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(54) Title: PROCESS OF PREPARING REGIOREGULAR POLYMERS

(57) Abstract: The invention relates to a process of preparing regioregular polymers, in particular head-to-tail (HT) poly-(3-substituted) thiophenes with high regioregularity, to novel polymers prepared by this process, to the use of the novel polymers as semiconductors or charge transport materials in optical, electrooptical or electronic devices including field effect transistors (FETs), electroluminescent, photovoltaic and sensor devices, to FETs and other semiconducting components or materials comprising the novel polymers, to a process of endcapping polymers and to endcapped polymers obtained thereof and their use in the above devices.

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Process of Preparing Regioregular Polymers

Field of Invention

5 The invention relates to a process of preparing regioregular polymers, in particular head-to-tail (HT) poly-(3-substituted) thiophenes with high regioregularity, and to novel polymers prepared by this process. The invention further relates to the use of the novel polymers as semiconductors or charge transport materials in optical,
10 electrooptical or electronic devices including field effect transistors (FETs), electroluminescent, photovoltaic and sensor devices. The invention further relates to FETs and other semiconducting components or materials comprising the novel polymers. The invention further relates to a process of endcapping polymers, to
15 polymers obtained by this process, and to their use in the above devices.

Background and Prior Art

20 Organic materials have recently shown promise as the active layer in organic based thin film transistors and organic field effect transistors (OFETs) [see H. E. Katz, Z. Bao and S. L. Gilat, *Acc. Chem. Res.*, 2001, **34**, 5, 359]. Such devices have potential applications in smart cards, security tags and the switching element in flat panel displays.
25 Organic materials are envisaged to have substantial cost advantages over their silicon analogues if they can be deposited from solution, as this enables a fast, large-area fabrication route.

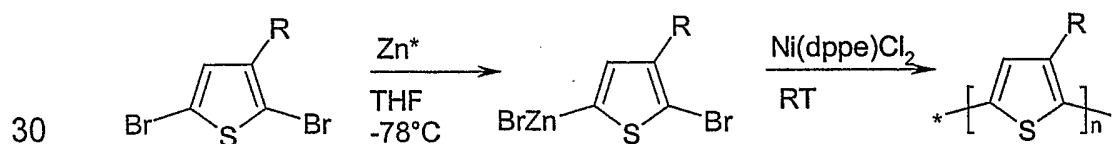
30 The performance of the device is principally based upon the charge carrier mobility of the semiconducting material and the current on/off ratio, so the ideal semiconductor should have a low conductivity in the off state, combined with a high charge carrier mobility ($> 1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). In addition, it is important that the semiconducting material is relatively stable to oxidation i.e. it has a high ionisation
35 potential, as oxidation leads to reduced device performance.

In prior art regioregular head-to-tail (HT) poly-(3-alkylthiophene), in particular poly-(3-hexylthiophene), has been suggested for use as semiconducting material, as it shows charge carrier mobility between 1×10^{-5} and $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Also, poly-(3-alkylthiophene) shows good solubility in organic solvents and is solution processable to fabricate large area films.

A high regioregularity of the poly-(3-alkylthiophene) is important for its electronic and photonic properties, as it leads to improved packing and optimised microstructure, leading to improved charge carrier mobility [see US 6,166,172, H. Sirringhaus et al., *Science*, 1998, **280**, 1741-1744; H. Sirringhaus et al., *Nature*, 1999, **401**, 685-688; and H. Sirringhaus, et al., *Synthetic Metals*, 2000, **111-112**, 129-132]. The regioregularity is strongly influenced by the method of preparing the polymer.

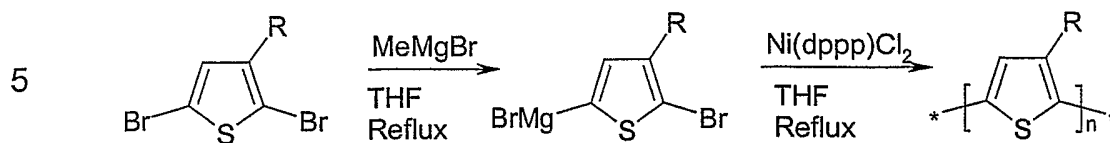
Several methods to produce highly regioregular HT-poly-(3-alkylthiophene) have been reported in prior art, for example in the review of R.D. McCullough, *Adv. Mater.*, 1998, **10(2)**, 93-116 and the references cited therein.

Known methods to prepare HT-poly(3-alkylthiophene) with a regioregularity $\geq 90 \%$ starting from 2,5-dibromo-3-alkylthiophene include for example the "Rieke method", by reacting the educt (wherein R is alkyl) with highly reactive zinc in THF as illustrated below.

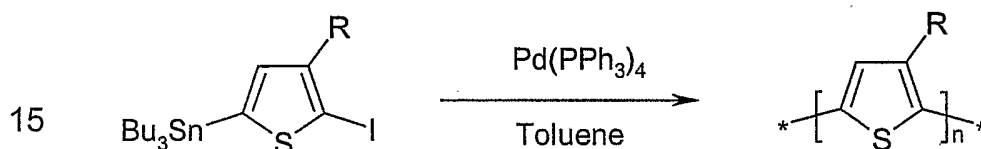


Also known is the method described in McCullough et al., *Adv. Mater.*, 1999, **11(3)**, 250-253 and in EP 1 028 136 and US 6,166,172, the entire disclosure of these documents being incorporated into this

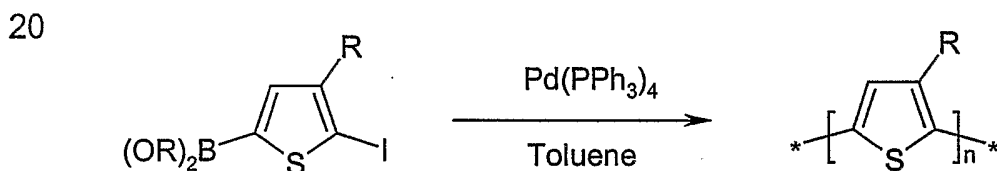
application by reference. According to this route the educt is reacted with methylmagnesium bromide in THF as shown below.



10 It was also reported to prepare regioregular poly(3-alkylthiophene) by the "Stille-method" (see Stille, Iraqi, Barker et al., *J. Mater. Chem.*, 1998, **8**, 25) as illustrated below



or by the "Suzuki-method" (see Suzuki, Guillerez, Bidan et al., *Synth. Met.*, 1998, **93**, 123) as shown below.



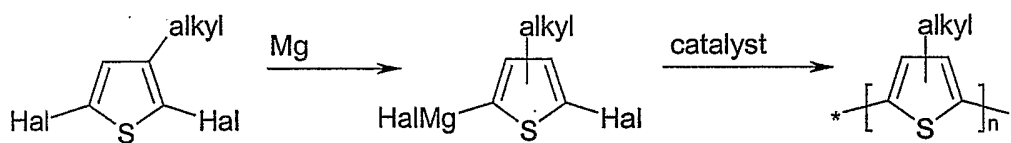
25 However, the methods described in prior art have several drawbacks. Thus, for example the Rieke method requires the costly and difficult preparation of the highly active "Rieke zinc". The Stille and Suzuki methods require an extra processing step which reduces the process efficiency. The McCullough method requires the costly Grignard reagent methylmagnesium bromide. Additionally, it produces methyl bromide as a by-product in stoichiometrical quantities which especially in large scale production causes environmental problems. As methyl bromide cannot be eliminated from the exhaust gases with a gas washer, costly techniques and means for exhaust air combustion are needed.

30

35

Prior art also reports the preparation of unsubstituted polythiophene by Nickel-catalysed coupling of a Grignard reagent that is formed from the reaction of a 2,5-dihalogenated thiophene with magnesium. This route was first reported in 1984 (J. P. Montheard; T. Pascal, *Synth. Met*, 1984, **9**, 389 and M. Kobayashi; J. Chen; T.-C. Chung; F. Moraes; A. J. Heeger; F. Wudl, *Synth. Met*, 1984, **9**, 77). However, this method yielded only low molecular weights. Also these polymers only have low solubility, compared to 3-alkyl substituted polythiophenes.

There are also reports on the preparation of poly (3-alkyl thiophene) using the Nickel-catalysed coupling of a Grignard reagent formed from 2,5-dihalogenated 3-alkylthiophene with magnesium as illustrated below.



T. Yamamoto; K.-I. Sanechika; A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 1497 and US 4,521,589 describe the Grignard coupling of 2,5-dihalo-3-alkylthiophene in THF, wherein the alkyl group is lower alkyl with 1 to 4 C-atoms, like methyl. However, the resulting polymers are reported to have low molecular weight (1,370 or 2,300) and low regioregularity (as can be seen from the $^1\text{H-NMR}$ spectra). US 4,521,589 also mentions a higher weight fraction with a degree of polymerization of 96 as concluded from IR spectra, but no molecular weight measurement data are given. A series of publications by Elsenbaumer et al. also describes the synthesis of poly (3-alkyl thiophenes) by Grignard coupling (R. L. Elsenbaumer; K. Y. Jen; R. Oboodi, *Synth. Met*, 1986, **15**, 169; furthermore K. Y. Jen; R. Oboodi; R. L. Elsenbaumer, *Polym. Mater. Sci. Eng.*, 1985, **53**, 79 and K.-Y. Jen; G. G. Miller; R. L. Elsenbaumer, *J Chem Soc, Chem Commun*, 1986, 1346). However, these polymers mostly have molecular weights (M_n) in the range of 3,000 to 8,000, with the exception of a homopolymer obtained from 2,5-diiodo-3,4-

dimethylthiophene and a copolymer obtained from 2,5-diiodo-3-methyl- and 2,5-diiodo-3-n-butylthiophene, which are reported to have a molecular weight of 26,000 and 35,000 respectively. US 4,711,742 (Elsenbaumer et al.) reports the synthesis of poly(3-butylthiophene) by Grignard coupling of the diiodo monomer in 2-methyl-tetrahydrofuran, giving a molecular weight of 41,400 corresponding to a degree of polymerization of 300. However, the poly (3-alkyl thiophenes) described in the above documents are regiorandom with relatively low amounts of the desired head-to-tail head-to-tail (HT-HT) triads (see e.g. K.-Y. Jen; G. G. Miller; R. L. Elsenbaumer, *J Chem Soc, Chem Commun*, 1986, 1346).

In a study of poly (3-decyl thiophene) made by three different routes (see P. C. Stein; C. Botta; A. Bolognesi; M. Catellani, *Synth. Met*, 1995, **69**, 305) a sample prepared using the Grignard polymerisation of the diiodo monomer was found to have a regioregularity of 70% by ¹H-NMR. A study of the synthesis of poly (3-hexyl thiophene) using the Grignard reaction of 2,5-diiodo-3-hexylthiophene with magnesium in ether (see H. Mao; S. Holdcroft, *Macromolecules*, 1992, **25**, 554) resulted in a molecular weight (M_n) of 5,200. No direct regioregularity data are given but the ¹H-NMR shows peaks from all four possible triads, suggesting relatively low regioregularity. Another study of the same authors (see H. Mao; S. Holdcroft, *Macromolecules*, 1993, **26**, 1163) reported only poly (3-hexyl thiophenes) with low regioregularities (up to 58 % HT-HT triads or up to 80 % HT dyads).

In conclusion, although the preparation of poly (3-alkyl thiophenes) by Grignard reaction with magnesium has been described in the literature, the polymers synthesised are reported to have low molecular weight and/or low or random regioregularity.

Therefore, there is still a need for an improved method of preparing polymers, in particular poly-(3-substituted) thiophenes with high regioregularity, high molecular weight, high purity and high yields in an

economical, effective and environmentally beneficial way, which is especially suitable for industrial large scale production.

5 It was an aim of the present invention to provide an improved process for preparing polymers with these advantages, but not having the drawbacks of prior art methods mentioned above.

10 Other aims of the present invention are immediately evident to the person skilled in the art from the following detailed description.

15 The inventors of the present invention have found that these aims can be achieved, and the above problems be solved, by providing a process of preparing polymers, in particular poly-(3-substituted) thiophenes according to the present invention as described below. According to this process, a 3-substituted thiophene monomer with at least two groups, wherein these groups are leaving groups that are capable of reacting with magnesium, is reacted with magnesium in a suitable solvent to form an intermediate, which is then polymerized in the presence of a suitable catalyst. It was surprisingly
20 found that, by choosing appropriate reagents and reaction conditions, it is possible to obtain polymers, in particular poly-(3-substituted) thiophenes, with high regioregularity, high molecular weight and high purity in good yields and avoiding large amounts of hazardous by-products that need to be eliminated.

25 The polymers prepared by the process according to the present invention are especially useful as charge transport materials for semiconductor or light-emitting materials, components or devices.

30 The above described routes of preparing polymers usually give a polymer that is terminated by reactive groups such as halogens, organometallic species such as boronate esters or trialkyl tins, or very reactive groups such as organo-magnesium or organo-zincs, which will be quenched under standard work up procedures. However, these
35 groups have a disadvantageous effect on the electrical properties of the polymer; for example in semiconducting applications they can trap

charges and thus reduce the charge carrier mobility of the polymer. It is therefore a further aim of this invention to further improve the electrical properties of the polymers obtained by the inventive process and also by the prior art methods as described above. The inventors
5 have found that this aim can be achieved by chemical modification ('endcapping') of the polymers as described above and below. Thus, replacing the end groups of the polymers for example with alkyl groups or hydrogen can give poly (3-alkylthiophenes) with improved electrical properties. Another aspect of the invention therefore relates
10 to a process of endcapping polymers, in particular regioregular poly (3-alkyl thiophenes) and to polymers obtained by this process.

Summary of the Invention

15 The invention relates to a process of preparing a polymer by providing a thiophene having at least two groups that are capable of reacting with magnesium, reacting said thiophene with magnesium to form a regiochemical Grignard intermediate or a mixture of regiochemical Grignard intermediates, and polymerising said
20 Grignard intermediate by adding a suitable catalyst.

The invention further relates to a process as described above and below, wherein the thiophene is a 3-substituted soluble thiophene having groups that are capable of reacting with magnesium in 2- and
25 5-position.

The invention further relates to a process as described above and below, wherein the polymer is a regioregular head-to-tail (HT) polymer having a regioregularity of $\geq 90\%$, preferably $\geq 95\%$, very
30 preferably $\geq 98\%$.

The invention further relates to a process as described above and below, by

35 a) dissolving a thiophene having two groups that are capable of reacting with magnesium in a solvent or a mixture of solvents,

- 5 b) adding magnesium in an at least molar amount of the thiophene to the solution, or adding the solution to said magnesium, wherein said magnesium reacts with the thiophene to form a regiochemical Grignard intermediate or a mixture of regiochemical Grignard intermediates,
- c) optionally removing the unreacted magnesium from the reaction mixture,
- 10 d) adding a catalyst to the reaction mixture, or adding the reaction mixture to a catalyst, and optionally agitating the resulting mixture, to form a polymer, and
- e) recovering the polymer from the mixture.

15 The invention further relates to novel polymers, in particular novel poly-3-substituted thiophenes, obtainable or obtained by a process as described above and below.

20 The invention further relates to polymers, in particular poly-3-substituted thiophenes, preferably with high regioregularity preferably obtained from the process as described above and below, wherein one or more of the terminal groups are chemically modified ('endcapped'), especially for use as semiconductors. The invention further relates to a process of chemically modifying the terminal group of a polymer, in particular of a poly-3-substituted thiophene,

25 during or after polymerisation ('endcapping').

30 The invention further relates to a semiconductor or charge transport material, component or device comprising one or more polymers as described above and below.

35 The invention further relates to the use of polymers according to the invention as semiconductors or charge transport materials, in particular in optical, electrooptical or electronic devices, like for example in field effect transistors (FET) as components of integrated circuitry, as thin film transistors in flat panel display applications or for Radio Frequency Identification (RFID) tags, or in semiconducting

components for organic light emitting diode (OLED) applications such as electroluminescent displays or backlights of e.g. liquid crystal displays (LCD), for photovoltaic or sensor devices, as electrode materials in batteries, as photoconductors and for electrophotographic applications like electrophotographic recording.

The invention further relates to the use of the polymers according to the present invention as electroluminescent materials, in photovoltaic or sensor devices, as electrode materials in batteries, as photoconductors, for electrophotographic applications or electrophotographic recording or for detecting and discriminating DNA sequences.

The invention further relates to an optical, electrooptical or electronic device, FET, integrated circuit (IC), TFT or OLED comprising a semiconducting or charge transport material, component or device according to the invention.

The invention further relates to a TFT or TFT array for flat panel displays, radio frequency identification (RFID) tag, electroluminescent display or backlight comprising a semiconducting or charge transport material, component or device or a FET, IC, TFT or OLED according to the invention.

The invention further relates to a security marking or device comprising a FET or an RFID tag according to the invention.

Brief Description of the Drawings

Figures 1 shows forward transfer characteristics for polymers with different endgroups according to example 1 and 2 of the present invention.

Figure 2 shows repeated forward transfer scans for polymers with different endgroups according to example 1 and 2 of the present invention.

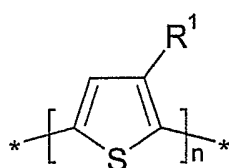
Figure 3 shows transistor output characteristics at low V_{sd} for polymers with different endgroups according to example 1 and 2 of the present invention.

5

Detailed Description of the Invention

The polymers prepared by the process according to the present invention are preferably selected of formula I

10



I

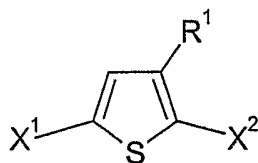
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wherein n is an integer > 1 and R^1 is a group that does not react with magnesium under the conditions as described for the process according to the present invention above and below. Preferably R^1 is an organic group which when it is unsubstituted and unmodified straight chained or branched alkyl has 5 or more C-atoms. Very preferably R^1 is an organic group having 5 or more C-atoms.

20

The thiophene used as educt in the process according to the present invention is preferably selected of formula II

25



II

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wherein R^1 has the meaning given in formula I and X^1 and X^2 are independently of each other a group that is capable of reacting with magnesium. Especially preferably X^1 and X^2 are Cl and/or Br, most preferably Br.

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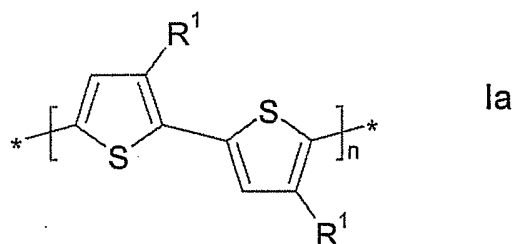
The process according to the present invention offers significant advantages over the methods disclosed in prior art especially

regarding economical and ecological aspects, whilst providing polythiophenes in comparable or even better yield and quality.

5 With the process according to the present invention it is possible to prepare polythiophenes, in particular HT-poly-(3-substituted) thiophenes with a regioregularity of 90 % or higher in a yield of 50 % or higher (related to the thiophene educt). As mentioned above, these highly regioregular HT-poly-(3-substituted) thiophenes are particularly suitable for use as charge-transport or semiconductor
10 material in electronic or optical devices.

The regioregular polymers of the present invention thus have a high number, and do preferably exclusively consist, of HT-linked repeating units as shown in formula Ia

15



20

Furthermore, the costly and difficult preparation of Grignard reagents like organomagnesium halides is not necessary, instead magnesium can be used as reagent. Also, the emission of large amounts of
25 hazardous by-products like methyl bromide can be avoided.

The general method of adding magnesium instead of Grignard reagents like organomagnesium halides has been described in prior art for the preparation of polythiophenes and poly-3-alkylthiophenes.
30 However, magnesium is generally not considered to be highly regioselective in conventional Grignard reactions. This is supported by the teaching of the prior art documents mentioned above, which do not report polymers with high regioregularity.

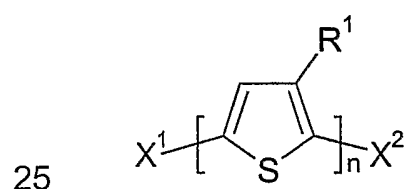
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The inventors of the present invention have found that polythiophenes with high regioregularity, high molecular weight and good

processability can be obtained by appropriate selection of the reaction conditions and the reagents, like the use of linear ethers as solvents and of thiophene monomers with bromo or chloro groups in 2/5-position as educts. Also, the use of 3-substituted thiophenes with organic substituents in 3-position that preferably have 5, 6 or more C-atoms improves the processability and solubility of the polythiophene. As a result, during polymerisation the growing polymer remains longer in solution and a high molecular weight and good regioregularity can be obtained.

After polymerisation the polymer is preferably recovered from the reaction mixture, for example by conventional work-up, and purified. This can be achieved according to standard methods known to the expert and described in the literature.

As a result of the process according to the present invention, the obtained polythiophenes are usually terminated by the leaving groups that are capable of reacting with magnesium in 2 and 5-position of the thiophene monomer, or derivatives thereof. In case thiophene educts of formula II are used, the obtained polymers correspond to formula I1



I1

wherein n, R¹, X¹ and X² have the meanings given in formula I and II.

Another object of the present invention is a process of chemically modifying the reactive terminal groups of a polymer, in particular a poly-3-substituted thiophene, during or after polymerisation. This process is hereinafter also referred to as 'endcapping'. Another object of the invention is a polymer, in particular a poly-3-substituted thiophene, wherein the terminal groups are chemically modified to replace monomer end groups, hereinafter also referred to as 'endcapped polymer'. Another object of the invention is the use of an

endcapped polymer, in particular an endcapped poly-3-substituted thiophene, as semiconductor or charge transport material, in particular for the uses and devices as described above and below.

5 Endcapping of polyalkylthiophene is known in the art and is described for example by B. M. W. Langeveld-Voss, R. A. J. Janssen et al., Chem Commun 2000 81-82, and J. Liu., R. S. Loewe and R. D. McCullough, Macromolecules, 1999, **32** 5777-5785, as an aid for understanding the reaction mechanism (Liu, Janssen) or to enable a
10 later reaction of the polymer or to encourage binding to a substrate (Janssen). Furthermore, US 6,602,974 describes the chemical modification of polyalkylthiophenes by replacing the terminal halogen groups with H or functional end groups for the preparation of block copolymers.

15 The inventors of the present invention have found that endcapping can also be used as a suitable method to provide a polymer with improved electrical properties. For example, by removing bromine end groups from the polymer chains, a source of charge carrier
20 trapping is eliminated and higher charge carrier mobilities can be observed. The main benefit concerns the improvement in transistor performance stability. The carbon - bromine bond is susceptible to undergo further reaction in the presence of charged species, which are present during transistor operation. These suspected chemical
25 reactions both change the properties of the semiconducting polymer, as well as release mobile ions, which lead to transistor hysteresis and threshold voltage drifts. Endcapping reduces the reactivity of the charged polymer and hence improves stability.

30 Thus, another aspect of the invention relates to a method of improving the electrical properties, like the charge carrier mobility, and the processability, of a polymer, in particular of a polyalkylthiophene, by chemically modifying the endgroups of the polymer (endcapping) as described above and below. Another
35 aspect of the invention relates to endcapped polymers and their use

as semiconductors, for example in the applications as described above and below.

5 The process of endcapping by conversion of, for example, residual halogen end groups into other groups or reactive species is not limited to polymers obtained by the method of the present invention. It can also be carried out with other polymers, for example those obtained by the methods of Rieke, McCullough, Suzuki or Stille as described above.

10 Endcapping can be carried out before or after recovering the polymer from the polymerisation reaction mixture, before or after work-up of the polymer or before or after its purification, depending on which is more suitable and more effective regarding the material costs, time and reaction conditions involved. For example, in case expensive co-
15 reactants are used for endcapping it may be more economical to carry out the endcapping after purification of the polymer. In case the purification effort is economically more important than the co-reactants it may be preferred to carry out the endcapping before
20 purification or even before recovering the polymer from the polymerisation reaction mixture.

Especially preferred are endcapped poly-3-substituted thiophenes obtained by a Grignard reaction with magnesium according to the
25 inventive process as described above and below, wherein the reactive terminal groups of the polymer are chemically modified during or after polymerisation, or after recovering the polymer from the mixture, or after purification of the polymer.

30 As a result of the process according to the present invention, at the end of the polymerisation step the end groups X^1 and X^2 are either a halogen or Grignard group. At this stage, an aliphatic Grignard reagent $RMgX$ or dialkyl Grignard reagent MgR_2 , wherein X is halogen and R is an aliphatic group, or active Magnesium is
35 preferably added to convert the remaining halogen end groups to Grignard groups. Subsequently, for example to give an alkyl end

group an excess of an ω -haloalkane is added which will couple to the Grignard. Alternatively, to give a proton end group the polymerisation is quenched into a non-solvent such as an alcohol.

5 To provide reactive functional end groups, like for example hydroxyl or amine groups or protected versions thereof, the halogen end groups are for example reacted with a Grignard reagent $R'MgX$, wherein R' is such a reactive functional group or protected reactive functional group.

10 Instead of a Grignard reagent it is also possible to carry out endcapping using an organo lithium reagent, followed by addition of an ω -haloalkane.

15 It is also possible to replace H end groups by reactive functional groups by using e.g. the methods described in US 6,602,974, such as a Vilsmeier reaction to introduce aldehyde groups followed by reduction with metal hydrides to form hydroxyl groups.

20 If the polymer has been fully worked up prior to endcapping, it is preferred to dissolve the polymer in a good solvent for Grignard coupling such as diethyl ether or THF. The solution is then treated for example with the above mentioned organo Grignard reagent $RMgX$ or MgR_2 or $R'MgX$ or with a zinc reagent, $RZnX$, $R'ZnX$ or ZnR_2 ,
25 where R and R' are as defined above. A suitable nickel or palladium catalyst is then added along with the haloalkane.

This method of endcapping is also effective for example for polymers prepared by the McCullough or Rieke route.

30 In the case of polymers prepared by the Suzuki or Stille route, these are preferably endcapped as follows: For the Suzuki reaction at the end of the polymerisation alkyl termination is preferably obtained by addition of a 2-boronic-5-alkyl thiophene to react with the bromine
35 end groups, followed by an excess of a 2-bromo-5-alkyl thiophene to react with the boronic end groups. To obtain a hydrogen endcapped

species, reaction with 2-boronic thiophene followed by an excess of 2-bromo thiophene is required. A similar process can be employed for the Stille route, but using a 2-trialkyl stannyl reagent, for example 2-trialkyl stannyl-5-alkyl thiophene, instead of boronic thiophene.

5 Similarly, if the endcapping is carried out after initial quenching and purification of the polymer, it is preferred to dissolve the polymer and add a suitable catalyst.

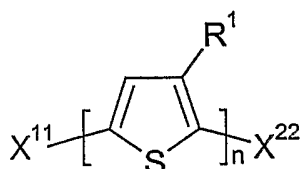
10 Very preferred are endcapped polymers wherein the terminal groups during or after polymerisation are replaced by H or an alkyl group (hereinafter also referred to as 'polymers endcapped by H or an alkyl group').

15 Preferably endcapping is carried out before purification of the polymer. Further preferably endcapping is carried out after step d) of the process as described above and below. In another preferred embodiment of the present invention the endcapper is added during polymerisation to remove the end groups and possibly control the molecular weight of the polymer.

20 Preferably, substantially all molecules in a polymer sample are endcapped in accordance with this invention, but at least 80 %, preferably at least 90 %, most preferably at least 98 % are endcapped.

25 By chemical modification of the terminal groups (endcapping) of the polymers according to the present invention, it is possible to prepare novel polymers with different terminal groups. These polymers are preferably selected of formula I2

30



I2

35

wherein n and R^1 have the meanings given in formula I and II, and X^{11} and X^{22} are independently of each other H, halogen, stannate, boronate or an aliphatic, cycloaliphatic or aromatic group that may also comprise one or more hetero atoms.

5

Especially preferably X^{11} and X^{22} are selected from H or straight-chain or branched alkyl with 1 to 20, preferably 1 to 12, very preferably 1 to 6 C-atoms, most preferably straight-chain alkyl or branched alkyl like isopropyl or tert. butyl. Aromatic groups X^{11} and X^{22} tend to be bulky and are less preferred.

10

As described above, the end groups X^{11} and X^{22} are preferably introduced by reacting the polymer of formula I1 with a Grignard reagent $MgRX$, MgR_2 or $MgR'X$ as described above, wherein R and R' are X^{11} or X^{22} as defined in formula I2.

15

By introducing suitable functional end groups X^{11} and/or X^{22} it is possible to prepare block copolymers from the polymers according to the present invention. For example, if one or both of the end groups X^{11} and X^{22} in a polymer of formula I2 is a reactive group or a protected reactive group, like for example an optionally protected hydroxy or amine group, they can be reacted (after removing the protective group) with the end group of another polymer of formula I2 (e.g. with different groups R^1 and/or X^{11} and/or X^{22}), or with a polymer of different structure. If one of X^{11} and X^{22} is a reactive group, diblock copolymers can be formed. If both X^{11} and X^{22} are reactive groups, a triblock copolymer can be formed.

20

25

30

Alternatively a block copolymer can be formed by introducing reactive or protected reactive groups X^{11} and/or X^{22} , adding a catalyst and one or monomers, and initiating a new polymerization reaction starting from the site of the groups X^{11} and/or X^{22} .

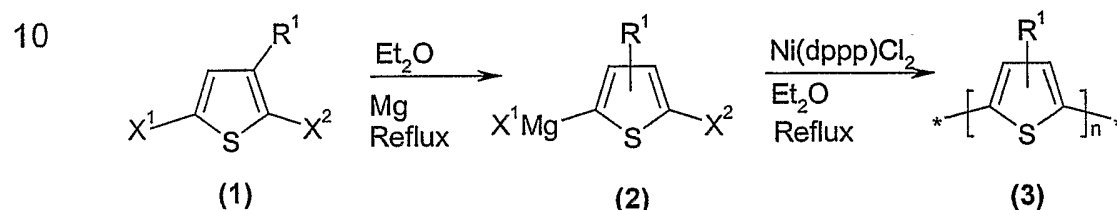
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Suitable functional end groups and methods of their introduction can be taken from the above disclosure and from prior art. Details how to prepare block copolymers can be taken e.g. from US 6,602,974, the

entire disclosure of which is incorporated into this application by reference.

5 The process according to the present invention is exemplarily illustrated in Scheme 1 below, wherein n , R^1 , X^1 and X^2 have the meaning of formula I and II.

Scheme 1



15 If R^1 is a group that is reactive with magnesium under the process conditions as described above and below, it is preferably transformed into, or coupled with, a protective group, in order not to take part in the reactions forming (2) and (3). Suitable protective groups are known to the expert and described in the literature, for example in Greene and Greene, "Protective Groups in Organic

20 Synthesis", John Wiley and Sons, New York (1981).

25 The starting materials and reagents used in the process according to the present invention are either commercially available (e.g. from Aldrich) or can be easily synthesized by methods well known to those skilled in the art.

30 In some cases it may be suitable to further purify the thiophene monomer and the other reagents before using them in the inventive process. Purification can be carried out by standard methods known to the expert and described in the literature.

35 The process according to the present invention as exemplarily depicted in Scheme 1 is preferably carried out as follows:

In a first step (step a)) a 3-substituted thiophene (1), preferably 3-substituted 2,5-dihalothiophene, most preferably 3-substituted 2,5-dibromothiophene, like for example 2,5-dibromo-3-alkylthiophene, which is a readily available starting material, is dissolved in a solvent or a solvent mixture, like for example diethyl ether.

The solvent or solvent mixture preferably consists of one or more polar aprotic solvents, which can be any solvent of this type, like for example dialkylethers such as diethyl ether, di-n-butyl ether, di-n-propyl ether, di-isopropyl ether, glycol ethers such as 1,2-dimethoxyethane, ethers with two different alkyl groups such as tert.-butylmethyl ether, or mixtures thereof, or mixtures of aromatic or aliphatic solvents such as mixtures of toluene with the above ethers.

Preferably the solvent is selected from linear ethers like diethyl ether, di-n-butyl ether, di-n-propyl ether, di-isopropyl ether, ethers with two different alkyl groups, 1,2-dimethoxyethane or tert.-butylmethyl ether or mixtures thereof, or a mixture of toluene with one or more of these ethers.

Especially preferably the solvent is diethyl ether.

The concentration of the thiophene educt (1) in the solvent is preferably from 40 to 200 g/l, very preferably from 80 to 130 g/l.

In a second step (step b)) magnesium is added to the reaction mixture in an at least molar amount of the thiophene educt (1), preferably in an excessive amount from more than 1 to 3, preferably from 1.01 to 2.00, very preferably from 1.02 to 1.50, most preferably from 1.02 to 1.20 times the molar amount of the thiophene educt.

The Grignard reaction is then started for example by heating the reaction mixture to reflux or by adding a suitable starting agent such as Br₂, I₂, DIBALH (diisobutylaluminium hydride) or others, or by other methods of activating the magnesium surface. The Grignard reaction is then allowed to proceed, optionally under agitating and/or heating

the reaction mixture, for a sufficient period of time to give the intermediate (2).

5 In an optional next step (step c)), the non-reacted magnesium is then removed from the reaction mixture e.g. by filtration. Preferably the magnesium is removed.

10 In the next step (step d)), a suitable catalyst is added to the reaction mixture in an effective amount to initiate the polymerisation via a Grignard metathesis reaction. Usually the catalyst is reactive enough to start the polymerisation without other means, however in practice the mixture is typically stirred while adding the catalyst.

15 Alternatively, it is possible to add the reaction mixture to the catalyst.

The catalyst in step d) can be any catalyst that is suitable for a reaction involving organometallic reagents, including for example Ni, Pd or other transition metal catalysts. Preferably it is selected from nickel catalysts, in particular Ni(II) catalysts like Ni(dppp)Cl₂ (1,3-diphenylphosphinopropane nickel(II) chloride) or Ni(dppe)Cl₂ (1,2-bis(diphenylphosphino)ethane nickel(II) chloride), furthermore e.g. copper catalysts like CuI, CuBr or Li₂CuCl₄ or Pd catalysts like Pd(PPh₃), PdCl₂(dppe).

25 The catalyst is preferably added in an amount from 0.1 to 5 %, preferably 0.5 to 2 mol % of the thiophene educt.

30 The polymerisation (Grignard metathesis) reaction is then allowed to proceed, optionally under agitating and/or heating the reaction mixture, for a sufficient period of time to give the polymer (3).

35 The process according to the present invention may be run at any temperature providing a sufficient conversion rate. It is preferred that the reaction is performed at a temperature between -5 °C and the solvent's reflux temperature, in particular at the temperatures as

specified above and below. The term "reflux temperature" includes temperatures at or slightly below the boiling point of the solvent.

5 The selection of a suitable reaction time depends on the actual rate of the individual reaction. Preferably the reaction times are as given above and below.

10 For the reaction of the thiophene educt with magnesium (step b)) the reaction temperature is preferably in the range from 10 °C to reflux temperature, most preferably from room temperature to reflux temperature. The reaction time is from 15 min to 24 h, preferably from 30 min to 6 h.

15 For the polymerisation reaction (step d)) the temperature is preferably in the range from -5 °C to reflux temperature, most preferably from room temperature to reflux temperature. The reaction time is from 15 min to 48 h, preferably from 45 min to 4h.

20 The reactions according to steps b) and d) are optionally carried out under agitating the reaction mixture, which can be achieved by known methods.

25 Steps a) to d), in particular steps b) and d) are preferably carried out under a dry and inert atmosphere, e.g. under nitrogen.

30 The reaction products (2) and (3) prepared by the process according to the present invention may be isolated by usual work-up and purification with standard procedures well known to those skilled in the art.

35 The intermediate (2) obtained in step b) is directly used in step d). However, for the purpose of e.g. investigating the proceeding of the reaction process or analysing the ratio of the regiochemical intermediates produced it may be suitable to quench the reaction mixture.

In the last step (step e)) the polymer (3) is recovered from the reaction mixture. Preferably the polymer is recovered from the mixture by quenching the reaction mixture with an alcoholic or aqueous solution or/and precipitating the polymer.

5

The polymer can then be purified by known methods to remove inorganic impurities as well as monomers and short-chain oligomers, or may also be used without further purification. Preferably the polymer is purified. Suitable and preferred purification methods include solid-phase extraction, liquid-liquid extraction, precipitation, adsorption and filtration. Preferably a combination of purification methods is selected to obtain a high-purity product best suitable for application,

10

For example a preferred purification method includes aqueous quenching, for example with a mixture of chloroform/water, optional liquid/liquid extraction or distilling off the original solvent, precipitation into a polar solvent like for example methanol, and washing with an unpolar solvent like for example heptane.

15

Suitable reagents and process conditions for the steps d) and e) including the reaction of the intermediate (2) to the polymer (3), can also be taken from McCullough et al., *Adv. Mater.*, 1999, **11(3)**, 250-253, EP 1 028 136 and US 6,166,172, the entire disclosure of these documents being incorporated into this application by reference.

20

An especially preferred embodiment relates to a process including the following steps

25

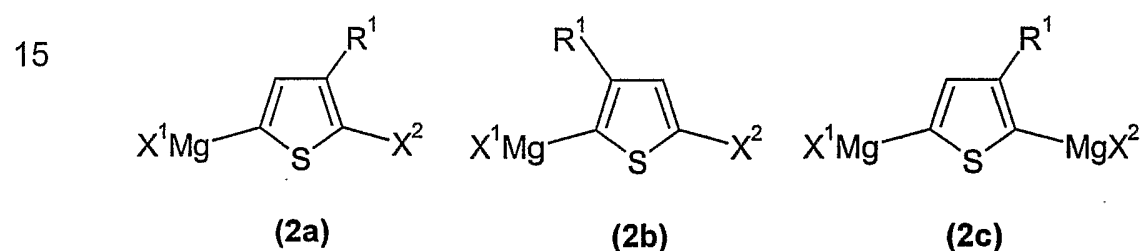
- a) dissolving a thiophene having two groups that are capable of reacting with magnesium, preferably a thiophene of formula II, very preferably in an amount of from 40 to 200 g/l, in diethyl ether,
- b) adding magnesium in 1.02 to 1.20 times the molar amount of the thiophene, or adding the thiophene solution to the magnesium, and heating the mixture to reflux to form a regiochemical Grignard intermediate,

30

35

- c) removing the unreacted magnesium from the reaction mixture,
d) adding a Ni(II) catalyst, preferably Ni(DPPP)Cl₂ or Ni(DPPE)Cl₂ to
the reaction mixture, or adding the reaction mixture to the Ni(II)
catalyst, and agitating the resulting mixture, preferably under
5 reflux, to form a polymer, and
e) recovering the polymer from the mixture.

The intermediate (2) is usually obtained as a mixture of
10 regiochemical isomers (2a) and (2b), and may also include a,
typically small, amount of the double-Grignard product (2c), as
shown below, wherein X¹, X² and R¹ have the meanings of formula I
and I1



20 The ratio of these intermediates is depending for example on the
molar excess of Magnesium, the solvent, temperature and reaction
time.

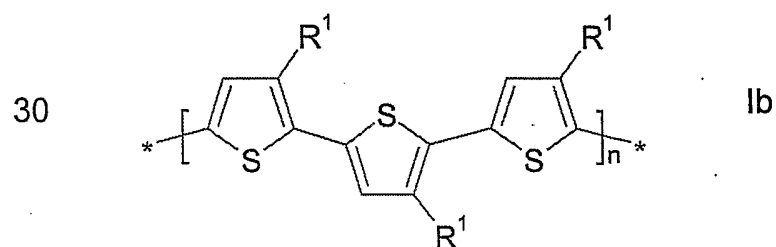
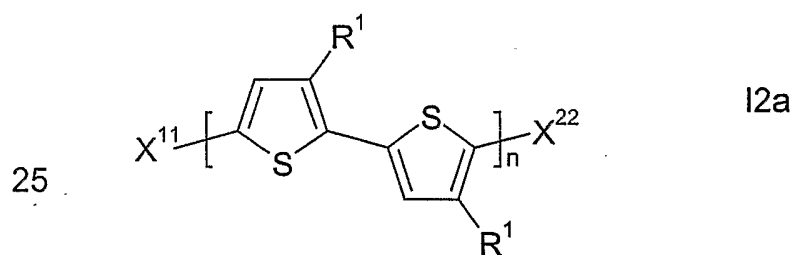
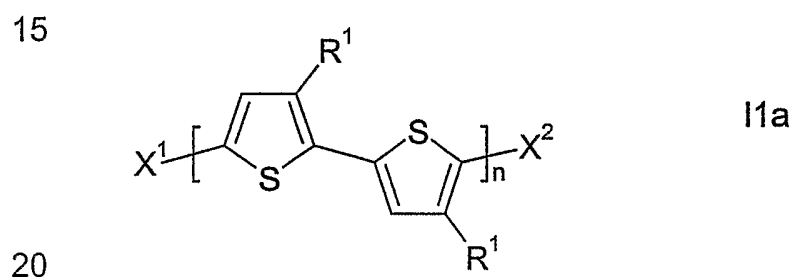
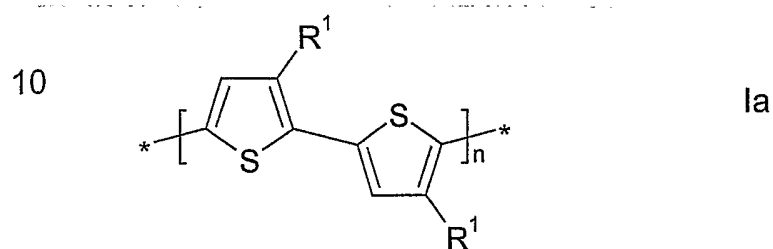
25 For example, if the reaction is carried out according to the especially
preferred embodiment described above, the intermediates 2a, 2b
and 2c can be obtained in a ratio of 85/5/10.

30 Depending on the processing conditions, like for example the solvent
and the amount of magnesium, the ratio of isomer intermediates
2a/2b/2c can be varied. A preferred process includes isomer
intermediate ratios 2a/2b/2c of 80-90/2-20/0-20.

35 The polymers according to the present invention are especially
preferably regioregular HT-poly-(3-substituted) thiophenes. The
regioregularity (=head-to-tail couplings divided by the total couplings,

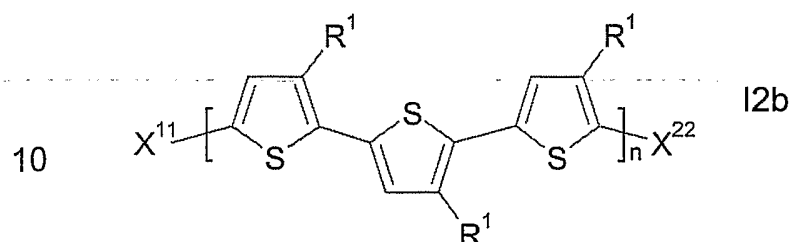
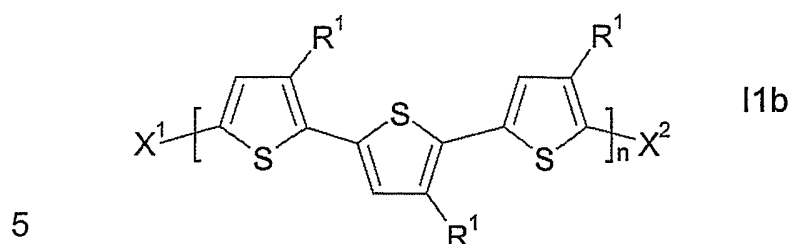
and expressed as a percentage), in these polymers is preferably at least 85 %, in particular 90% or more, very preferably 95% or more, most preferably from 98 to 100%.

- 5 Polymers of formula I, I1 and I2 having a high percentage of HT-couplings accordingly have a corresponding high number of HT dyads or HT-HT-triads formula Ia/b, I1a/b and I2a/b shown below.



30

35



wherein R^1 , X^1 , X^2 , X^{11} , X^{22} have the meanings given above.

15 Regioregular poly-(3-substituted) thiophenes are advantageous as they show strong interchain pi-pi-stacking interactions and a high degree of crystallinity, making them effective charge transport materials with high carrier mobilities, as described for example in US
20 6,166,172.

The polymers according to the present invention preferably have a degree of polymerisation (or number n of recurring units) from 2 to 5,000, in particular from 10 to 5,000 or from 110 to 5,000, very
25 preferably from 50 to 1,000, most preferably from above 100 to 1,000.

Further preferred are polymers having a molecular weight from 5,000 to 300,000, in particular from 10,000 to 100,000, preferably from
30 15,000 to 100,000, very preferably from 20,000 to 100,000.

R^1 in formula I, I1 and II is preferably an organic group, preferably a non-reactive or protected reactive organic group, which has preferably 5 or more C-atoms.

35

Especially preferably R^1 is straight chain, branched or cyclic alkyl with 1 or more, preferably 5 or more, very preferably 1 to 20 C-atoms, which may be unsubstituted, mono- or poly-substituted by F, Cl, Br, I or CN, it being also possible for one or more non-adjacent
 5 CH_2 groups to be replaced, in each case independently from one another, by -O-, -S-, -NH-, -NR⁰-, -SiR⁰R⁰⁰-, -CO-, -COO-, -OCO-, -OCO-O-, -SO₂-, -S-CO-, -CO-S-, -CY¹=CY²- or -C≡C- in such a manner that O and/or S atoms are not linked directly to one another, optionally substituted aryl or heteroaryl preferably having 1 to 30 C-atoms, or P-Sp, with
 10

R^0 and R^{00} being independently of each other H or alkyl with 1 to 12 C-atoms,

15 Y^1 and Y^2 being independently of each other H, F, Cl or CN,

P being a polymerisable or reactive group which is optionally protected, and

20 Sp being a spacer group or a single bond.

X^1 and X^2 in formula I1 and II are preferably independently of each other selected from halogen, very preferably Cl or Br, most preferably Br.

25 X^{11} and X^{22} in formula I2 are preferably independently of each other selected from H, halogen, B(OR')(OR'') or SnR⁰R⁰⁰R⁰⁰⁰ or straight chain, branched or cyclic alkyl with 1 to 20 C-atoms, which may be unsubstituted, mono- or poly-substituted by F, Cl, Br, I, -CN and/ or -
 30 OH, it being also possible for one or more non-adjacent CH_2 groups to be replaced, in each case independently from one another, by -O-, -S-, -NH-, -NR⁰-, -SiR⁰R⁰⁰-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S-, -CY¹=CY²- or -C≡C- in such a manner that O and/or S atoms are not linked directly to one another, optionally substituted aryl or
 35 heteroaryl, or P-Sp, with R^0 , R^{00} , Y^1 , Y^2 , P and Sp having the meanings given above,

R^{000} being H or alkyl with 1 to 12 C-atoms, and

5 R' and R'' being independently of each other H or alkyl with 1 to 12 C-atoms, or OR' and OR'' together with the boron atom may also form a cyclic group having 2 to 10 C atoms.

Especially preferred are polymers and compounds of formula I, II, I1 and I2 wherein

- 10
- R^1 is an organic group, preferably an alkyl group with 5 or more C-atoms,
 - R^1 is a straight-chain alkyl group with 1 to 12, preferably 5 to 12 C-atoms,
 - 15 - R^1 is n-hexyl,
 - R^1 is selected from C_1 - C_{20} -alkyl that is optionally substituted with one or more fluorine atoms, C_1 - C_{20} -alkenyl, C_1 - C_{20} -alkynyl, C_1 - C_{20} -alkoxy, C_1 - C_{20} -thioalkyl, C_1 - C_{20} -silyl, C_1 - C_{20} -ester, C_1 - C_{20} -amino, C_1 - C_{20} -fluoroalkyl, optionally substituted aryl or
 - 20 heteroaryl, or P-Sp-, in particular C_1 - C_{20} -alkyl or C_1 - C_{20} -fluoroalkyl, preferably straight-chain groups,
 - R^1 is selected from alkyl that is optionally substituted with one or more fluorine atoms, alkenyl, alkynyl, alkoxy, thioalkyl or
 - 25 fluoroalkyl, all of which are straight-chain and have 1 to 12, preferably 5 to 12 C-atoms,
 - R^1 is selected from pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl or dodecyl,
 - X^1 and X^2 have the same meaning,
 - 30 - X^1 and X^2 denote Br,
 - X^{11} and X^{22} have the same meaning,
 - X^{11} and X^{22} denote H,
 - 35 - X^{11} and X^{22} are selected from alkyl that is optionally substituted with one or more fluorine atoms, alkenyl, alkynyl, alkoxy,

thioalkyl, silyl, ester, amino or fluoroalkyl, all of these groups being straight-chain or branched and having 1 to 20, preferably 1 to 12, most preferably 1 to 6 C atoms, or optionally substituted aryl or heteroaryl, or P-Sp as defined above, in particular
 5 straight-chain or branched C₁-C₆-alkyl, most preferably isopropyl, tert.butyl, or 2-methylbutyl,

- n is an integer from 2 to 5000, in particular 50 to 1000.

10 If in formula I, II, I1 and I2 R¹ is an alkyl or alkoxy radical, i.e. where the terminal CH₂ group is replaced by -O-, this may be straight-chain or branched. It is preferably straight-chain, has 2 to 8 carbon atoms and accordingly is preferably ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, ethoxy, propoxy, butoxy, pentoxy, hexyloxy, heptoxy, or octoxy,
 15 furthermore methyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, nonoxy, decoxy, undecoxy, dodecoxy, tridecoxy or tetradecoxy, for example. Especially preferred are n-hexyl and n-dodecyl.

20 If in formula I, II, I1 and I2 R¹ is oxaalkyl, i.e. where one CH₂ group is replaced by -O-, is preferably straight-chain 2-oxapropyl (=methoxymethyl), 2- (=ethoxymethyl) or 3-oxabutyl (=2-methoxyethyl), 2-, 3-, or 4-oxapentyl, 2-, 3-, 4-, or 5-oxahexyl, 2-, 3-, 4-, 5-, or 6-oxaheptyl, 2-, 3-, 4-, 5-, 6- or 7-oxaoctyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-oxanonyl or 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-oxadecyl, for example.

25 If in formula I, II and I1 R¹ is thioalkyl, i.e. where one CH₂ group is replaced by -S-, is preferably straight-chain thiomethyl (-SCH₃), 1-thioethyl (-SCH₂CH₃), 1-thiopropyl (= -SCH₂CH₂CH₃), 1- (thiobutyl), 1-(thiopentyl), 1-(thiohexyl), 1-(thioheptyl), 1-(thiooctyl), 1-(thiononyl),
 30 1-(thiododecyl), 1-(thioundecyl) or 1-(thiododecyl), wherein preferably the CH₂ group adjacent to the sp² hybridised vinyl carbon atom is replaced.

35 If in formula I, II, I1 and I2 R¹ is fluoroalkyl, it is preferably straight-chain perfluoroalkyl C_iF_{2i+1}, wherein i is an integer from 1 to 15, in

particular CF_3 , C_2F_5 , C_3F_7 , C_4F_9 , C_5F_{11} , C_6F_{13} , C_7F_{15} or C_8F_{17} , very preferably C_6F_{13} .

Halogen is preferably F, Br or Cl.

5

$-\text{CY}^1=\text{CY}^2-$ is preferably $-\text{CH}=\text{CH}-$, $-\text{CF}=\text{CF}-$ or $-\text{CH}=\text{C}(\text{CN})-$.

10

Aryl and heteroaryl preferably denote a mono-, bi- or tricyclic aromatic or heteroaromatic group with up to 25 C atoms that may also comprise condensed rings and is optionally substituted with one or more groups L, wherein L is halogen or an alkyl, alkoxy, alkylcarbonyl or alkoxy carbonyl group with 1 to 12 C atoms, wherein one or more H atoms may be replaced by F or Cl.

15

Especially preferred aryl and heteroaryl groups are phenyl in which, in addition, one or more CH groups may be replaced by N, naphthalene, thiophene, thienothiophene, dithienothiophene, alkyl fluorene and oxazole, all of which can be unsubstituted, mono- or polysubstituted with L as defined above.

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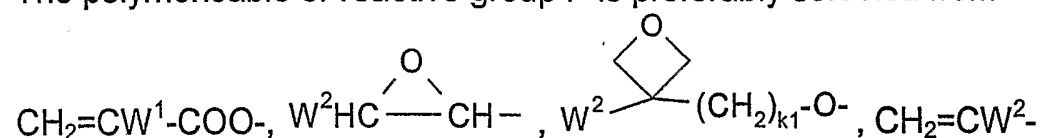
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Another preferred embodiment of the present invention relates to polythiophenes that are substituted in 3-position with a polymerisable or reactive group, which is optionally protected during the process of forming the polythiophene. Particular preferred polymers of this type are those of formula I, I1 or I2 wherein R^1 denotes P-Sp. These polymers are particularly useful as semiconductors or charge transport materials, as they can be crosslinked via the groups P, for example by polymerisation in situ, during or after processing the polymer into a thin film for a semiconductor component, to yield crosslinked polymer films with high charge carrier mobility and high thermal, mechanical and chemical stability.

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The polymerisable or reactive group P is preferably selected from


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$(O)_{k1}-$, $CH_3-CH=CH-O-$, $(CH_2=CH)_2CH-OCO-$, $(CH_2=CH)_2CH-O-$,
 $(CH_2=CH-CH_2)_2CH-OCO-$, $(CH_2=CH-CH_2)_2N-$, $HO-CW^2W^3-$, $HS-$
 CW^2W^3- , HW^2N- , $HO-CW^2W^3-NH-$, $CH_2=CW^1-CO-NH-$, $CH_2=CH-$
 $(COO)_{k1}-Phe-(O)_{k2}-$, $Phe-CH=CH-$, $HOOC-$, $OCN-$, and $W^4W^5W^6Si-$,
 5 with W^1 being H, Cl, CN, phenyl or alkyl with 1 to 5 C-atoms, in
 particular H, Cl or CH_3 , W^2 and W^3 being independently of each
 other H or alkyl with 1 to 5 C-atoms, in particular methyl, ethyl or n-
 propyl, W^4 , W^5 and W^6 being independently of each other Cl,
 oxalkyl or oxacarbonylalkyl with 1 to 5 C-atoms, Phe being 1,4-
 10 phenylene and k_1 and k_2 being independently of each other 0 or 1, or
 a protected derivative of these groups which is non-reactive with
 magnesium under the conditions described for the process according
 to the present invention. Suitable protective groups are known to the
 expert and described in the literature, for example in Greene and
 15 Greene, "Protective Groups in Organic Synthesis", John Wiley and
 Sons, New York (1981), like for example acetals or ketals.

Preferably, however, the polymerisable group is added to the
 inventive polymers as the last step, after polymerisation.

20 Especially preferred groups P are $CH_2=CH-COO-$, $CH_2=C(CH_3)-$
 $COO-$, $CH_2=CH-$, $CH_2=CH-O-$, $(CH_2=CH)_2CH-OCO-$, $(CH_2=CH)_2CH-$

25 O-, and W^2  $(CH_2)_{k1}-O-$, or protected derivatives thereof.

Polymerisation of group P can be carried out according to methods
 that are known the expert and described in the literature, for example
 in D. J. Broer; G. Challa; G. N. Mol, *Macromol. Chem*, 1991, **192**, 59.

30 As spacer group Sp all groups can be used that are known for this
 purpose to the skilled in the art. The spacer group Sp is preferably of
 formula $Sp'-X'$, such that $P-Sp-$ is $P-Sp'-X'-$, wherein

35 Sp' is alkylene with up to 30 C atoms which is unsubstituted
 or mono- or polysubstituted by F, Cl, Br, I or CN, it being

also possible for one or more non-adjacent CH₂ groups to be replaced, in each case independently from one another, by -O-, -S-, -NH-, -NR⁰-, -SiR⁰R⁰⁰-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S-, -CH=CH- or -C≡C- in such a manner that O and/or S atoms are not linked directly to one another,

5 X' is -O-, -S-, -CO-, -COO-, -OCO-, -O-COO-, -CO-NR⁰-, -NR⁰-CO-, -OCH₂-, -CH₂O-, -SCH₂-, -CH₂S-, -CF₂O-, -OCF₂-, -CF₂S-, -SCF₂-, -CF₂CH₂-, -CH₂CF₂-, -CF₂CF₂-, -CH=N-, -N=CH-, -N=N-, -CH=CR⁰-, -CY¹=CY²-, -C≡C-, -CH=CH-COO-, -OCO-CH=CH- or a single bond,

10 R⁰ and R⁰⁰ are independently of each other H or alkyl with 1 to 12 C-atoms, and

Y¹ and Y² are independently of each other H, F, Cl or CN.

20 X' is preferably -O-, -S-, -OCH₂-, -CH₂O-, -SCH₂-, -CH₂S-, -CF₂O-, -OCF₂-, -CF₂S-, -SCF₂-, -CH₂CH₂-, -CF₂CH₂-, -CH₂CF₂-, -CF₂CF₂-, -CH=N-, -N=CH-, -N=N-, -CH=CR⁰-, -CY¹=CY²-, -C≡C- or a single bond, in particular -O-, -S-, -C≡C-, -CY¹=CY²- or a single bond. In another preferred embodiment X' is a group that is able to form a conjugated system, such as -C≡C- or -CY¹=CY²-, or a single bond.

25 Typical groups Sp' are, for example, -(CH₂)_p-, -(CH₂CH₂O)_q-CH₂CH₂-, -CH₂CH₂-S-CH₂CH₂- or -CH₂CH₂-NH-CH₂CH₂- or -(SiR⁰R⁰⁰-O)_p-, with p being an integer from 2 to 12, q being an integer from 1 to 3 and R⁰ and R⁰⁰ having the meanings given above.

30 Preferred groups Sp' are ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, undecylene, dodecylene, octadecylene, ethyleneoxyethylene, methyleneoxybutylene, ethylene-thioethylene, ethylene-N-methyl-iminoethylene, 1-methylalkylene, ethenylene, propenylene and
35 butenylene for example.

The polymers of the present invention are useful as optical, electronic and semiconductor materials, in particular as charge transport materials in field effect transistors (FETs), e.g., as components of integrated circuitry, ID tags or TFT applications. Alternatively, they may be used in organic light emitting diodes (OLEDs) in electroluminescent display applications or as backlight of, e.g., liquid crystal displays, as photovoltaics or sensor materials, for electrophotographic recording, and for other semiconductor applications.

The polymers according to the present invention show especially advantageous solubility properties which allow production processes using solutions of these compounds. Thus films, including layers and coatings, may be generated by low cost production techniques, e.g., spin coating. Suitable solvents or solvent mixtures comprise alkanes and/ or aromatics, especially their fluorinated or chlorinated derivatives.

The polymers of the present invention are especially useful as charge transport materials in FETs. Such FETs, where an organic semiconductive material is arranged as a film between a gate-dielectric and a drain and a source electrode, are generally known, e.g., from US 5,892,244, WO 00/79617, US 5,998,804, and from the references cited in the background and prior art chapter and listed below. Due to the advantages, like low cost production using the solubility properties of the compounds according to the invention and thus the processibility of large surfaces, preferred applications of these FETs are such as integrated circuitry, TFT-displays and security applications.

In security applications, field effect transistors and other devices with semiconductive materials, like transistors or diodes, may be used for ID tags or security markings to authenticate and prevent counterfeiting of documents of value like banknotes, credit cards or ID cards, national ID documents, licenses or any product with money

value, like stamps, tickets, shares, cheques etc..

Alternatively, the polymers according to the invention may be used in organic light emitting devices or diodes (OLEDs), e.g., in display applications or as backlight of e.g. liquid crystal displays. Common OLEDs are realized using multilayer structures. An emission layer is generally sandwiched between one or more electron-transport and/or hole-transport layers. By applying an electric voltage electrons and holes as charge carriers move towards the emission layer where their recombination leads to the excitation and hence luminescence of the lumophor units contained in the emission layer. The inventive compounds, materials and films may be employed in one or more of the charge transport layers and/ or in the emission layer, corresponding to their electrical and/ or optical properties.

Furthermore their use within the emission layer is especially advantageous, if the polymers according to the invention show electroluminescent properties themselves or comprise electroluminescent groups or compounds. The selection, characterization as well as the processing of suitable monomeric, oligomeric and polymeric compounds or materials for the use in OLEDs is generally known by a person skilled in the art, see, e.g., Meerholz, Synthetic Materials, 111-112, 2000, 31-34, Alcala, J. Appl. Phys., 88, 2000, 7124-7128 and the literature cited therein.

According to another use, the polymers according to the present invention, especially those which show photoluminescent properties, may be employed as materials of light sources, e.g., of display devices such as described in EP 0 889 350 A1 or by C. Weder et al., Science, 279, 1998, 835-837.

A further aspect of the invention relates to both the oxidised and reduced form of the polymers according to this invention. Either loss or gain of electrons results in formation of a highly delocalised ionic form, which is of high conductivity. This can occur on exposure to common dopants. Suitable dopants and methods of doping are

known to those skilled in the art, e.g., from EP 0 528 662, US 5,198,153 or WO 96/21659.

5 The doping process typically implies treatment of the semiconductor material with an oxidating or reducing agent in a redox reaction to form delocalised ionic centres in the material, with the corresponding counterions derived from the applied dopants. Suitable doping methods comprise for example exposure to a doping vapor in the atmospheric pressure or at a reduced pressure, electrochemical
10 doping in a solution containing a dopant, bringing a dopant into contact with the semiconductor material to be thermally diffused, and ion-implantation of the dopant into the semiconductor material.

When electrons are used as carriers, suitable dopants are for
15 example halogens (e.g., I₂, Cl₂, Br₂, ICl, ICl₃, IBr and IF), Lewis acids (e.g., PF₅, AsF₅, SbF₅, BF₃, BCl₃, SbCl₅, BBr₃ and SO₃), protonic acids, organic acids, or amino acids (e.g., HF, HCl, HNO₃, H₂SO₄, HClO₄, FSO₃H and ClSO₃H), transition metal compounds (e.g., FeCl₃, FeOCl, Fe(CIO₄)₃, Fe(4-CH₃C₆H₄SO₃)₃, TiCl₄, ZrCl₄, HfCl₄,
20 NbF₅, NbCl₅, TaCl₅, MoF₅, MoCl₅, WF₅, WCl₆, UF₆ and LnCl₃ (wherein Ln is a lanthanoid), anions (e.g., Cl⁻, Br⁻, I⁻, I₃⁻, HSO₄⁻, SO₄²⁻, NO₃⁻, ClO₄⁻, BF₄⁻, PF₆⁻, AsF₆⁻, SbF₆⁻, FeCl₄⁻, Fe(CN)₆³⁻, and anions of various sulfonic acids, such as aryl-SO₃⁻). When holes are used as carriers, examples of dopants are cations (e.g., H⁺, Li⁺, Na⁺, K⁺, Rb⁺
25 and Cs⁺), alkali metals (e.g., Li, Na, K, Rb, and Cs), alkaline-earth metals (e.g., Ca, Sr, and Ba), O₂, XeOF₄, (NO₂⁺) (SbF₆⁻), (NO₂⁺) (SbCl₆⁻), (NO₂⁺) (BF₄⁻), AgClO₄, H₂IrCl₆, La(NO₃)₃ · 6H₂O, FSO₂OOSO₂F, Eu, acetylcholine, R₄N⁺; (R is an alkyl group), R₄P⁺ (R is an alkyl group), R₆As⁺ (R is an alkyl group), and R₃S⁺ (R is an
30 alkyl group).

The conducting form of the polymers of the present invention can be used as an organic "metal" in applications, for example, but not limited to, charge injection layers and ITO planarising layers in
35 organic light emitting diode applications, films for flat panel displays and touch screens, antistatic films, printed conductive substrates,

patterns or tracts in electronic applications such as printed circuit boards and condensers.

5 According to another use the polymers according to the present invention, especially their water-soluble derivatives (for example with polar or ionic side groups) or ionically doped forms, can be employed as chemical sensors or materials for detecting and discriminating DNA sequences. Such uses are described for example in L. Chen, D. W. McBranch, H. Wang, R. Helgeson, F. Wudl and D. G. Whitten, 10 Proc. Natl. Acad. Sci. U.S.A. 1999, **96**, 12287; D. Wang, X. Gong, P. S. Heeger, F. Rininsland, G. C. Bazan and A. J. Heeger, Proc. Natl. Acad. Sci. U.S.A. 2002, **99**, 49; N. DiCesare, M. R. Pinot, K. S. Schanze and J. R. Lakowicz, Langmuir 2002, **18**, 7785; D. T. McQuade, A. E. Pullen, T. M. Swager, Chem. Rev. 2000, **100**, 2537.

15 The examples below serve to illustrate the invention without limiting it. In the foregoing and the following, all temperatures are given in degrees Celsius, and all percentages are by weight, unless stated otherwise.

20

Example 1

a) Polymerisation:

25 9,7g of 2,5-dibromo-3-hexylthiophene are dissolved in 100 ml diethylether. To 10 % of this prepared solution 0,8 g magnesium are added and heated to reflux. The Grignard reaction is started by adding one drop of bromine. The rest (90%) of the prepared solution is added to the reaction mixture during 30 minutes and refluxed for 30 further 2 hours. Then the excess magnesium is filtered off, the reaction cooled down to 0 °C and 0,2 g of Ni(dppp)Cl₂ are added to start the polymerisation, and the reaction heated to reflux.

b) Work-up and Purification:

35

After 2 more hours of refluxing, 4 ml of isopropylmagnesium chloride (2 mol/l in diethyl ether) is added for H-endcapping.

5 After a reaction time of 2 hours the endcapping is finished and the reaction mixture is quenched with aqueous methanol. Extracting the product from the aqueous phase with chloroform and precipitating it into methanol gives the crude polymer which is further purified by Soxhlet extractions with methanol and heptane. Thus, 2.5g (50%) of pure poly-3-hexylthiophene ($^1\text{H-NMR}$ regioregularity > 95 %) are
10 obtained. The molecular weight determined by GPC is $M_n = 12,600$, $M_w = 21,700$, the polydispersity is 1,7.

Comparison Example 1 (diiodo instead of dibromo monomer)

15 Example 1 is repeated but with using 2,5-diiodo-3-hexylthiophene instead of 2,5-dibromo-3-hexylthiophene in the same molar amounts. However the mixture of Grignard intermediates precipitates and cannot be polymerised. Changing the concentration keeps the intermediate products in solution but after polymerisation an oily
20 product is obtained which cannot be precipitated from methanol and is soluble in hot heptane, indicating a low molecular weight. Regioregularity is only around 70%.

Comparison Example 2 (THF instead of linear ether as solvent)

25 Example 1 is repeated but with using THF instead of diethyl ether as solvent. As a result a low molecular weight product is obtained that is soluble in hot heptane and has a regioregularity only around 90%.

Example 2 - Endcapping (replacing Br by H)

Poly-3-hexylthiophene is prepared as described in example 1a). At the end of the polymerisation reaction a portion of the reaction mixture is end capped with H as described in example 1b) and a
35 portion is worked up without endcapping by immediate precipitation prior to the addition of the Grignard reagent. Analysis by MALDI-TOF

mass spectroscopy (Matrix-Assisted Laser-Desorption/Ionization Time-Of-Flight, see M. Karas and F. Hillenkamp, Anal. Chem. 1988, **60**, 2299 and J. Liu., R. S. Loewe and R. D. McCullough, Macromolecules, 1999, **32**, 5777) indicate that the endcapped
5 sample has predominantly H end groups, whereas the non-end-capped sample has a much higher amount of bromine end groups.

Example 3 - Endcapping (replacing Br by Propyl)

10 Poly-3-hexylthiophene is prepared as described in example 1a). At the end of the polymerisation reaction a portion of the reaction mixture is end capped with an alkyl group by first adding isopropylmagnesium chloride (2 mol/L in diethylether) and after two
15 hours adding 1-Bromopropane. The other portion is worked up with out endcapping. MALDI-TOF MS analysis indicates that the endcapped sample has predominantly propyl end groups where as the non-endcapped sample has a much higher amount of bromine end groups.

20 Example 4 - Use of endcapped polymer in a transistor

Measurements of the maximum current versus voltage are carried out for Br-terminated and H-endcapped polymers of examples 1 and 2 using substrates and processing conditions as follows.

25 Thin-film organic field-effect transistors (OFETs) are fabricated on highly doped silicon substrates with a thermally grown silicon oxide (SiO_2) insulating layer, where the substrate served as a common gate electrode. Transistor source-drain gold electrodes are
30 photolithographically defined on the SiO_2 layer. Prior to organic semiconductor deposition, FET substrates are treated with a silylating agent hexamethyldisilazane (HMDS). Thin semiconductor films are then deposited by spin-coating polymer solutions in
35 chloroform on to the FET substrates. The electrical characterization of the transistor devices, is carried out in a dry nitrogen atmosphere

using computer controlled Agilent 4155C Semiconductor Parameter Analyser.

5 The results are shown in **Figures 1-3**. The effect of the end groups can be seen in the following ways:

10 As can be seen in **Figure 1**, maximum current (and hence mobility) is higher for samples with H end capping with respect to Br end capping. Samples with H have a higher sub threshold slope.

15 As can be seen in **Figure 2A and 2B**, stability of the samples to repeated scanning is superior for samples with H end caps (2B) than for those with bromine end caps (2A).

20 Finally, as can be seen in the transistor output scans **Figure 3A and 3B**, at low source-drain voltage H-capped samples (3B) show good ohmic contact behaviour. The sample with H capping shows perfect linear behaviour. The Br capped sample (3A) however displays significant contact resistance as can be seen by the non-linear behaviour of the current-voltage plot around 0V.

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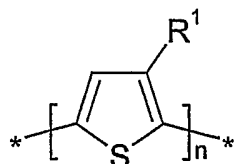
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Patent Claims

1. Process of preparing a regioregular poly (3-substituted
thiophene) having a regioregularity of $\geq 95\%$ head-to-tail (HT)
couplings, by providing a 3-substituted thiophene having chloro
and/or bromo groups in 2- and 5-position, reacting said
thiophene with magnesium in a solvent comprising a linear ether
or a mixture of linear ethers to form a regiochemical Grignard
intermediate or a mixture of regiochemical Grignard
intermediates, and polymerising said Grignard intermediate by
adding a suitable catalyst.
2. Process according to claim 1, by
- a) dissolving the 3-substituted thiophene in a solvent or a
mixture of solvents,
- b) adding magnesium in an at least molar amount of the
thiophene to the solution, or adding the solution to said
magnesium, wherein said magnesium reacts with said
thiophene to form a regiochemical Grignard intermediate or a
mixture of regiochemical Grignard intermediates,
- c) optionally removing the unreacted magnesium from the
reaction mixture,
- d) adding a catalyst to the reaction mixture, or adding the
reaction mixture to a catalyst, and optionally agitating the
mixture, to form a polymer, and
- e) recovering the polymer from the mixture.
3. Process according to claim 1 or 2, characterized in that the
substituent in 3-position of the thiophene is an organic group
which when it is unsubstituted and unmodified straight chained
or branched alkyl has 5 or more C-atoms.

4. Process according to at least one of claims 1 to 3, characterized in that the 3-substituted thiophene is a 3-substituted 2,5-dibromo-thiophene.
- 5 5. Process according to at least one of claims 1 to 4, characterized in that the poly (3-substituted thiophene) has a regioregularity of $\geq 98 \%$.
- 10 6. Process according to at least one of claims 1 to 5, characterized in that the solvent is selected from diethyl ether, di-n-butyl ether, di-n-propyl ether, di-isopropyl ether, ethers with two different alkyl groups, 1,2-dimethoxyethane or t-butylmethyl ether, or mixtures thereof, or mixtures of toluene with one or more of the above ethers.
- 15 7. Process according to claim 6, characterized in that the solvent is diethyl ether.
- 20 8. Process according to at least one of claims 2 to 7, characterized in that the concentration of the thiophene in the solution in step a) is from 40 to 200 grams per litre.
- 25 9. Process according to at least one of claims 1 to 8, characterized in that the amount of the magnesium is from > 1 to 3 times the molar amount of the thiophene educt.
- 30 10. Process according to claim 9, characterized in that the amount of the magnesium is from 1.02 to 1.20 times the molar amount of the thiophene educt.
- 35 11. Process according to at least one of claims 1 to 10, characterized in that the unreacted magnesium is removed from the reaction mixture before adding the catalyst.
12. Process according to at least one of claims 1 to 11, characterized in that the catalyst is a Ni(II) catalyst.

13. Process according to claim 12, characterized in that the catalyst is selected from Ni(dppp)Cl₂ (1,3-diphenylphosphinopropane nickel(II) chloride) or Ni(dppe)Cl₂ (1,2-bis(diphenylphosphino)ethane nickel(II) chloride).
14. Process according to at least one of claims 1 to 13, characterized in that the formation of the regiochemical Grignard intermediate and the polymerisation (steps a) and d)) are carried out at a temperature from room temperature to reflux temperature.
15. Process according to claim 14, characterized in that the formation of the regiochemical Grignard intermediate and the polymerisation (steps a) and d)) are carried out at reflux temperature.
16. Process according to at least one of claims 1 to 15, characterized in that the polymer is purified after being recovered from the reaction mixture.
17. Process according to at least one of claims 1 to 16, characterized in that one or more of the terminal groups of the polymer are chemically modified ('endcapped').
18. Process according to at least one of claims 1 to 17, characterized in that the polymer is selected of formula I

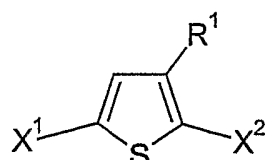


I

wherein n is an integer > 1 and R¹ is a group that does not react with magnesium under the conditions of the process according to any of the preceding or following claims.

19. Process according to at least one of claims 1 to 18, characterized in that the 3-substituted thiophene is selected of formula II

5



II

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wherein R^1 has the meaning of claim 18, and X^1 and X^2 are independently of each other Br or Cl.

15

20. Process according to claim 18 or 19, characterized in that R^1 is straight chain, branched or cyclic alkyl with 1 or more C-atoms, which may be unsubstituted, mono- or poly-substituted by F, Cl, Br, I or CN, it being also possible for one or more non-adjacent CH_2 groups to be replaced, in each case independently from one another, by $-O-$, $-S-$, $-NH-$, $-NR^0-$, $-SiR^0R^{00}-$, $-CO-$, $-COO-$, $-OCO-$, $-OCO-O-$, $-SO_2-$, $-S-CO-$, $-CO-S-$, $-CY^1=CY^2-$ or $-C\equiv C-$ in such a manner that O and/or S atoms are not linked directly to one another, optionally substituted aryl or heteroaryl, or P-Sp, with

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25

R^0 and R^{00} being independently of each other H or alkyl with 1 to 12 C-atoms,

Y^1 and Y^2 being independently of each other H, F, Cl or CN,

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P being a polymerisable or reactive group which is optionally protected, and

Sp being a spacer group or a single bond.

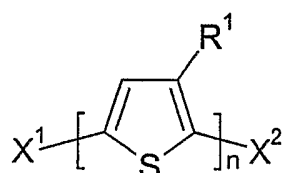
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21. Process according to claim 20, characterized in that R^1 is selected from C_1 - C_{20} -alkyl that is optionally substituted with one or more fluorine atoms, C_1 - C_{20} -alkenyl, C_1 - C_{20} -alkynyl, C_1 - C_{20} -

alkoxy, C₁-C₂₀-thioalkyl, C₁-C₂₀-silyl, C₁-C₂₀-ester, C₁-C₂₀-amino, C₁-C₂₀-fluoroalkyl.

- 5 22. Process according to claim 21, characterized in that R¹ is selected from straight-chain or branched pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl or dodecyl.
23. Process according to claim 22, characterized in that R¹ is n-hexyl.
- 10 24. Process according to at least one of claims 18 to 23, characterized in that X¹ and X² are Br.
25. Process according to at least one of claims 18 to 24, characterized in that n is an integer from 50 to 1,000.
- 15 26. Process according to at least one of claims 1 to 25, characterized in that the polymer is selected of formula I1

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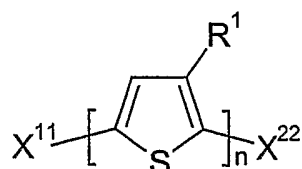
I1

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wherein n, R¹, X¹ and X² have the meanings of claims 18 to 24.

27. Process according to claim 17, characterized in that the polymer after endcapping is of formula I2

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I2

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wherein n and R¹ have the meanings of claims 18 to 24,

5 X^{11} and X^{22} are independently of each other H, halogen, $Sn(R^0)_3$ or straight chain, branched or cyclic alkyl with 1 to 20 C-atoms, which may be unsubstituted, mono- or poly-substituted by F, Cl, Br, I, -CN and/or -OH, it being also possible for one or more non-adjacent CH_2 groups to be replaced, in each case independently from one another, by -O-, -S-, -NH-, - NR^0 -, - SiR^0R^{00} -, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S-, - $CY^1=CY^2$ - or - $C\equiv C$ - in such a manner that O and/or S atoms are not linked directly to one another, optionally substituted aryl or heteroaryl, or P-Sp,

15 R^0 and R^{00} are independently of each other H or alkyl with 1 to 12 C-atoms, and

Y^1 and Y^2 are independently of each other H, F, Cl or CN.

20 28. Process according to claim 27, characterized in that X^{11} and X^{22} are independently of each other alkyl that is optionally substituted with one or more fluorine atoms, alkenyl, alkynyl, alkoxy, thioalkyl, silyl, ester, amino or fluoroalkyl, all of these groups being straight-chain or branched and having 1 to 20 C atoms, or optionally substituted aryl or heteroaryl, or P-Sp as defined in claim 20.

 29. Process according to claim 28, characterized in that X^{11} and X^{22} denote straight-chain or branched alkyl with 1 to 6 C atoms.

30 30. Process according to claim 27, characterized in that one or both of X^{11} and X^{22} denote a reactive group or a protected reactive group.

35 31. Process according to claim 30, characterized in that the polymer of formula I2 is further reacted via end group X^{11} and/or X^{22} with

the same or a different polymer of formula I2, or with another polymer, to form a block copolymer.

- 5 32. Polymer or copolymer obtained by a process according to at least one of claims 1 to 31.
- 10 33. Poly-3-substituted thiophene for use as semiconducting component in an electrical device, a field effect transistor, OLED, photovoltaic cell or sensor, wherein the terminal groups are chemically modified ('endcapped polymer').
34. Poly-3-substituted thiophene according to claim 33, characterized in that it is endcapped with H or alkyl groups.
- 15 35. Polymer according to claim 33 or 34, characterized in that it has improved oxidative stability and/or improved charge carrier properties.
- 20 36. Process of chemically modifying ('endcapping') the terminal group of a poly-3-substituted thiophene, during or after polymerisation, for use as semiconducting component in an electrical device, field effect transistor, OLED, photovoltaic cell or sensor.
- 25 37. Process of preparing a block copolymer from an endcapped polymer according to claim 33, wherein one or both of the endgroups have been modified into a reactive or protected reactive group, by reacting said polymer via one or both of said reactive or protected reactive groups with another monomer or polymer.
- 30 38. Use of a polymer according to at least one of claims 32 to 35 as semiconductor or charge transport material, in particular in optical, electrooptical or electronic devices, like for example in field effect transistors (FET) as components of integrated circuitry, as thin film transistors in flat panel display applications
- 35

- or for Radio Frequency Identification (RFID) tags, or in semiconducting components for organic light emitting diode (OLED) applications such as electroluminescent displays or backlights of e.g. liquid crystal displays (LCD), for photovoltaic or sensor devices, as electrode materials in batteries, as photoconductors, for electrophotographic applications like electrophotographic recording or for detecting and discriminating DNA sequences.
39. Use of a polymer according to at least one of claims 32 to 35 as electroluminescent material, in photovoltaic or sensor devices, as electrode materials in batteries, as photoconductors, for electrophotographic applications or electrophotographic recording.
40. Semiconductor or charge transport material, component or device comprising one or more polymers according to at least one of claims 32 to 35.
41. Optical, electrooptical or electronic device, FET, integrated circuit (IC), TFT or OLED comprising a semiconducting or charge transport material, component or device according to claim 40.
42. TFT or TFT array for flat panel displays, radio frequency identification (RFID) tag, electroluminescent display or backlight comprising a semiconducting or charge transport material, component or device or a FET, IC, TFT or OLED according to claim 40 or 41.
43. Security marking or device comprising a FET or an RFID tag according to claim 42.
44. Polymer according to at least one of claims 32 to 35 which is oxidatively or reductively doped to form conducting ionic species.

45. Charge injection layer, planarising layer, antistatic film or conducting substrate or pattern for electronic applications or flat panel displays, comprising a polymer according to claim 44.

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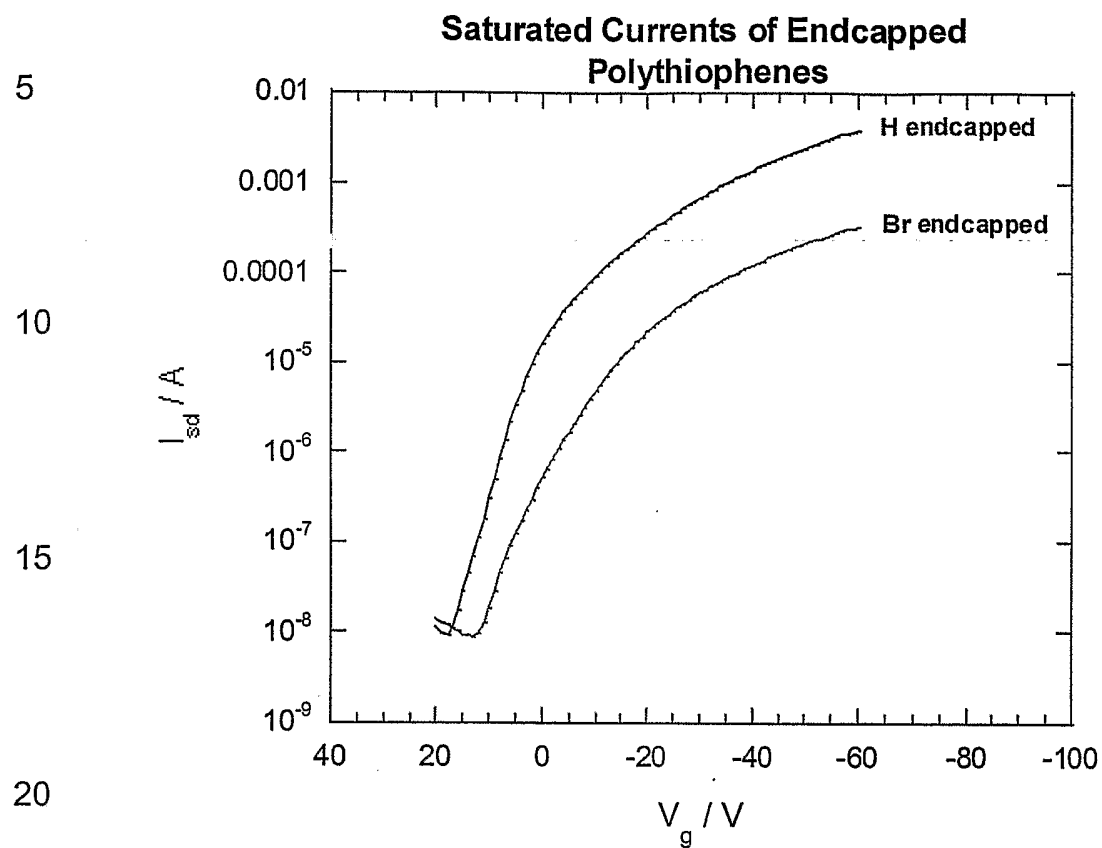


Figure 1

Br Endcapped

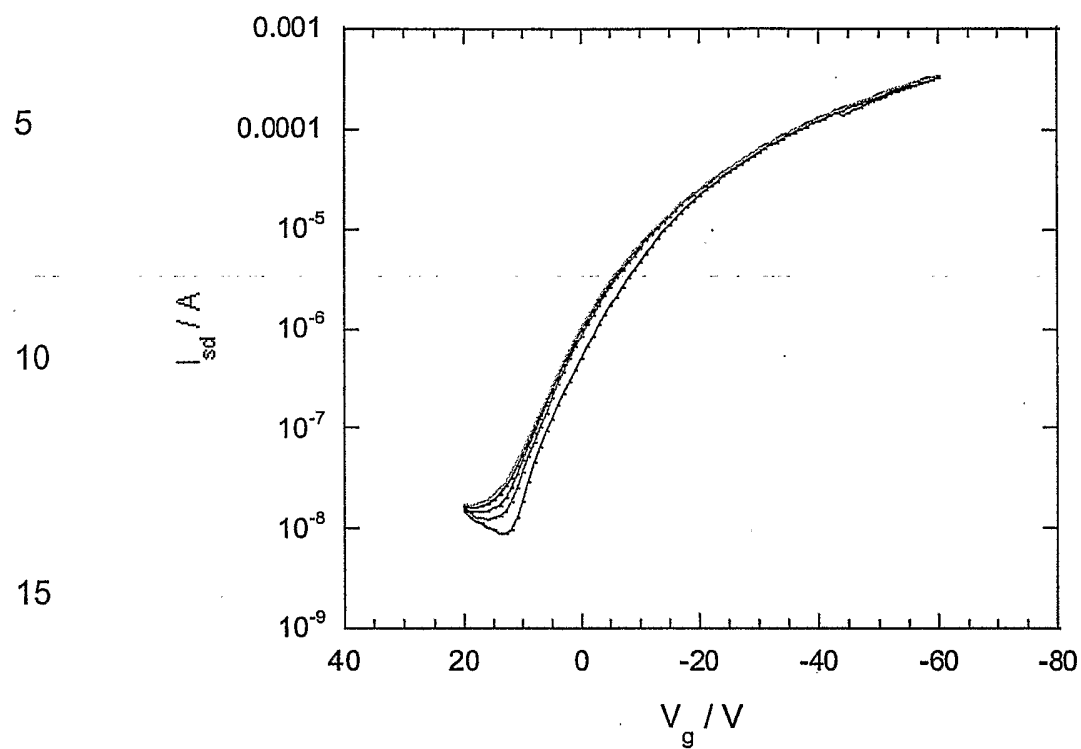


Figure 2A

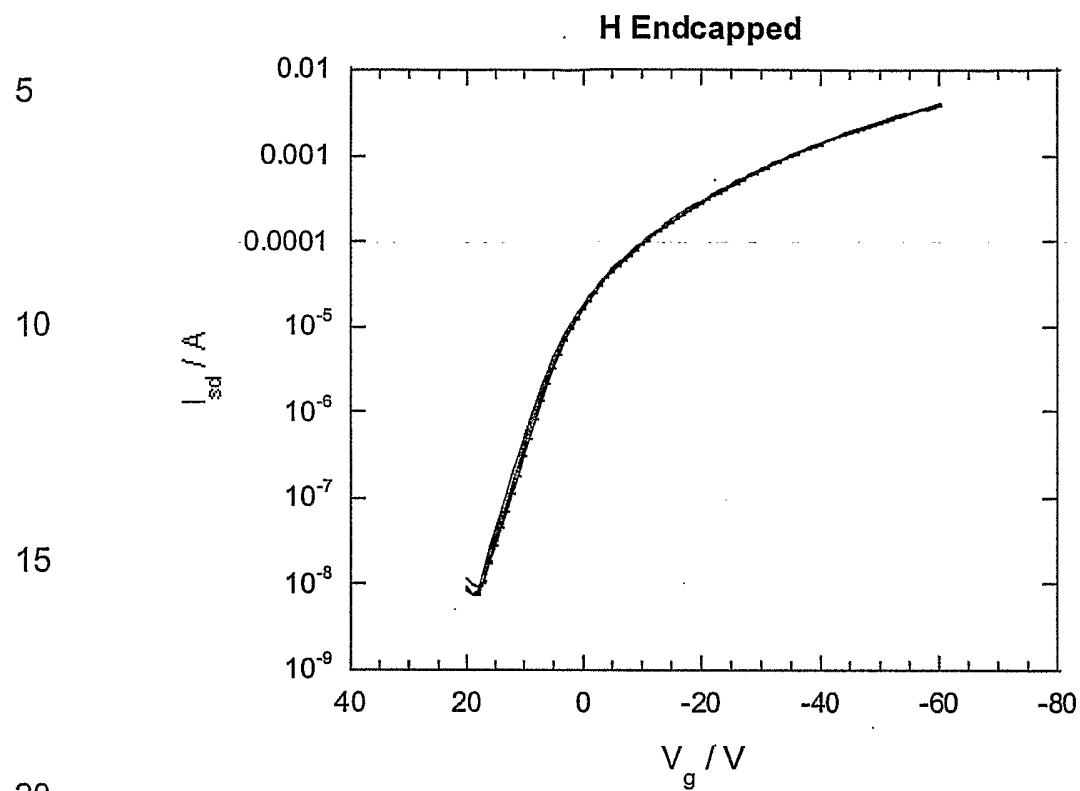


Figure 2B

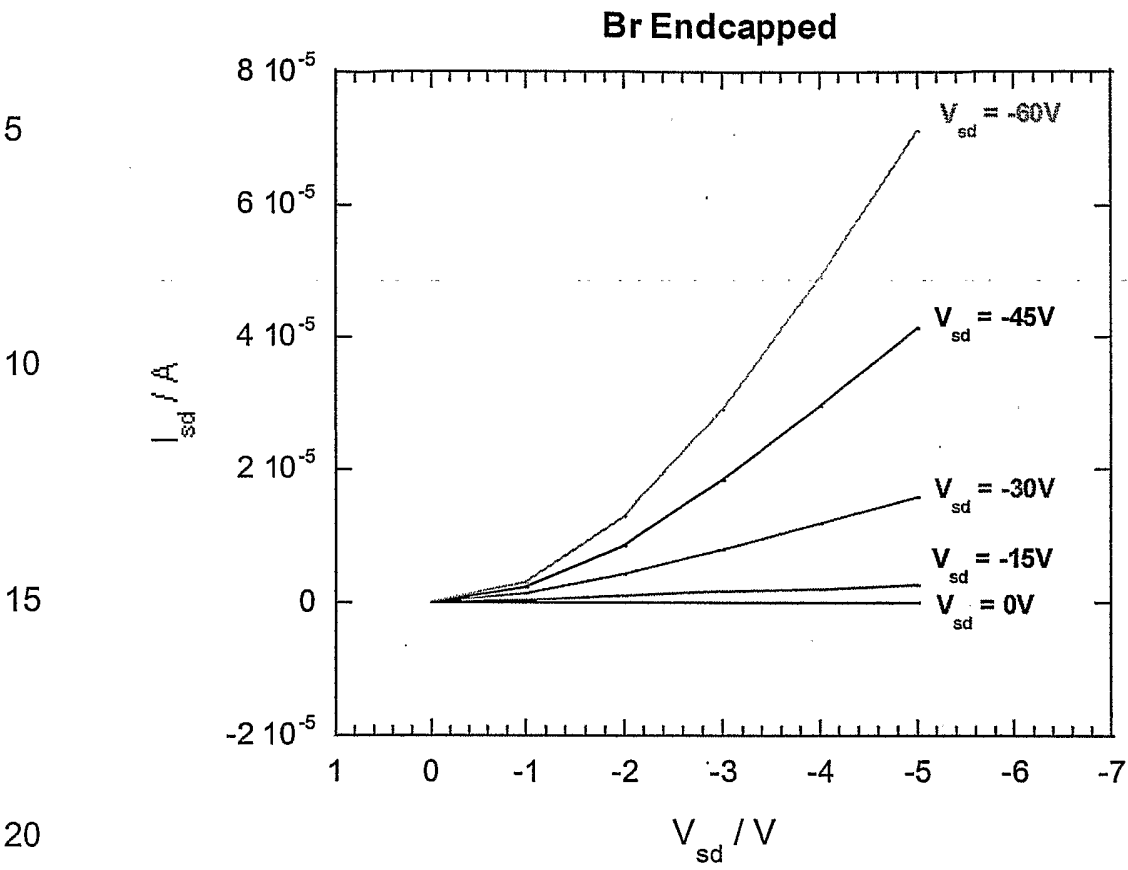


Figure 3A

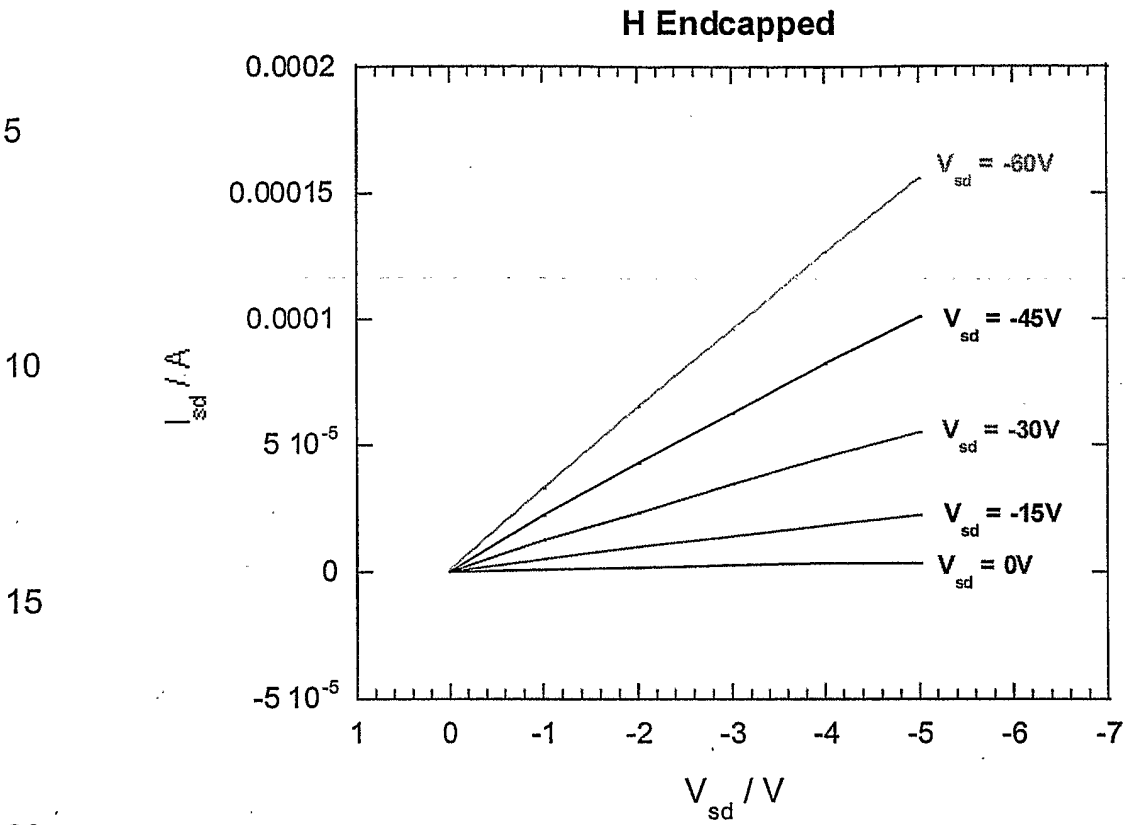


Figure 3B