The influence of branching on the Kumada catalyst transfer condensative polymerization of 3-alkylthiophenes

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To study the influence of branching of the side chain on the Kumada catalyst transfer condensative polymerization (KCTCP) of 3-alkylthiophenes, a new, severely branched precursor monomer, 2-bromo-5-iodo-3-(2-octyldodecyl)thiophene, was designed. The controlled character of its polymerization was investigated and rate studies for both poly(3-hexylthiophene) (P3HT) and poly(3-(2-octyldodecyl)thiophene) (P3ODT) were performed. Second, the influence of non-covalent gelation on the controlled character of the polymerization was studied through the determination of the maximal degree of polymerization that could be obtained in a controlled manner. Next, nona-stage polymers were synthesized and the lifetime of the active chain ends for P3HT and P3ODT was studied. Last, the nature of the occurring termination reactions was established. Combined, these results point out the difference in polymerization behavior between branched and linear alkyl substituents and, related to this, between gelated and non-gelated polymerization mixtures.

Introduction

In the last decade, the mechanism of the catalyst transfer condensative polymerization (CTCP) of especially thiophene monomers has thoroughly been investigated.¹ This includes the influence of the ligand of the catalyst^{2–4}, the halogen on the monomer^{5,6}, the use of different precursor monomers and synthetic methods for obtaining the monomers^{6–10}. Concerning the initiation, apart from the originally used NiL_2X_2 (L = ligand, X is Cl or acetylacetonate) also external initiators^{11–14} were developed, which allow to introduce functional groups at the beginning of each polymer chain. In contrast to NiL_2Cl_2 , they are soluble in THF, which results in a faster initiation and, hence, lower dispersities. The influence of the reactive ligand of external initiators^{15,16} was also examined. One property that has received much less attention, is the nature of the alkyl substituent, although it has important consequences for the resulting properties. While changing the length of linear alkyl chains is straightforward, also branching^{17,18} influences the polymer characteristics. Although poly(3-alkylthiophene)s (P3ATs) with branched side chains can be used for inducing microphase separation¹⁷ or optimizing the performance of solar cells¹⁹, and various studies about the effect of branched side chains on the behaviour of the polymers were already performed^{17–20}, none of them focussed on the influence of this branching on the polymerization characteristics. The only

study on the influence of branching on CTCP was performed on poly(3-alkyltellurophene)s (P3ATes) by Ye *et al.* and they concluded that branching on the 2-position of the alkyl side chain leads to a significant reduction of the propagation rate constant and premature termination reactions.²¹ However, when the branching point was shifted to the 3-position of the alkyl side chain, the propagation rate constant increased and control over the polymerization was obtained.

Branching of the side chain cannot only influence the polymerization directly, but also indirectly via the lower capability of the polymers to stack, preventing precipitation or non-covalent gelation during the polymerization. The non-covalent gelation behaviour of P3ATs in certain solvents or solvent mixtures *after* polymerization and the potential applications of these gels have already been investigated. For example, gels can be formed in xylene^{22,23} and mixtures of dodecane and 1,2-dichlorobenzene²⁴ and they can be used in thin-film organic electronic devices²⁴ or as an electrode active material in secondary batteries²⁵. However, the non-covalent gelation of P3HT in THF during the polymerization is not yet described, although one can assume that it significantly affects the controlled nature of the polymerization and polymerization rate, since branching, especially close to the P3AT backbone, slows down crystallization and, hence, non-covalent gelation.^{20,26}

In this manuscript, we design a thiophene monomer with a severely branched alkyl substituent and study (1) the influence of branching on the rate of polymerization and hence, dispersity, and (2) the influence of non-covalent gelation on the controlled character of the polymerization and nature of termination reactions.

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Scheme 1 - Reaction scheme for the monomer synthesis.

Results and discussion

To study the influence of branching and the occurrence of non-covalent gelation in the KCTCP of thiophene monomers, monomer **5** was designed. The severely branched and long 2-octyldodecyl side chain was chosen to enlarge the difference with the commonly used hexyl side chain compared to already existing side chains.²⁶ The monomer was synthesized according to existing protocols (Scheme 1).²⁷

Because poly(3-(2-octyldodecyl)thiophene) (P3ODT) was never synthesized before, a preliminary test reaction was performed to verify whether it is possible to obtain high molar mass polymer based on the KCTCP protocol. Therefore, **5** was combined with Ni(dppp)Cl₂ (dppp: 1,3-bis(diphenylphosphino)propane) in a 100/1 ratio (P3ODT-1). After 1 hour of polymerization the reaction mixture was analysed with gel permeation chromatography (GPC) ($\bar{M}_{n,P3ODT-1}$ = 22 kg/mol and $\bar{P}_{P3ODT-1}$ = 1.05). Especially the very low dispersity was remarkable, since systematically a dispersity of 1.2 is obtained when Ni(dppp)Cl₂ is used as initiator in the poly(3-hexylthiophene) (P3HT) synthesis (S6-S8). So, in contrast to the synthesis of P3ATes, where branching on the 2-position of the alkyl side chain gives rise to a reduced propagation rate constant, termination reactions and hence a higher dispersity compared to P3ATe with a linear side chains²¹, it seems that branching does not necessarily destroy the controlled nature of the synthesis of P3ATs. We hypothesize that this is due to (1) a reduced propagation rate constant, which, in combination with an unchanged initiation rate - this essentially depends on the dissolution of the Ni(dppp)Cl₂ initiator -, resulting in a remarkably low dispersity and (2) the absence of a larger amount of termination reactions, in contrast to branched P3ATes. In order to test this hypothesis, two experiments were performed. First, a chain extension experiment was conducted to verify the absence of termination reactions and, second, kinetic experiments were performed to determine the propagation rate constants of P3HT and P3ODT.

To exclude termination reactions at the later stage of the polymerization, the chain extension experiment was performed on a polymer with a degree of polymerization (DP) of 100 (**P3ODT-2a**) to which monomer was added equivalent to an additional 100 monomeric units (**P3ODT-2b**) (Scheme 2). As can be derived from the GPC analysis of the crude polymerization mixtures before ($\bar{M}_{n,P3ODT-2a}$ = 22 kg/mol and $\bar{P}_{P3ODT-2a}$ = 1.05) and after ($\bar{M}_{n,P3ODT-2b}$ = 38 kg/mol and $\bar{P}_{P3ODT-2b}$ = 1.1) chain extension (Figure 1), the polymer peak shifts completely to lower elution volumes and no new

Scheme 2 - Reaction scheme for a chain extension experiment.

Figure 1 - GPC elution curves of P3ODT before (**P3ODT-2a**) and after chain extension (**P3ODT-2b**).

Figure 2 - Plot of $\ln([M]_t/[M]_0)$ in function of reaction time for P3HT and P3ODT.

polymer chains were initiated. From this experiment it can be concluded that, in contrast to P3ATes, almost no termination or transfer reactions occur at least until a DP of 100 is reached. To determine whether also for P3ATs the propagation rate constant decreases by introducing (severe) branching in the side chain, as is the case for P3ATe²¹, the propagation rate constant was measured. The rate determining step in the synthesis of P3AT with a Ni(dppp)Cl₂-catalyst is the transmetalation, as previously described by Lanni *et al.*³ Therefore, the reaction rate can be described by equation 1 or, equivalently, by equation 2, making it possible to determine the rate constant if the monomer concentration in function of time during the polymerization is known.

$$-\frac{d[M]}{dt} = k[\text{In}][M] \quad \text{Eq. 1}$$

$$\ln \frac{[M]_t}{[M]_0} = -k[\text{In}]t \quad \text{Eq. 2}$$

The monomer concentration during the polymerization was determined by GPC analysis. A polystyrene standard with a peak molar mass of 174 kg/mol is used as external standard to avoid overlap with any signal. To exclude the effect of initiation, which can be significant due to the insolubility of Ni(dppp)Cl₂, the polymerization was preinitiated with 10 equivalents of monomer, as described previously by Lanni *et al.*³ In figure 2, $\ln([M]_t/[M]_0)$ was plotted in function of time and from the linear regression the propagation rate constant was calculated. A clear distinction between P3HT and P3ODT can be observed, as the rate constant of P3HT ($40 \pm 4 \text{ L mol}^{-1} \text{ s}^{-1}$)

¹) is almost double of the rate constant of P3ODT ($23 \pm 4 \text{ L mol}^{-1} \text{ s}^{-1}$). This can be explained by a slower rate-determining transmetalation due to more steric hindrance when branched side chains are present. When assumed that the initiation rate in the synthesis of P3HT and P3ODT is similar - it mainly depends on the dissolution of Ni(dppp)Cl₂ -, this lower propagation rate for P3ODT, together with the almost absence of termination and transfer reactions, can explain the very low dispersity observed for P3ODT. The obtained linear relationship between $\ln([M]_t/[M]_0)$ and time for P3ODT confirms the assumption that also in the polymerization of 5 the rate determination step is the transmetalation.

The severe branching can also affect the crystallisation of P3ODT and, hence, possible non-covalent gelation. Therefore, we assumed that a higher DP for P3ODT could be obtained compared to P3HT, since premature precipitation of P3HT was thought to terminate its polymerization. To validate this hypothesis, the maximal DP obtained in a controlled manner was determined. For this purpose, polymerizations with different monomer over initiator ratios were performed and the obtained polymers were analysed with GPC. As long as the polymerization proceeds in a controlled manner, the $\bar{M}_n$ should increase linearly with $[M]_0/[\text{In}]$. For both polymers this relationship is found to be linear until a DP of 150, but the deviation at the monomer over initiator ratio of 200 is clearly smaller for P3HT (P3HT-3a-e) than for P3ODT (P3ODT-3a-e) (figure 3, A and B). In the GPC elution curves also more tailing to lower molar masses is visible for P3ODT with a high DP than for P3HT (figure 3, C and D). This indicates that control over the polymerization can be maintained longer for P3HT. However, this result is remarkable since the polymerization mixtures of P3HT with a DP of 100, 150 and 200 were non-covalently gelled. Crystallization of P3HT chains brings polymer ends into close proximity, hence facilitating disproportionation reactions and leading to loss of control over the polymerization. However, this is not at all observed.

Due to the high polymerization rate, it is of course possible that the polymerization was already finished before the non-covalent gelation occurred. Therefore, a new set of experiments was designed, in which a multiple chain extension is performed. During this experiment, first 20 equivalents of monomer and then 8 times 10 equivalents of monomer were added after different times. In this way, non-covalent gelation could set in before all the monomer was consumed. The monomer concentration used in this experiment (0.2 M) is double the concentration used in the previous experiments to increase the polymerization and gelation rate.

Figure 3 - A) and B) Plot of $\bar{M}_n$ in function of $[M]_0/[In]$ for P3HT and P3ODT, respectively. C) and D) Plot of normalized absorption in function of elution volume for P3HT and P3ODT, respectively (a: $[M]_0/[In] = 15$; b: $[M]_0/[In] = 50$; c: $[M]_0/[In] = 100$; d: $[M]_0/[In] = 150$; e: $[M]_0/[In] = 200$)

Figure 4 - Representation of the increase in molar mass after different amounts of monomer added for P3HT (A) and P3ODT (B). (a: $[M]_0/[In] = 20$; b: $[M]_0/[In] = 30$; c: $[M]_0/[In] = 40$; d: $[M]_0/[In] = 50$; e: $[M]_0/[In] = 60$; f: $[M]_0/[In] = 70$; g: $[M]_0/[In] = 80$; h: $[M]_0/[In] = 90$; i: $[M]_0/[In] = 100$)

When **5** was polymerized, no sign of crystallization or non-covalent gelation was observed, as was expected, and the polymer chains were able to grow each time new monomer was added, allowing the construction of a nona-stage polymer (**P3ODT-4a-i**) (figure 4, B: Note that the molar mass is plotted and not the elution volume to more clearly show the chain extension). For **6** non-covalent gelation was observed after the addition of 60 equivalents of monomer compared to

$Ni(dppp)Cl_2$. Nevertheless, the polymer chains were able to grow each time monomer was added (**P3HT-4a-i**) (Figure 4, A). This means that, even though the propagating chain ends are brought closer together in the formed gel, no disproportionation or other termination reaction occur, in contrast to what we assumed. For P3HT, higher dispersities are measured towards the highest molar masses, although theoretically the dispersity should decrease with increasing DP.

Figure 5 - Attempted chain extension for P3ODT (A: $[M]_0 = 0.2$ M; B: $[M]_0 = 0.05$ M) and P3HT (C: $[M]_0 = 0.2$ M; D: $[M]_0 = 0.05$ M). (a: without chain extension; b: chain extension after 48 hours; c: chain extension after 72 hours; d: chain extension after 96 hours)

This discrepancy could be attributed to the non-covalently gelled state of the polymerization mixture, preventing a thorough mixing (in fact, the polymerization tube was shaken instead of stirred when a DP of 60 was reached, since stirring was impossible), or to termination reactions. Also for P3ODT the dispersity increases (slightly) towards the end, suggesting the occurrence of a small amount of termination reactions.

Since the occurrence of non-covalent gelation does not destroy the controlled character of the polymerization, one could wonder whether non-covalent gelation has an influence on the stability of the propagation chain ends in solution. For this purpose new experiments were designed in which the polymerization mixture was kept under inert atmosphere for several days before chain extension was attempted. Low DPs were targeted to prevent the occurrence of termination reactions. P3HT as well as P3ODT were synthesized with a monomer concentration of 0.05 M and 0.2 M in order to distinguish between the influence of non-covalent gelation and branching in the side chain of the monomer. When this experiment is performed with **5** in a 0.2 M concentration, dead polymer chains are already present after two days (**P3ODT-5b**) and after three days, half of the polymer chains were not able to grow further (**P3ODT-5c**) (figure 5, A). When the monomer concentration is lowered to 0.05 M, tailing is still visible after 2 days (**P3ODT-6b**) (figure 5, B). However, when this experiment is repeated with **6**, a complete chain extension for both monomer concentrations is still observed after 3 days (**P3HT-5c** (gelled) and **P3HT-6c** (non-gelled)) (figure 5, C and D).

After 4 days however, the polymerization showed signs of non-controlled behaviour. For the lowest monomer concentration tailing was visible and the obtained molar mass was much higher than expected (**P3HT-6d**). For the higher monomer concentration, the increase in molar mass was much smaller than expected (**P3HT-5d**). Therefore it could be hypothesized that the introduction of side chain branching diminishes the long term controlled character of the polymerization, but that the occurrence of non-covalent gelation does not have an influence.

To characterize the origin of the occurring termination reactions, polymerization mixtures of P3HT and P3ODT were kept for one week under inert atmosphere before they were terminated with acidified THF (**P3HT-7** and **P3ODT-7**). Different termination reactions are possible, i.e. decomplexation of the catalyst (A), reaction with moisture (or other protic entities) (B) and disproportionation (C) (scheme 3). To exclude the occurrence of disproportionation reactions, GPC analysis was performed on two samples: one was taken after one hour of polymerization and the other after one week. Since no difference was observed for the two samples (S12), disproportionation reactions could be excluded as the main termination reaction. In order to distinguish between termination reactions induced by impurities or due to decomplexation, ^1H NMR was measured to characterize the end groups. This is possible because the terminal α -methylenes have different chemical shifts depending on the

Scheme 3 - Representation of the possible termination reactions during KCTCP: A) dissociation of the catalyst, B) reaction with protic impurities and C) disproportionation.

Figure 6 - Designation of the NMR signals of the terminal α -methylenes in (A) **P3HT-7** and (B) **P3ODT-7**, in which A designates the α -methylenes coupled to Br-terminated polymer chain ends and B the α -methylenes coupled to H-terminated polymer chain ends.

presence of a Br- or H-end group and this was previously done in our group for P3HT.²⁸ In the ^1H NMR spectrum, mainly H- and Br-end groups (two signals are expected for Br-end groups: one for an external tail-to-tail diad and one for an internal tail-to-tail diad) are visible (figure 6), but not in a 1/1 ratio, indicating that termination induced by protic impurities cannot be the only termination pathway. The excess of Br-end groups can be explained by the decomplexation of the Ni-catalyst from the polymer backbone, if one could assume an equilibrium between the oxidatively inserted Ni in the terminal C-Br bond and Ni complexed to the polymer backbone is set in. Based on signals A and B, the percentage of termination by decomplexation can be calculated and equals 39 % for P3HT

and 61 % for P3ODT (eq. 3). The amount of decomplexation can also be calculated based on the aromatic signals for P3HT²⁹ and was found to be 38 %. This is in good agreement with the result based on the aliphatic region (S12).

$$\%(\text{decomplexation}) = \frac{\left(\frac{A-B}{2}\right)}{\left(\frac{A+B}{2}\right)} \cdot 100 \% \quad \text{Eq. 3}$$

This is surprising, as the final state in a polymerization prior to termination, was found to be oxidatively inserted catalyst.³ The fact that a considerable part of the chains were found to be terminated by dissociation of the catalyst, shows that an equilibrium is set in between the complexated catalyst and the oxidatively inserted catalyst (scheme 3). The larger amount of decomplexation in the P3ODT synthesis compared to P3HT is in line with the previous results, indicating the more controlled character of the polymerization on long term for P3HT. In the NMR spectra of both P3HT and P3ODT, a small signal is present not corresponding to terminal α -methylenes on a thiophene with a Br- or H-end group. To elucidate the nature of the end groups, MALDI-ToF analysis was performed on **P3HT-7** and **P3ODT-7**, but unfortunately the assignment of the peaks was not possible.

Conclusions

First, a new thiophene monomer with a severely branched side chain was designed and polymerized. Especially the very low dispersity compared to other P3ATs was remarkable and was attributed to a reduced propagation rate constant compared to the one of P3HT, and the absence of a larger amount of termination reactions upon the introduction of branching in the side chain. Second, it was determined that complete control over the polymerization could be maintained until a DP of 150 for P3HT and P3ODT and that the synthesis of a nona-stage polymer for both polymers was possible. For P3HT these results were unexpected since non-covalent gelation sets in from a DP of 60. Third, it was established that a branched side chain diminishes the long term controlled character of the polymerization compared to a linear side chain. Last, the character of the occurring termination reactions was investigated. Decomplexation of the Ni-catalyst from the polymer backbone was found to be the main termination reaction, implying an equilibrium between the complexed and the oxidatively inserted catalyst. Disproportionation does not occur, not even in the non-covalently gelated state where the polymer chain ends are in close proximity.

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