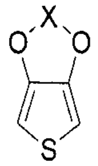
ABSTRACT

New aqueous dispersible polymers of 3,4-alkylenedioxythiophene. Also a process for the preparation of the polymers. The process comprises polymerizing at least one monomer comprising 2,5-dihalo derivative of 3,4-alkylenedioxythiophene with at least one monomer comprising derivative of the formula

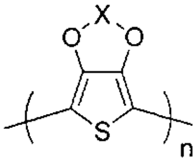


in 1:1 molar ratio in an organic solvent in the presence of palladium (II) compound catalyst in a concentration of 0.01 to 20 mol % of the monomers at 60°C to the boiling point of the solvent. The polymers are purified by precipitating with an organic solvent and the precipitate is dried to obtain the polymers as powder.

12 OCT 2010

We claim

1. New aqueous dispersible polymers of 3,4-alkylenedioxythiophene of the formula IV:

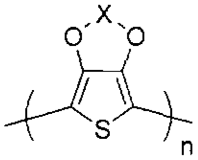


Formula IV

wherein X represents $-CH_2CH_2-$ or $CH_2C(RR')CH_2-$, wherein R represents a $-CH_2-O-(CH_2)_A-B$, wherein A represents 0 to 10 and B represents a hydrogen or a C_1-C_5 linear or branched alkyl or aryl group optionally substituted by one or more groups selected from amines, carboxylic acids, alcohols, ethers, sulfonic acids, thiols or amides; R' represents R as defined above or hydrogen or C_1-C_3 linear or branched alkyl group or aryl group optionally substituted by one or more groups selected from aryl, propargyl or azide and n is the number of recurring or repeating polymer units.

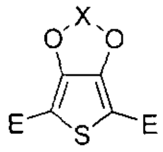
2. The polymers 3,4-alkylenedioxythiophene as claimed in claim 1, in powder form.

3. A process for the preparation of aqueous dispersible polymers of 3,4-alkylenedioxythiophene of the formula IV:



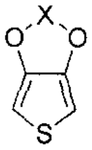
Formula IV

wherein X represents $-CH_2CH_2-$ or $CH_2C(RR')CH_2-$, wherein R represents a $-CH_2-O-(CH_2)_A-B$, wherein A represents 0 to 10 and B represents a hydrogen or a C_1-C_5 linear or branched alkyl or aryl group optionally substituted by one or more groups selected from amines, carboxylic acids, alcohols, ethers, sulfonic acids, thiols or amides; R' represents R as defined above or hydrogen or C_1-C_3 linear or branched alkyl group or aryl group optionally substituted by one or more groups selected from aryl, propargyl or azide and n is the number of recurring or repeating polymer units, which process comprises polymerizing at least one monomer comprising 2,5-dihalo derivative of 3,4-alkylenedioxythiophene of the formula V



Formula V

wherein E represents Cl, Br or I and X is as defined above with at least one monomer comprising derivative of the formula VI



Formula VI

wherein X is as defined above in 1:1 molar ratio in an organic solvent in the presence of palladium (II) compound catalyst in a concentration of 0.01 to 20 mol % of the monomers at 60°C to the boiling point of the solvent and purifying the polymers by precipitating with an organic solvent and drying the precipitate to obtain the polymers as powder.

4. The process as claimed in claim 3, wherein the palladium (II) compound catalyst is selected from salts of palladium (II) compounds and is preferably palladium acetate.

5. The process as claimed in claim 3 or 4, wherein the concentration of the catalyst is 1 mol % of the monomers.

6. The process as claimed in any one of claims 3 to 5, wherein the organic solvent is selected from dimethylformamide (DMF), dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF), toluene or haloromatics selected from chlorobenzene or dichlorobenzene and is preferably dimethylformamide (DMF).

7. The process as claimed in any one of claims 3 to 6, wherein the polymerization is carried out at 70°C.

8. The process as claimed in any one of claims 3 to 7, wherein the polymer is precipitated with an organic solvent selected from alcohols, ketones, haloalkanes or alkanes, preferably methanol.

9. The process as claimed in any one of claims 3 to 8, wherein the precipitate is dried in vacuum at room temperature.

Dated this 11th day of October 2010.

Indian Institute of Technology, Bombay
By their Agent & Attorney

(Jose M A)
of Khaitan & Co
Reg No IN/PA-44

FIELD OF THE INVENTION

This invention relates to aqueous dispersible polymers of 3,4-alkylenedioxythiophene and process for the preparation thereof.

The term polymers as used in the specification in relation to 3, 4-alkylenedioxythiophene in the context of the invention includes oligomers and copolymers thereof.

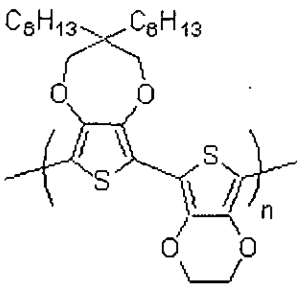
BACKGROUND OF THE INVENTION

Polymers of 3,4-alkylenedioxythiophene exhibit excellent chemical and thermal stability in their reduced and oxidized forms. They also exhibit high conductivity and are transparent in their conducting form. Because of the above properties, polymers of 3,4-alkylene dioxythiophene are used for various applications in diverse fields. For instance, they are used in display devices, photovoltaics, electrochromic devices, chemical and biological sensors, antistatic, transparent or conducting coatings, conducting paints or adhesives or as hole transparent layer in thin film devices like LEDs [Electrochemistry of Poly(3,4-alkylenedioxythiophene) derivatives, Groenendaal,L.; Zotti,Gianni; Aubert,Pierre Henri; Waybright,Shane M.; Reynolds,John R; Advanced Materials, 15,11,2003, pp 855-879].

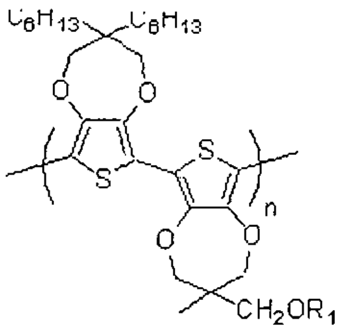
Polymers of 3,4-alkylenedioxythiophenes are prepared by polymerizing the 3,4-alkylenedioxythiophene monomers oxidatively using oxidizing agents like ferric salt such as ferric chloride or tosylate or sodium peroxydisulphate or reductively using Grignard Metathesis Polymerization or Palladium(II) compounds catalyzed coupling reaction [Spray Coatable Electrochromic Dioxythiophene Polymers with High Coloration Efficiencies, Reeves,B.D.; Grenier,C.R.G.; Argun,A.A.; Cirpan,A.; McCarley,T.D.; Reynolds,J.R.; Macromolecules, 37, 20, pp 7559-7569; Single Step Reductive Polymerization of Functional 3,4-Propylenedioxythiophenes via Direct C-H Arylation Catalyzed by Palladium Acetate, Anshu Kumar, Anil Kumar, Polymer Chemistry, 2010, 1, 286-288]. In case ferric salt is used in the oxidative polymerisation, the polymers will contain iron impurity and this may not be acceptable in some applications, in which case the iron impurity will have to be removed by ion exchange treatment.

Reductive polymerization generally gives polymers with improved material properties and hence is the preferred method for polymerization. However, Grignard Metathesis reductive polymerization requires extremely dry solvents like tetrahydrofuran and drastic reaction conditions. Therefore, it is uneconomical and cumbersome to carry out. Palladium (II) compounds catalysed coupling polymerisation is carried out in organic solvents under normal conditions. Further the palladium (II) compounds catalysed coupling polymerisation gives polymers with functional groups which play a very important role in tailoring or adapting the properties of the polymers to suit various applications. Therefore, within the reductive polymerisation, palladium (II) compounds catalysed coupling is preferred as it is versatile, easy and convenient to carry out and economical.

Organic soluble polymers of 3,4-alkylenedioxythiophenes of the formulae I and II:



Formula I

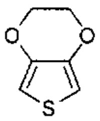


Formula II

wherein R_1 is H, CH_2CH_2CN, CH_2COOEt, $C_6H_{12}Br$ or $C_6H_{12}N_3$ and n is the number of repeating or recurring units of the polymer are prepared by palladium (II) compounds catalysed polymerization. [Single Step Reductive Polymerization of Functional 3,4-Propylenedioxythiophenes via Direct C-H Arylation Catalyzed by Palladium Acetate, Anshu Kumar, Anil Kumar, Polymer Chemistry, 2010, 1, 286-288].

Many of the important applications or uses of the polymers of 3,4-alkylenedioxythiophene are in their conducting form. In order to make effective use of the polymers for variouos applications it is, therefore, essential that the polymers are dispersible in solvents in their conducting state. The conducting forms of the polymers of 3,4-alkylenedioxythiophene are generally insoluble in non-polar organic solvents. In order to make formulations of conducting forms of the above polymers, highly polar organic solvents are required. As a result, the choice of the solvents is limited and the potential use or versatility of use of the polymers is limited. Use of organic solvents for dissolution of the polymers also increases the cost. Further the formulations are monomer specific in that each formulation is formulated starting with a specific monomer. The monomers are few and therefore the number of polymers that can be made are also limited thereby limiting the number of applications of the polymers.

Aqueous dispersions of the polymers of 3,4-ethylenedioxythiophene of the formula III

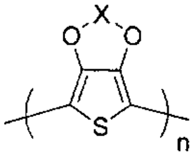


Formula III

are prepared by in situ oxidative polymerization of the monomer in the presence of anionic surfactant. A commonly used oxidising agent is a combination of sodium peroxydisulphate and ferric salt like ferric chloride. A commonly used anionic surfactant is electrolyte like polyanionic polystyrene sulfonate (PSS) sodium salt. Such dispersions are available under the trade name "CLEVIOS" (www.clevios.com). Oxidative polymerisation has the disadvantage as stated earlier. Use of surfactant like PSS sodium salt in the polymerisation reaction gives rise to acid formulation which may not be acceptable in some applications of the polymeric formulations.

DETAILED DESCRIPTION OF THE INVENTION

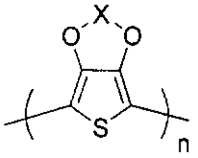
According to the invention there is provided new aqueous dispersible polymers of 3,4-alkylenedioxythiophene of the formula IV:



Formula IV

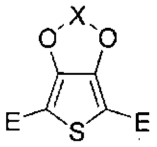
wherein X represents $–CH_2CH_2–$ or $CH_2C(RR')CH_2–$, wherein R represents a $-CH_2-O-(CH_2)_A-B$, wherein A represents 0 to 10 and B represents a hydrogen or a C_1-C_5 linear or branched alkyl or aryl group optionally substituted by one or more groups selected from amines, carboxylic acids, alcohols, ethers, sulfonic acids, thiols or amides; R' represents R as defined above or hydrogen or C_1-C_3 linear or branched alkyl group or aryl group optionally substituted by one or more groups selected from aryl, propargyl or azide and n is the number of recurring or repeating polymer units.

According to the invention there is also provided a process for the preparation of aqueous *dispersible polymers of 3, 4-alkylenedioxythiophene of the formula IV:*



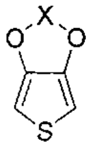
Formula IV

wherein X represents $–CH_2CH_2–$ *or* $CH_2C(RR')CH_2–$, *wherein* R *represents a* $-CH_2-O-(CH_2)_A-B$, wherein A represents 0 to 10 and B represents a hydrogen or a C_1-C_5 linear or branched alkyl or aryl group optionally substituted by one or more groups selected from amines, carboxylic acids, alcohols, ethers, sulfonic acids, thiols or amides; R' represents R as defined above or hydrogen or C_1-C_3 linear or branched alkyl group or aryl group optionally substituted by one or more groups selected from aryl, propargyl or azide and n is the number of recurring or repeating polymer units, which process comprises polymerizing at least one monomer comprising 2,5-dihalo derivative of 3,4-alkylenedioxythiophene of the formula V



Formula V

wherein E represents Cl, Br or I and X is as defined above with at least one monomer comprising derivative of the formula VI



Formula VI

wherein X is as defined above in 1:1 molar ratio in an organic solvent in the presence of palladium(II) compound catalyst in a concentration of 0.01 to 20 mol % mole of the monomers at 60°C to the boiling point of the solvent and purifying the polymers by precipitating with an organic solvent and drying the precipitate to obtain the polymers as powder.

The palladium (II) compound catalyst is selected from salts of palladium (II) compounds and is preferably palladium acetate and the concentration of the catalyst is preferably 1 mol % of the monomers. The organic solvent used for polymerization is selected from dimethylformamide (DMF), dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF), toluene or haloromatics selected from mono or dichlorobenzene and is preferably dimethylformamide (DMF). The polymerization is preferably carried out at 70°C. The organic solvent used for precipitating the polymer is selected from alcohols, ketones, haloalkanes or alkanes and is preferably methanol. The number of recurring units 'n' of the polymers is selected depending on the end use of the polymers by controlling the reaction rate in known manner.

According to the invention there is provided new water dispersible polymers 3,4-alkylenedioxythiophene which can be used for various applications in diverse fields as such or as aqueous formulation as described in our Indian Patent Application No ______________. Because of the dispersability of the polymers in water, it is easy and economical to handle them and make formulations thereof. Further, the potential use or versatility of areas of use of the polymers is increased. The polymers of the invention have a variety of uses, for example, they may be used in display devices, photovoltaics, electrochromic devices, chemical and biological sensors, antistatic, transparent or conducting coatings, conducting paints or conducting adhesives or as hole transport layer in thin film devices like LEDs.

According to the invention there is also provided a process for the preparation of the polymers which is easy and convenient to carry out and is economical as it does not require dry solvents and drastic reaction conditions. It is also versatile as the polymers obtained by the process have several functional groups which can be manipulated to control the properties of the polymers to suit various applications.

The following experimental examples are illustrative of the invention but not limitative of the scope thereof :

Example 1

1 mmol of 2,5-dibromo-3,4-ethylenedioxythiophene was stirred with 1 mmol of ProDOT-OH [3-methyl-3,4-dihydro-2H-thieno(3,4-b)(1,4)dioxepin-3-yl)-methanol] in 5 ml of DMF in the presence of 1 mol % of palladium acetate at 70 °C for 24 hrs. The resulting reaction mixture was poured in methanol to precipitate the polymeric powder. The polymeric powder was purified by washing with methanol and dried in a vacuum oven at room temperature to get dark solid powder.

Example 2

1 mmol of 2,5-dibromo-3,4-propylenedioxythiophene was stirred with 1 mmol of ProDOT-OH in 5 ml of DMF in the presence of 1 mol % of palladium acetate at 70 °C for 24 hrs. The resulting reaction mixture was processed as described in Example 1 to get dark solid powder.

Example 3

*1 mmol of 2,5-dibromo-*ProDOT-OH *was stirred with 1 mmol of* ProDOT-OH *in 5 ml of* DMF in the presence of 1 mol % of palladium acetate at 70 °C for 24 hrs. The resulting reaction mixture was processed as described in Example 1 to get dark solid powder.

Example 4

1 mmol of 2,5-dibromo-3,4-ethylenedioxythiophene was stirred with 1 mmol of ProDOT-Sultone [sulfuric acid mono-[3-(3-methyl-3,4-dihydro-2H-thieno(3,4-b)(1,4)dioxepin-3-ylmethoxy)-propyl] ester in 5 ml of DMF in the presence of 1 mol % of palladium acetate at 70

°C for 24 hrs. The resulting reaction mixture was processed as described in Example 1 to get dark solid powder.

Example 5

1 mmol of 2,5-dibromo-3,4-propylenedioxythiophene was stirred with 1 mmol of ProDOT-Sultone in 5 ml of DMF in the presence of 1 mol % of palladium acetate at 70 °C for 24 hrs. The resulting reaction mixture was processed as described in Example 1 to get dark solid powder.

Example 6

1 mmol of 2,5-dibromo-3,4-propylenedioxythiophene-dimethyl was stirred with 1 mmol of ProDOT-OH in 5 ml of DMF in the presence of 1 mol % of palladium acetate at 70 °C for 24 hrs. The resulting reaction mixture was processed as described in Example 1 to get dark solid powder.

Example 7

1 mmol of 2,5-dibromo-3,4-propylenedioxythiophene-dimethyl and 1 mmol of 2,5-dibromo-3,4-ethylenedioxythiophene were stirred with 2 mmol of ProDOT-OH in 7 ml of DMF in the presence of 1 mol % of palladium acetate at 70 °C for 24 hrs. The resulting reaction mixture was processed as described in Example 1 to get dark solid powder.

Example 8

1 mmol of 6,8-Dibromo-3-methyl-3-prop-2-ynyloxymethyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine was stirred with 1 mmol of ProDOT-OH in 5 ml of DMF in the presence of 1

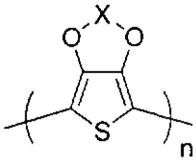
mol % of palladium acetate at 70 °C for 24 hrs. The resulting reaction mixture was processed as described in Example 1 to get dark solid powder.

Example 9

1 mmol of 2,5-dibromo-3,4-propylenedioxythiophene-dimethyl and 1 mmol of 2,5-dibromo-3,4-propylenedioxythiophene were stirred with 2 mmol of ProDOT-OH in 7 ml of DMF in the presence of 1 mol % of palladium acetate at 70 °C for 24 hrs. The resulting reaction mixture was processed as described in Example 1 to get dark solid powder.

We claim

1. New aqueous dispersible polymers of 3,4-alkylenedioxythiophene of the formula IV:

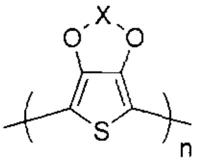


Formula IV

wherein X represents $-CH_2CH_2-$ or $CH_2C(RR')CH_2-$, wherein R represents a $-CH_2-O-(CH_2)_A-B$, wherein A represents 0 to 10 and B represents a hydrogen or a C_1-C_5 linear or branched alkyl or aryl group optionally substituted by one or more groups selected from amines, carboxylic acids, alcohols, ethers, sulfonic acids, thiols or amides; R' represents R as defined above or hydrogen or C_1-C_3 linear or branched alkyl group or aryl group optionally substituted by one or more groups selected from aryl, propargyl or azide and n is the number of recurring or repeating polymer units.

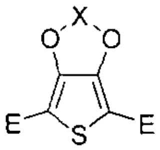
2. The polymers 3,4-alkylenedioxythiophene as claimed in claim 1, in powder form.

3. A process for the preparation of aqueous dispersible polymers of 3,4-alkylenedioxythiophene of the formula IV:



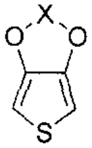
Formula IV

wherein X represents $-CH_2CH_2-$ or $CH_2C(RR')CH_2-$, wherein R represents a $-CH_2-O-(CH_2)_A-B$, wherein A represents 0 to 10 and B represents a hydrogen or a C_1-C_5 linear or branched alkyl or aryl group optionally substituted by one or more groups selected from amines, carboxylic acids, alcohols, ethers, sulfonic acids, thiols or amides; R' represents R as defined above or hydrogen or C_1-C_3 linear or branched alkyl group or aryl group optionally substituted by one or more groups selected from aryl, propargyl or azide and n is the number of recurring or repeating polymer units, which process comprises polymerizing at least one monomer comprising 2,5-dihalo derivative of 3,4-alkylenedioxythiophene of the formula V



Formula V

wherein E represents Cl, Br or I and X is as defined above with at least one monomer comprising derivative of the formula VI



Formula VI

wherein X is as defined above in 1:1 molar ratio in an organic solvent in the presence of palladium (II) compound catalyst in a concentration of 0.01 to 20 mol % of the monomers at 60°C to the boiling point of the solvent and purifying the polymers by precipitating with an organic solvent and drying the precipitate to obtain the polymers as powder.

4. The process as claimed in claim 3, wherein the palladium (II) compound catalyst is selected from salts of palladium (II) compounds and is preferably palladium acetate.

5. The process as claimed in claim 3 or 4, wherein the concentration of the catalyst is 1 mol % of the monomers.

6. The process as claimed in any one of claims 3 to 5, wherein the organic solvent is selected from dimethylformamide (DMF), dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF), toluene or haloromatics selected from chlorobenzene or dichlorobenzene and is preferably dimethylformamide (DMF).

7. The process as claimed in any one of claims 3 to 6, wherein the polymerization is carried out at 70°C.

8. The process as claimed in any one of claims 3 to 7, wherein the polymer is precipitated with an organic solvent selected from alcohols, ketones, haloalkanes or alkanes, preferably methanol.

9. The process as claimed in any one of claims 3 to 8, wherein the precipitate is dried in vacuum at room temperature.

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