiation step. The value found k_p = 45 $mol^{-1}L\ s^{-1}$ is of the same magnitude as the one determined for monomer **5**. Nevertheless the polydispersity (PDI = 1.5) is high and implies that the initiation reaction is slower than the propagation reaction. This phenomenon is amplified when the LiCl salt is added before the introduction of the catalyst. For instance, Figure 5 presents the graph of relation 4 versus time for a polymerization carried out with a higher concentration of Ni(dppp)Cl_2 and a catalyst introduced after the salt addition. It can be observed that the stabilization of the propagation rate constant occurs after 150 s corresponding to the consumption of 30% of the monomer engaged. The polymerization rate constant remains of the same order of magnitude but the polydispersity increases sharply, PDI = 1.8.

All these experiments show that initiation and polymerization of **2** can take place upon addition of LiCl in the reaction medium, despite the steric hindrance around the active center in the initiation reaction. To elucidate the role of the salt on this step, a study was done using different techniques of characterization: UV−vis spectroscopy, ^{31}P NMR and SEC.

INITIATION STEP STUDY

To facilitate this study, the reaction shown in eq 4 was achieved by adding two equivalents of Grignard compounds per catalyst. Higher concentration of reagents was used to obtain a sufficient signal in ^{31}P NMR but also to increase the rate of adduct formation.

Initially, the experiment was conducted from Grignard of monohalogenated thiophene, the 2-iodo-3-hexylthiophene **3** (I_{2I}) or the 2-bromo-3-hexylthiophene (I_{2Br}). These compounds, after activation by *i*-PrMgCl l constitute model molecules (I_{2I}*, I_{2Br}*) of activated monomer **2*** without bromine atom on carbon 5. The lack of this halogen atom on the thiophene ring removes any possibility of polymerization and limits

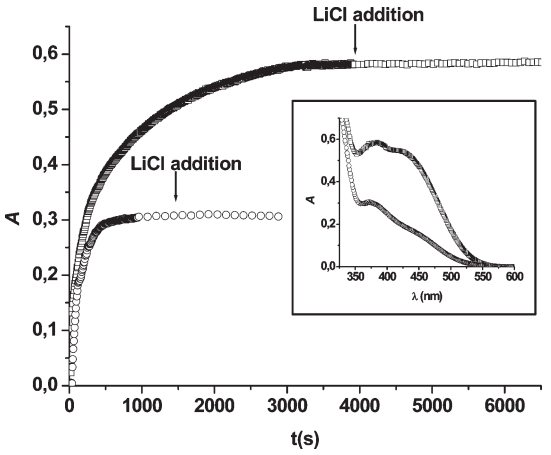


Figure 7. UV−vis spectra of the final solution obtained after addition of two equivalents of Grignard compounds on Ni(dppp)Cl_2: evolution of the absorbance (λ = 375 nm) versus time (○) [I_{2Br}*] = 3 x10^{-2} mol L^{-1}, [Ni] = 1.5 × 10^{-2} M; (□) [2*] = 2.4 × 10^{-2} mol L^{-1} [Ni] = 1.2 × 10^{-2} mol L^{-1}, T = 20 °C.

the reaction to the formation of the Ni adducts.

$$2RMgCl + Ni(dppp)Cl_2 \rightarrow Ni(dppp)RR \text{ or } Ni(dppp)RCl \quad (4)$$

In Figure 6, it is clear that the reaction leads to the formation of the Ni(dppp)RX adduct characterized by the presence of two doublets associated with a different environment for the two phosphorus atoms of the dppp. However, two types of pair of doublets can be observed in each experiment. The main pair with chemical shifts at 17.7 and −3.9 ppm (J_{PP} = 62 Hz), is common to all spectra and can be related to the Ni(dppp)RCl adduct. The other pairs present different chemical shifts implying that the nickel atom is associated with another halogen atom generated by the precursors. This was confirmed by the spectra obtained after addition of various salts (LiI, LiBr, LiCl) in excess in the reaction medium (Figure 6); these experiments lead to the exchange of the halogen on the nickel center and thereby permit to identify the corresponding chemical shifts: two doublets are observed for Ni(dppp)RI at 18.2 and −1.1 ppm - (J_{PP} = 62 Hz)and for Ni(dppp)RBr at 18.8 and −3.3 ppm (J_{PP} = 62 Hz).

It has to be noted that the addition of the different salts, in each experiment, does not change the total concentration of the species formed (internal standard solution of H_3PO_4, see Experimental Section). In the case of LiCl, the same observation was done on the UV−vis spectrum (Figure 7), this latter is not modified and the absorbance at λ = 375 nm remains constant. This reveals that the excess of Grignard reactants present in the medium does not lead to the formation of a diadduct or other compounds when LiCl is added. The spectrum represented in Figure 7 can be attributed to the monoadduct species: Ni(dppp)RCl. As expected the addition of concentrated hydrochloric acid in the solution leads mainly to the formation of hexylthiophene.

When the same reaction is carried out with the activated reverse monomer **2***, under the same experimental conditions (similar concentration in reagents), the evolution of UV−vis spectrum with time is quite different. A shown in Figure 7, it appears a major absorption peak at 430 nm while the final

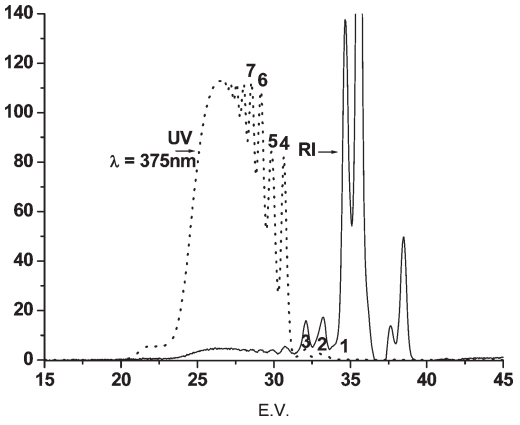


Figure 8. SEC traces of compounds formed during the addition of **2*** on Ni(dppp)Cl_2 ; [**2**] = 2.4 × 10^{-2} L^{-1}, [Ni(dppp)Cl_2] = 1.2 × 10^{-2} mol L^{-1}.

absorbance at 375 nm reaches a higher level than the one observed in the previous experiment. However the reaction time is much longer t = 3000 s compared to t = 800 s for I_{2Br}*. The ^{31}P NMR spectrum of the solution (Figure 6) shows two main pairs of doublets corresponding to Ni(dppp)ClR, chemical shifts at 17.4 and −4.2 ppm (J_{PP} = 68 Hz), and to Ni(dppp)BrR, chemical shifts at 18.2 and −3.6 ppm (J_{PP} = 65 Hz). Both species have nearly equivalent integrations implying similar concentrations in the reaction medium. This is unexpected because the presence of bromine salt in the medium, coming from the precursor monomer, and leading to an halogen exchange on the monoadduct Ni(dppp)ClR cannot be envisaged at a such concentration. Only a low exchange between the chlorine and iodine atoms can be observed in Figure 6: it can be seen a pair of doublets of small intensity corresponding to Ni(dppp)IR (chemical shifts at 17.8 and −1.23 ppm (J_{PP}= 63 Hz)) . Therefore, it was necessary to assume that the formation of Ni(dppp)BrR is due to the formation of oligomers Ni(dppp)BrR_n: this reaction could explain the ^{31}P NMR spectrum since the living ends present a bromine atom on the nickel center. It could explain also the higher final absorbance at 375 nm since the monoadduct is still present in the solution. The final spectrum is then the sum of absorbances of the monoadduct species and of the conjugated oligomers (λ_{max} = 430 nm) at each wavelength. The lack of change of the UV spectrum, upon addition of LiCl, is a result of the complete consumption of monomer **2*** in the oligomerization reaction. To check this hypothesis, SEC using special columns for low molecular weight samples (see Experimental Section) was used to characterize withdrawals (deactivation with concentrated HCl)) done before and after addition of LiCl.

Both solutions give the same SEC traces represented in Figure 8. It can be observed the presence of the deactivated monomer and oligomers of various DPn, highlighted by the UV traces. This reaction was repeated several times with the same results in disagreement with a previous study.[5a]

All these characterizations allow us to conclude that the initiation of the reverse monomer by Ni(dppp)Cl_2 is possible even without LiCl in the medium. However the reaction rate is extremely slow in particularly the formation of the dimer adduct. This initiation step and the formation of oligomers were observed because the concentrations of reactants were much higher than those used in a polymerization experiment. Moreover, the time necessary to achieve monomer completion implies that the

Table 2. Characteristics of Poly(dodecylthiophene) Prepared by Polymerization of 2-Bromo-3-dodecyl-5-iodothiophene with Ni(dppp)Cl_2 in the Presence of LiCl Salt (R = [LiCl]/[M*] = 4)[a]

	[Ni],	[M*],				M_n	
no.	mol L^{-1}	mol L^{-1}	M_w	M_n	PDI	theor	% yield
1	$8 \times 10-5$	1.05×10^{-2}	34 000	32 000	1.05	35 000	100
2	4×10^{-5}	1.07×10^{-2}	64 500	59 500	1.1	68 600	95
3	2×10^{-5}	1.23×10^{-2}	109 000	86 000	1.25	158 000	62
4	1×10^{-5}	1.09×10^{-2}	174 000	130 000	1.34	270 000	50

[a] M_w and M_n were determined by light scattering (SEC) using dn/dc = 0.2205.

propagation rate constant for the reverse monomer, without LiCl addition, is also very low. This is in accordance to the result mentioned recently on the polymerization of **2** by using Ph−Ni(dppp)Br as initiator. The aggregation of the Grignard activated monomer **2*** is the main reasons of these observations. As it was shown, the addition of LiCl enhances the reactivity of the Grignard species probably by deaggregation of **2*** and formation of new complex but it modifies also the Nickel center through a halogen exchange reaction. This exchange is probably at the origin of the kinetics observed for the polymerization of **5*** according to the ratio R; each addition of a monomer on a growing chain consumes one molecule of LiCl. An excess of LiCl is then necessary to obtain a constant value for k_p.

SYNTHESIS OF HIGH MOLECULAR WEIGHT POLYMERS

The difficulty to prepare high molecular weight polymers is related to the low concentration of Ni(dppp)Cl_2 used which leads to a major increase of the reaction time. Thus, it is necessary that the active center and the activated monomer remain stable during all the process. Our study has shown that the addition of LiCl salt in the medium permits one to increase by a factor of 20 the propagation rate constant and therefore to correspondingly reduce the time needed to consume all the monomer.

Therefore, it was interesting to attempt the synthesis of high molecular weight samples. In this aim, the new process was applied to the polymerization of the 2-bromo-3-dodecyl-5-iodothiophene. This monomer was chosen because it leads to soluble polymer, whatever the molecular weight, due to the long alkyl chain. Different samples of various molecular weight were prepared by decreasing the catalyst concentration relative to that of the monomer.

Data collected in Table 2 show that well-defined polymers can be obtained until 60000 g of molar mass. However, when the catalyst concentration diminishes the polydispersity of the samples increases regularly while the yield decreases and the experimental molecular weight deviates from the theoretical value. All these observations correspond mainly to a deactivation reaction of the active center and to a stop of the polymerization reaction before the monomer completion. The mechanism involved in this deactivation reaction was not identified.

CONCLUSION

In this study, we have shown that the propagation rate constant of the 2-bromo-chloromagnesio-3-hexyl thiophene mediated by Ni(dppp)Cl_2 catalyst is considerably increased by addition of LiCl salt in the medium. It was established that k_p depends on the ratio R (R = [LiCl]/[M*]) and reaches a maximum value (20 times higher) for R = 4. This additive permits also the polymerization of the reverse monomer with a similar polymerization rate constant (R = 4). This result suggests that both monomers, under their nonaggregated Grignard form, lead to a similar intermediate state on the Ni center during the polymerization step. Nevertheless the initiation step is quite different and the steric hindrance involved in the intermediate state for the reverse monomer explains the slow initiation rate compared to the propagation rate. This sterically hindered intermediate is the same during the initiation step of monomer **2** by a growing chain of monomer **5**. It is at the origin of the formation of block "copolymer" ($k_{52} \approx 0$) during the polymerization of a mixture of both activated monomers. By using different techniques of characterization, we have shown that LiCl, in addition to its effect on deaggregation and activation of the Grignard monomers, plays probably a role on the reactivity of the Ni center through an halogen exchange reaction. This process was applied to the synthesis of well-defined of poly(dodecylthiophene) of high molecular weight.

ACKNOWLEDGMENT

The authors thank Dr. E. M. Ribstein and Dr. L. M. Atrahi for helpful discussions on this work.

REFERENCES

(1) (a) Yokoyama, A.; Miyakoshi, R.; Yokazawa, T. *Macromolecules* **2004**, *37*, 1169–1171. (b) Miyakoshi, R.; Yokoyama, A.; Yokazawa, T. *Macromol. Rapid Commun.* **2004**, *25*, 1663–1666. (c) Miyakoshi, R.; Yokoyama, A.; Yokazawa, T. *J. Am. Chem. Soc.* **2005**, *127*, 17552–17547.

(2) (a) Sheina, E. E.; Liu, J.; Iovu, M. C.; Laird, D. W.; McCullough, R. D. *Macromolecules* **2004**, *37*, 3526–3528. (b) Iovu, M. C.; Sheina, E. E.; Gil, R. R.; McCullough, R. D. *Macromolecules* **2005**, *38*, 8649–8656.

(3) (a) Beryozkina, T.; Sen kovskyy, V.; Kaul, E.; Kiriy, A. *Macromolecules* **2008**, *41*, 7817–7823. (b) Tkachov, R.; Senkovskyy, V.; Komber, H.; Sommer, J. U.; Kiriy, A. *J. Am. Chem. Soc.* **2010**, *132*, 7803–7810.

(4) Achord, B. C.; Rawlins, J. W. *Macromolecules* **2009**, *42*, 8634.

(5) (a) Boyd, S. D.; Jen, A.K.-Y.; Luscombre, C. K. *Macromolecules* **2009**, *42*, 9387. (b) Tkachov, R.; Senkovskyy, V.; Komber, H.; Kiriy, A. *Macromolecules* **2011**, *44*, 2006.

(6) (a) Krasovski, A.; Knochel, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 733–738. (b) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *Chem. Lett.* **2008**, *37*, 1022–1023. (c) Lanni, E. L.; McNeil, A. J. *J. Am. Chem. Soc.* **2009**, *131*, 16573–16579. (d) Lanni, E. L.; McNeil, A. J. *Macromolecules* **2010**, *43*, 8039.

(7) Takahashi, A.; Rho, A.; Higashihara, T.; Ahn, B.; Ree, M.; Ueda, M. *Macromolecules* **2010**, *43*, 4843.

(8) Lohwasser, R.; Thelakkat, H. M. *Macromolecules* **2011**, *44*, 3388.

(9) Lamps, J.-P.; Catala, J.-M. *Macromolecules* **2009**, *42*, 7282.