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Electrically conductive alternating copolymer and method of preparing such a copolymer.

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The invention relates to a new group of intrinsically electrically conductive alternating copolymers.

The invention also relates to a method of preparing such polymers.

The invention further relates to the application of such copolymers.

Organic polymers are generally electrical insulators and therefore they are used as insulating material in electrical and electronic components. It is known that the polymer obtains electrically conductive properties if it contains a poly-conjugated bond system of, for example, double bonds, triple bonds, aromatic or hetero-aromatic rings. Said conductivity is termed intrinsic conductivity. Examples of such polymers are polyacetylene, polythiophene and polypyrrole. In general, the conductivity of these polymers is low because these polymers are semiconductors having a relatively large band gap of 1.5-4 eV. The conductivity can be increased by (electro)chemically oxidizing or reducing the polymer. Said oxidation or reduction treatment is termed doping. By oxidation p-type conductors are formed; by reduction n-type conductors are formed. In the oxidation or reduction treatment, charge carriers are formed on the polymer chains, which charges are compensated for by oppositely charged counterions. The expression "alternating copolymer" is to be understood to mean a polymer which is composed of two different monomers which are alternately incorporated in the polymer chain. In general, polymers are cheap and can be readily processed, so that it is attractive to use conductive polymers in conductive and semiconductive structures in (integrated) electronic circuits, electrodes for batteries, antistatic coatings and electromagnetic protective layers.

A conductive alternating copolymer is known from an article by J. Kowalik et al., Synthetic Metals, 41-43 (1991) 435-438. In said article, a description is given of a semiconductive alternating copolymer on the basis of benzoquinone and pyrrole which are reacted to form poly(2-pyrrolyl-1,4-benzoquinone). The polymer obtained is p-type semiconductive and "disordered" and is produced by oxidative



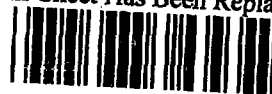
polymerization of pyrrole and benzoquinone. The band gap of the polymer formed is not mentioned in said article.

A disadvantage of the known method is the presence of an oxidizing agent, namely p-chloranil, during the polymerization reaction, which causes the polymer obtained to be doped and p-type conductive. It is impossible or very difficult to obtain the undoped, *i.e.* intrinsically conductive polymer, from said polymer. A further disadvantage is the "disordered" polymer structure which adversely affects the conductivity.

It is an object of the invention to provide, *inter alia*, a new group of electrically (semi)conductive alternating copolymers which have a band gap of maximally 1.5 eV and which can be obtained by means of a simple condensation polymerization (polycondensation) process which, in addition, initially yields an undoped copolymer.

A further object of the invention is to provide a method of preparing such copolymers without using an oxidizing agent.

According to the invention, this object is achieved by an alternating copolymer which is characterized in that the (semi)conductive copolymer can be obtained by reacting an acceptor monomer unit A having an unsaturated ring structure which is substituted with at least two double-bonded oxygen atoms and at least one hydroxy group, with a donor monomer unit D formed by a homo or heterocyclic aromatic compound comprising at least two active hydrogen atoms, a polycondensation reaction taking place in the presence of a solvent, thereby forming said alternating (semi)conductive copolymer. The term "acceptor" is to be understood to mean a unit which is capable of accepting a negative charge, and the term "donor" is to be understood to mean a unit which is capable of donating a negative charge. In this connection, the expression "active hydrogen atom" is to be understood to mean a hydrogen atom which can be readily separated from the monomer during the polycondensation reaction. Examples of donor monomer units D comprising at least two active hydrogen atoms are given below. By virtue of the polycondensation reaction a strictly alternating and ordered structure of acceptors and donors ...ADADADA... is obtained, the choice of the monomer units A and D resulting in the formation of a poly-conjugated bond system. The polymers obtained have a small to very small band gap, which leads to a substantial increase of the intrinsic conductivity. Said intrinsic



conductivity, *i.e.* conductivity obtained without doping, is obtained at room temperature.

Suitable acceptor monomer units A are squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione; see formula I of Fig. 1), croconic acid (4,5-dihydroxy-4-cyclopentene-1,2,3-trione; see formula II of Fig. 1) and 5,6-dihydroxy-5-cyclohexene-1,2,3,4-tetraone (see formula III of Fig. 1).

Suitable donor monomer units D are compounds having (5-6-5) or (6-6-6) heterocyclic ring systems which are, for example, used in dye chemistry. A few examples thereof can be found in J. Fabian et al., "Light Absorption of Organic Colorants", Springer Verlag, Berlin, 1980, page 189. In said publication, these compounds are used to prepare biscyanine dyes. The general class of said suitable donor monomers D is shown in formulae IVA and IVB and VA, VB and VC in Fig. 2. In said Figure, X_1 represents an -NR- group; X_2 represents an O-, S- or Se atom or an -NR-, -CR=CH-, -CHR-CH₂- or -C(alkyl)₂-group and X_3 represents a -CR= or -N= group. In said Figure, X_1 may also represent an S- or O-atom, where X_2 represents an S-atom or a -CR=CH- group and X_3 has the above-mentioned meaning. R represents an H-atom or an alkyl or alkoxy substituent having 1-18 C-atoms. These compounds have an extensive, conjugated structure and two active hydrogen atoms which react, during the polycondensation reaction, with the OH groups of the acceptor monomer units, such as squaric acid. A few special examples are shown in formulae VI and VII of Fig. 3.

The substituents R_1 and R_2 of the benzodihydropyrrole in accordance with formula VI of Fig. 3 denote a C₁-C₁₈ alkyl group such as a methyl, butyl, or octadecyl group. The substituents R_3 and R_4 of the benzodithiazole in accordance with formula VII of Fig. 3 also denote a C₁-C₁₈ alkyl group such as a methyl, n-heptyl, n-dodecyl or n-octadecyl group. By virtue of the choice of the substituents R, those skilled in the art can widely vary the properties of the final copolymer, such as solubility, processibility and conductivity. A special example of a compound in accordance with formula VC of Fig. 2 is neocuproine (formula VIII of Fig. 3).

Another suitable donor monomer D is azulene (an aromatic 5-7 ring) which may or may not be substituted with, for example, an alkyl group.

Other suitable donor monomers D are thiophene oligomers such as bithienyl and terthienyl (formula IX of Fig. 3). The thiophene ring may be substituted with a group R_5 , which is a C₁-C₁₈ alkyl group or a C₁-C₁₈ alkoxy group.



Another class of suitable donor monomers D is that of the aromatic diamines. The general formula is shown in formula X of Fig. 4. In said formula, A denotes an aromatic core and R_6 and R_7 denote an H-atom or a C_1 - C_{18} alkyl group. A few examples of the aromatic core A are shown in formulae XI, XII, XIII and XIV of Fig. 4. In said formulae R_8 and R_9 represent an H-atom or a C_1 - C_{18} alkyl group; X_1 represents a $-N=$ or $-CR=$ group and X_2 and X_3 represent an $-NH-$ or an $-N(alkyl)-$ group or an S-, Se- or O-atom. The alkyl group contains 1-18 carbon atoms. R represents an H-atom or an alkyl or alkoxy substituent containing 1-18 carbon atoms. Representatives thereof are, for example, p-phenylene diamine, 3,6-diamino acridine (formula XV of Fig. 4) and thionine (formula XVI of Fig. 4). The polycondensation product of diamines and, for example, squaric acid surprisingly gives an electrically conductive polymer; after all, the polymer formed is a polyamide which, as a class, is known as an insulator.

An example of an alternating copolymer in accordance with the invention is the polycondensation product of squaric acid (formula I of Fig. 1) and the compound in accordance with formula VI of Fig. 3, where R_1 and R_2 represent an n-octadecyl group ($n-C_{18}H_{37}$). The polymer formed has formula XVII of Fig. 5 as the repeating unit. The squaric acid unit is negatively charged and serves as the charge acceptor. The benzo(1,2,4,5)bis(N-octadecyl-2-methyl-3-bis-methyldihydropyrrole) unit is positively charged and serves as the charge donor. The alternating sequence of donor units and acceptor units in combination with an extensive conjugated system gives an intrinsically conductive "self-doped" polymer. The conductivity of the polymer in accordance with formula XVII of Fig. 5 is $3 \cdot 10^5$ S/cm at room temperature and the band gap is 1.0 eV. The polymer can be readily dissolved in various solvents, such as chlorobenzene. Instead of octadecyl groups, other alkyl groups, such as the methyl, n-heptyl and n-dodecyl group, can be chosen for R_1 and R_2 . In general, the solubility of the polymer in solvents increases as the length of the alkyl groups increases.

Another example of an alternating copolymer in accordance with the invention is the polycondensation product of croconic acid (formula II of Fig. 1) and the compound in accordance with formula VII of Fig. 3, where R_3 and R_4 represent a methyl group. The polymer formed has formula XVIII of Fig. 5 as the repetitive unit. The croconic acid unit is negatively charged and serves as the charge acceptor. The benzo(1,2,4,5)bis(N-methyl-2-methylthiazole) unit is positively charged and serves as



the charge donor. This "self-doped" polymer in accordance with formula XVIII of Fig. 5 has a conductivity of 10^{-5} S/cm at room temperature and of $2.5 \cdot 10^{-3}$ S/cm at 250°C . The band gap of this polymer is 0.5 eV and, hence, this polymer has semiconductive properties. Instead of methyl groups, other alkyl groups such as the n-heptyl-, the n-dodecyl- and the n-octadecyl group can be chosen for R_3 and R_4 .

In accordance with the invention, squaric acid, croconic acid and 5,6-dihydroxy-5-cyclohexene-1,2,3,4-tetraon (formula III of Fig. 1) can also be copolymerized using neocuproine (formula VIII of Fig. 3), terthienyl (formula IX of Fig. 3) and 3,6 diamino acridine (formula XV of Fig. 4). Also in this case polycondensation leads to the formation of electrically conductive alternating copolymers, the compounds in accordance with formulae VIII, IX and XV serving as the donor unit in the polymer chains.

The object of providing a method of preparing an alternating copolymer is achieved in accordance with the invention by a method which is characterized in that equimolar quantities of bifunctional acceptor monomer units A and bifunctional donor monomer units D are mixed in a solvent and polymerized by polycondensation, thereby forming the alternating copolymer comprising repeating unit AD. As the acceptor monomer unit A a compound having an unsaturated ring structure is used which is substituted with at least two double-bonded oxygen atoms and at least one hydroxy group. As the donor monomer unit D a homo or heterocyclic aromatic compound having at least two active hydrogen atoms is used. Examples of the monomer units A and D have been mentioned above. The polycondensation reaction is carried out in a suitable solvent such as propanol, butanol, toluene or dimethyl sulfoxide.

In general, the alternating copolymers manufactured in accordance with the above method exhibit great thermal stability. In most of said copolymers no change can be observed after heating to 300°C in air. Consequently, the sensitivity to oxygen is very small.

The conductivity of the alternating copolymers in accordance with the invention can be increased by means of dopants which are known *per se*. Dopants which are suitable for obtaining p-type conduction are, for example, I_2 , AsF_5 , SbF_5 , HBF_4 , perchlorate, sulphonate, SO_3 and FeCl_3 . With certain copolymers p-doping causes the absorption band to pass to the infrared portion of the spectrum. As a result, said copolymers become colourless. As semiconductive polymers are available, circuits

can be manufactured which can be used in electronic devices. Also conductor tracks can be manufactured from the alternating copolymer in accordance with the invention and form an alternative to metal conductor tracks.

5 The alternating copolymers in accordance with the invention can also be used in antistatic layers or electromagnetic protective layers by dissolving the copolymer in question in a suitable solvent and, subsequently, providing it on the desired substrate by means of, for example, spin coating.

It is noted that in German Patent Application DE-A-3246319, a description is given of the preparation of a copolymer of pyrrole and squaric acid by anodic oxidation of a solution of said compounds in the presence of a conducting salt. The polymer obtained is p-doped and also contains the anion of the conducting salt as the counterion. By anodic oxidation, squaric acid is incorporated in the polypyrrole formed. In this manner no strictly alternating copolymer is formed but a block copolymer which, in addition to a sequence of pyrrole units, comprises squaric acid units, or a homopolymer is formed which consists of pyrrole doped with squaric acid.

The invention will be explained in greater detail by means of exemplary embodiments and drawings, in which

Fig. 1 represents formulae I, II and III of monomer units A which can be used as acceptor units in alternating copolymers in accordance with the invention, and

20 Fig. 2 represents formulae IV and V of monomer units D which can be used as donor units in alternating copolymers in accordance with the invention, and

Fig. 3 represents formulae VI, VII, VIII and IX of a few special examples of monomer units D which can be used as donor units in alternating copolymers in accordance with the invention, and

25 Fig. 4 represents formulae X, XI, XII, XIII, XIV, XV and XVI of aromatic diamines which can be used as donor monomer units D in alternating copolymers in accordance with the invention, and

Fig. 5 represents formulae XVII and XVIII of repetitive units of representatives of electrically conductive alternating copolymers in accordance with the invention.

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Exemplary embodiment 1.Preparation of a compound in accordance with formula VI, where $R_1 = R_2 = n-C_{18}H_{37}$

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The compound in accordance with formula VI of Fig. 3 is prepared using a benzodipyrrole and stearyl-p-chlorobenzene sulphonate. Said dipyrrole is prepared according to the method described in Chemical Abstracts, Vol. 76, 1972, abstract No. 72434m, where it is indicated by formula III. The stearyl-p-chlorobenzene sulphonate is prepared from p-chlorobenzene sulphonchloride and stearyl alcohol.

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A mixture of 99 grams of stearyl-p-chlorobenzene sulphonate, 18 grams (75 mmol) of said dipyrrole and 100 ml of chlorobenzene are heated for three hours at a temperature of 120°C - 140°C. A quantity of 100 ml of chlorobenzene is added to the paste formed, thereby forming a suspension. Said suspension is heated at a temperature of 120°C-130°C for 16 hours and then cooled, after which 200 ml of toluene are added. The solid is filtrated by vacuum filtration after which said solid is stirred with 250 ml of toluene and then filtered again. The solid obtained is stirred with a mixture of 16 grams of NaOH, 500 ml of water and 500 ml of toluene for 5 hours after which all of the solid has dissolved. The liquid layers are separated and the organic layer is washed with 500 ml of water, after which said layer is dried over Na_2SO_4 and evaporated. The residue is crystallized from 500 ml of 96% ethanol thereby forming 13.75 grams (18,48 mmol) of the desired product VI, i.e. benzodihydropyrrole, where $R_1 = R_2 = n-C_{18}H_{37}$.

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Preparation of alternating copolymer in accordance with formula XVII.

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A mixture of the benzodihydropyrrole in accordance with formula VI (2.40 grams, 3.23 mmol) which is prepared according to the above method, squaric acid (370 mg, 3.25 mmol), 150 ml of n-butanol, 100 ml of toluene and 3 drops of quinoline is refluxed for 20 hours while removing water by means of azeotropic distillation. After the mixture has cooled, it is filtered off by suction, after which the solid is washed with toluene. After drying at 90°C, the alternating copolymer in accordance with formula XVII thus obtained weighs 1.76 grams.



The conductivity of said copolymer in accordance with formula XVII, measured on a film by means of a four-point measurement (also termed potential-probe measurement) is $3 \cdot 10^{-5}$ S/cm. The band gap is 1.0 eV and is determined by the threshold of the continuous optical absorption in the near infrared (see C. Kittel, Introduction to Solid State Physics, 5th ed., John Wiley and Sons, 1976, page 210). The absorption spectrum is measured on a thin layer of the polymer on a glass plate, said polymer being provided from a solution in chlorobenzene.

10 Exemplary embodiment 2.

Preparation of the salt of the compound in accordance with formula VII, where $R_3 = R_4 = CH_3$.

15 The salt of the compound in accordance with formula VII of Fig. 3 is prepared according to the method described in Chemical Abstracts, Vol. 71, 1969, abstract No. 81344f, where it is indicated by formula III (dithiazole salt of methyl sulphate). In this form the compound is used in the polycondensation reaction with croconic acid.

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Preparation of alternating copolymer in accordance with formula XVIII.

25 A mixture of 324 mg (2.0 mmol) of croconic acid-monohydrate, 945 mg (2.0 mmol) of the above-mentioned dithiazole salt, 30 ml of n-propanol, 800 mg of pyridine and 30 ml of dimethyl sulphoxide are refluxed for 3 hours. After evaporation a residue is obtained which is further concentrated under a vacuum at 100°C to remove dimethyl sulphoxide. The residue thus obtained is mixed with a mixture of 50 ml of water and 50 ml of toluene for half an hour. Filtration by suction gives 900 mg of the alternating copolymer in accordance with formula XVIII of Fig. 5. The conductivity at room temperature is 10^{-5} S/cm and $2.5 \cdot 10^{-3}$ S/cm at 250°C. The band gap is 0.5 eV.

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Exemplary embodiment 3.

Alternating copolymer of squaric acid and the compound in accordance with formula VI, where $R_1 = R_2 = n-C_4H_9$.

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In a manner analogous to that described in exemplary embodiment 1, the compound is prepared in accordance with formula VI of Fig. 3, where $R_1 = R_2 = n-C_4H_9$ (n-butyl). In a manner analogous to that of said exemplary embodiment, an alternating copolymer is obtained by using squaric acid. The conductivity of the copolymer formed is $5 \cdot 10^{-5}$ S/cm. After doping with iodine vapour at a temperature of 80°C the conductivity is 10^{-2} S/cm.

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Exemplary embodiment 4.

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Alternating copolymer of squaric acid with p-phenylene diamine.

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Polycondensation of squaric acid, using p-phenylene diamine in cyclohexanol as the solvent, gives an alternating copolymer having a conductivity of 10^{-6} S/cm. After doping with iodine vapour the conductivity is $5 \cdot 10^{-3}$ S/cm. The band gap of the copolymer obtained is 0.4 eV.

Further exemplary embodiments.

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The Table below gives a summary of the results of alternating copolymers obtained from the indicated acceptor monomer units A and donor monomer units D. The conductivity is measured on the undoped copolymer at room temperature.

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monomer A	monomer D	conductivity copolymer (S/cm)	band gap (eV)
squaric acid	VI where $R_1=R_2=CH_3$	10^{-8}	1,0
squaric acid	VI where $R_1=R_2=C_4H_9$	$3 \cdot 10^{-6}$	1,0
squaric acid	VI where $R_1=R_2=C_{18}H_{37}$	$3 \cdot 10^{-5}$	1,0
croconic acid	VI where $R_1=R_2=CH_3$	$2 \cdot 10^{-8}$	
squaric acid	VII where $R_3=R_4=C_4H_9$	$5 \cdot 10^{-7}$	
croconic acid	VII where $R_3=R_4=CH_3$	10^{-5}	0,5
croconic acid	VII where $R_3=CH_3$ and $R_4=C_{12}H_{25}$	10^{-4}	
squaric acid	neocuproine (VIII)	$2 \cdot 10^{-7}$	
squaric acid	terthienyl (IX) with $R_5=H$	$2 \cdot 10^{-6}$	
squaric acid	p-phenylenediamine	10^{-6}	0,4
croconic acid	p-phenylenediamine	10^{-8}	
squaric acid	diamino acridine (XV)	10^{-4}	
squaric acid	thionine (XVI)	$2 \cdot 10^{-6}$	

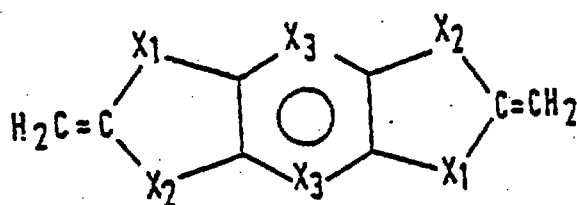
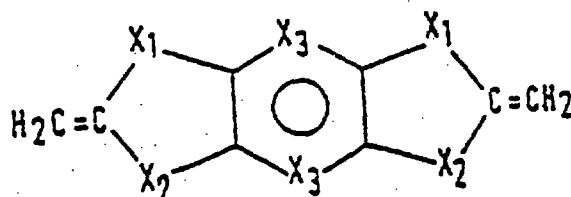
Alternating copolymers in accordance with the invention are intrinsically electrically conductive and have a band gap of maximally 1.5 eV.

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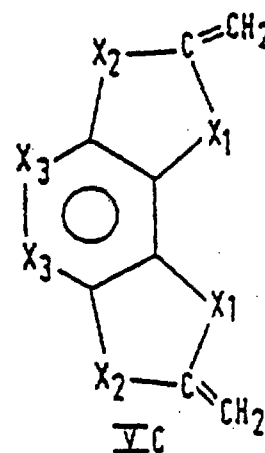
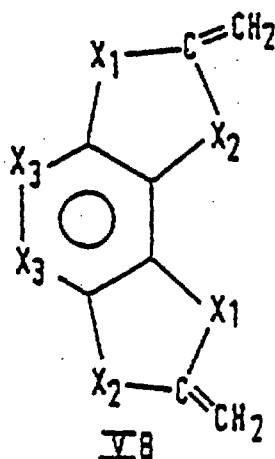
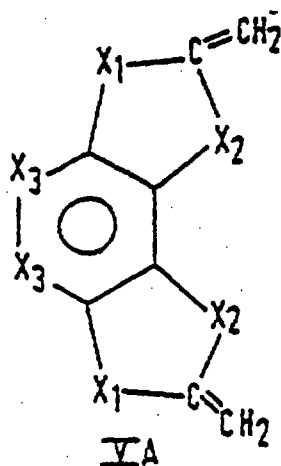
CLAIMS:

1. A (semi)conductive copolymer of alternating donor and acceptor monomer units, characterized in that the (semi)conductive copolymer can be obtained by reacting an acceptor monomer unit A having an unsaturated ring structure which is substituted with at least two double-bonded oxygen atoms and at least one hydroxy group, with a donor monomer unit D formed by a homo or heterocyclic aromatic compound comprising at least two active hydrogen atoms, a polycondensation reaction taking place in the presence of a solvent, thereby forming said alternating (semi)conductive copolymer.
2. An alternating copolymer as claimed in Claim 1, characterized in that the monomer unit A is selected from the group formed by squaric acid, croconic acid and 5,6-dihydroxy-5-cyclohexene-1,2,3,4-tetraone.
3. An alternating copolymer as claimed in Claim 1, characterized in that the monomer unit D is selected from the group formed by

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where:

$X_1 = -NR-$ and

$X_2 = O, S, Se, -NR-, -CR=CH-, -CHR-CH_2-$ or $-C(alkyl)_2-$, where the alkyl group contains 1-18 C-atoms and

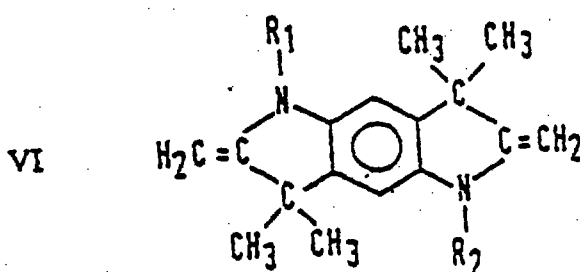
15 $X_3 = -CR=$ or $-N=$, where R is an H-atom or a C_1-C_{18} alkyl or alkoxy group; or

$X_1 = S$ or O and

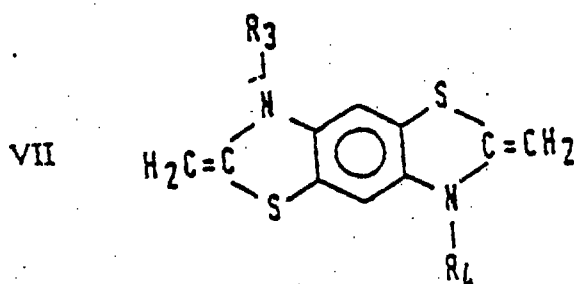
$X_2 =$ or $-CR=CH-$ and

$X_3 = -CR=$ or $-N=$, where R has the above-mentioned meaning.

4. An alternating copolymer as claimed in Claim 3, characterized in that the
20 monomer unit D is selected from the group formed by



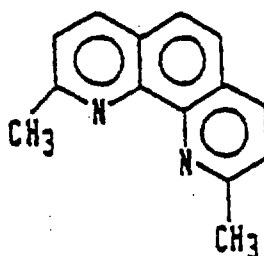
where R_1 and R_2 represent a C_1-C_{18} alkyl group;



where R_3 and R_4 represent a C_1-C_{18} alkyl group;



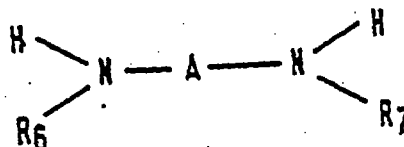
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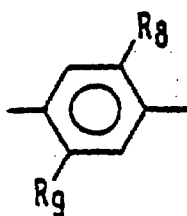
5. An alternating copolymer as claimed in Claim 4, characterized in that the monomer unit A is croconic acid and the monomer unit D corresponds to formula VII, where R_3 represents a methyl group and R_4 represents a dodecyl group.

6. An alternating copolymer as claimed in Claim 1, characterized in that the monomer unit D is an aromatic diamine of the general formula

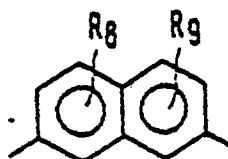
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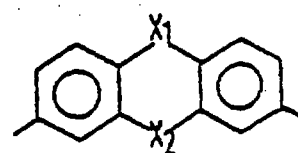
where R_6 and R_7 represent an H-atom or a C_1 - C_{18} alkyl group and A is an aromatic core selected from the group formed by



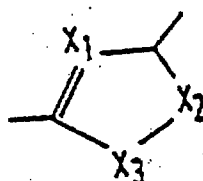
XI



XII



XIII



XIV

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where R_8 and R_9 represent an H-atom or a C_1 - C_{18} alkyl group and $X_1 = -N=$ or $-CR=$, where R represents an H-atom or a C_1 - C_{18} alkyl or alkoxy group, and X_2 and $X_3 = S, O, Se, -NH-$ or $-N$ (alkyl)-, where the alkyl group contains 1-18 C-atoms.

- 5 7. An alternating copolymer as claimed in Claim 6, characterized in that the monomer unit D is selected from the group formed by p-phenylenediamine, thionine and 3,6-diamino acridine.
8. A method of preparing an alternating copolymer in accordance with one of the preceding Claims, in which equimolar quantities of bifunctional acceptor
- 10 monomer units A and bifunctional donor monomer units D are mixed in a solvent and polymerized by polycondensation, thereby forming the alternating copolymer comprising repeating unit AD.
9. The use of an alternating copolymer as claimed in one of the Claims 1-7, or obtained by using the method as claimed in Claim 9, as a conductor or
- 15 semiconductor in an electronic circuit.
10. The use of an alternating copolymer as claimed in one of the Claims 1-7 in an antistatic layer or electromagnetic protective layer.

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