

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
6 March 2003 (06.03.2003)

PCT

(10) International Publication Number
WO 03/018648 A1

- (51) International Patent Classification⁷: **C08F 126/06**, 26/06, 234/04
- (21) International Application Number: PCT/US02/28064
- (22) International Filing Date:
3 September 2002 (03.09.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/316,607 31 August 2001 (31.08.2001) US
- (71) Applicant: **TDA RESEARCH, INC.** [US/US]; 12345 West 52nd Avenue, Wheat Ridge, CO 80033 (US).
- (72) Inventors: **LUEBBEN DEVITO, Sylvia**; 18855 West 59th Drive, Golden, CO 80403 (US). **ELLIOTT, Brian**; 1637 S. Riverbend Lane, Superior, CO 80027 (US). **WILSON, Carolina**; 6775 Coors Court, Arvada, CO 80004 (US).
- (74) Agents: **SULLIVAN, Sally, A.** et al.; Greenlee, Winner and Sullivan P.C., Suite 201, 5370 Manhattan Circle, Boulder, CO 80303 (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 03/018648 A1

(54) Title: POLY(HETEROAROMATIC) BLOCK COPOLYMERS WITH ELECTRICAL CONDUCTIVITY

(57) Abstract: The present invention provides block copolymers containing at least one block of a poly(heteroaromatic) polymer and at least two blocks of a non-conjugated polymer. The chemically different blocks of the copolymer are covalently bonded to each other in an alternating fashion through an appropriate linkage group. The poly(heteroaromatic) block may exist in its neutral or oxidized form, and when in the oxidized form, it associates with organic or inorganic counter-anions to balance the charge. The poly(heteroaromatic) polymer is an intrinsically conducting polymer (IPC), and when in the oxidized form it is electrically conducting. When the IPC block or blocks of the block copolymer are in the doped form, the block copolymer is electrically conducting. Preferably the conducting block copolymers have conductivities in the range 10^{-6} - 10^3 S/cm. Block copolymers of this invention are soluble or dispersible in water, one or more organic solvents, or in a mixture thereof at a level of at least about 0.1g/liter.

POLY(HETEROAROMATIC) BLOCK COPOLYMERS WITH ELECTRICAL CONDUCTIVITY

5

BACKGROUND OF THE INVENTION

This invention relates to block copolymers comprising one or more blocks of a poly(heteroaromatic) polymer and two or more blocks of a non-conjugated polymer and to methods for their preparation. The poly(heteroaromatic) blocks can be either in the neutral state or in the doped state. When the blocks of the poly(heteroaromatic) polymer are in the doped state the resulting block copolymer is electrically conducting and soluble or dispersible in water, an organic solvent, or a mixture thereof. In this invention the poly(heteroaromatic) blocks are referred to as "A", while the non-conjugated blocks are referred to as "B". This invention relates to tri-block copolymers of the structure BAB, multi-block copolymers of a minimum of four blocks and structure of ABAB (or longer), and end-capped multi-block copolymers of structure BABAB (or longer).

Intrinsically conducting polymers (ICP) are polymers whose electrical and optical properties can be reversibly controlled by changing their oxidation state. Most ICPs are conjugated polymers with extended π conjugation along the molecular backbone. By chemical or electrochemical oxidation or reduction of the polymer backbone (doping) it is possible to systematically vary the electrical conductivity of these materials from the insulating state to the conducting state. In the doped (conducting) state, ICPs consist of rather rigid planar polyionic chains in which the charges are delocalized over a segment of the backbone. The chains are polycationic when they are doped through oxidation (p-doping) and polyanionic when they are doped through reduction (n-doping). Counter-ions (anions for p-doped polymers and cations for n-doped polymers) are present within the polymeric matrix to compensate for the charges on the polymer.

Representative ICPs include polyacetylene, polyaniline, polypyrrole, polythiophene, poly(phenylenesulfide), poly(paraphenylene), poly(phenylenevinylene), and many others (P. Chandrasekhar, *Conducting*

Polymers, fundamental and Applications, Kluwer Academic Publishers, Boston, 1999). Because of their extended π conjugation, conducting polymer chains behave like rigid rods, have poor flexibility, and hence do not flow or melt. Therefore, traditional melt processing cannot be employed to process these materials.

5 Moreover, because of the strong ionic interactions among polymer chains and counterions, most conducting polymers do not dissolve in either aqueous or organic solvents and, as a result, cannot be processed from solution (Wessling B.; "Dispersion as the key to Processing Conducting Polymers", in *Handbook of Conducting Polymers, 2nd Ed.*, Ed. T.A. Skotheim, RL Eisenbauer, J.R. Reynolds,

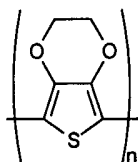
10 (1998), Marcel Dekker, New York, p-471-473). The poor processability of conducting polymers is a major impediment to their commercial use.

_____A few exotic solvents have been discovered for some conducting polymers. For example, polyaniline doped with organic sulfonic acids is soluble in *m*-cresol or

15 hexafluoroisopropanol solutions. These solvents are toxic or expensive, and difficult to handle in a large scale process (Rasmussen P., Hopkins A., Basheer R., *Macromolecules*, **29**, (1996) 7838-7846). Other conducting polymers have been stabilized as diluted dispersions in water. For example, a 1.3% aqueous dispersion of poly(3,4-ethylenedioxythiophene), PEDOT (Formula 1) doped with polystyrene sulfonic acid is commercially available from Bayer AG and is sold under the trade name of Baytron

20 (Trademark, Bayer AG) P (L. Groenendaal, F Jonas, D. Freitag, H. Pielartzik, J. Reynolds, *Advanced Materials*, **12**, (2000) 481-494). Conducting polymers containing long solubilizing side-chains such as poly(3-hexylthiophene) are soluble in many common organic solvents such as chloroform, but the side chains often disrupt the conjugation and conductivity is greatly reduced, except for the case of regioregular poly(3-

25 hexylthiophene) which has highly ordered crystal packing. Also the thermal and oxygen



PEDOT

Formula 1. Poly(ethylenedioxythiophene).

stability of these ICPs substituted with solubilizing chains is often much worse than the parent polymer. Finally, substituted monomers are much more expensive than unsubstituted monomers.

5 François and Oliga reported the preparation of polystyrene-polythiophene (PSt-PTh) copolymers by polymerization of thiophene or 2-bromothiophene and polystyrene chains terminated with thiophene or 2-bromothiophene groups. Soluble and insoluble fractions were recovered after synthesis. The soluble fraction was doped in solution after purification by iron chloride. The doping of the copolymer was
10 observed by measuring the optical density of the doping band as a function of the iron chloride loading, but no conductivity data were presented for the copolymer. The copolymer was used to cast films from solution, and these films were then pyrolyzed at 380°C to de-polymerize the polystyrene. The conductivity of the pyrolyzed films containing only the PTh, was reported to be up to 60S/cm (B. François, T. Olinga, *Synthetic Metals*, **55-57** (1993) 3489-3494). François and others also described the synthesis of poly(*paraphenylene*) (PPP), polythiophene (PTh), and poly(3-hexylthiophene) block copolymers with polystyrene (PSt) or polymethylmethacrylate (PMMA) by a similar method. Although they stated that
15 "FeCl₃ doped PSt-PPP copolymers" formed "exceptionally regular porous and conducting membranes", no conductivity data were reported (B. François, G. Widawski, M. Rawiso, B Cesar, *Synthetic Metals*, **69** (1995) 463-466; B. François, R Lazzaroni, Ph. Leclere, V. Parente, A. Couturiaux, J. Bredas, *Synthetic Metals*, **102** (1999) 1279-1282).

25 Xue and others reported the electrochemical copolymerization in nitromethane of pyrrole and styrene at different feed ratios. The formation of block copolymers was reported. The products deposited as insoluble films at the electrode during synthesis, and were insoluble in both nitromethane and dichloromethane. Conductivities ranging from 0.2 to 0.007 S/cm were reported (G. Xue, S. Jin, X. Liu,
30 W. Zhang Y. Lu, *Macromolecules*, **33**, (2000) 4805-4808).

Hadziioannou and others reported the synthesis of block copolymers by regularly alternating a block of oligothiophene with a block of oligosilanylene. The

oligothiophene blocks with a specific and definite number of monomer units (thiophene) were first prepared using organometallic chemistry (Ni-catalyzed Grignard coupling of mono- or di-bromothiophenes or by oxidative coupling of lithiated thiophenes). The oligothiophene blocks were then joined with thiophene terminated silanylene blocks (G. Hadziioannou, P. Hutten, R. Gill, J. Herrema; *J. Phys. Chem.*, **99**, (1995) 3218-3224). Hadziioannou and others describe using the silanylene group to limit the conjugation length of conducting polymer segments as a method of controlling the luminescence wavelength. The silanylene blocks contain only one or two silicon atoms and are described solely to break the conjugation of oligothiophenes.

Leung and Ho Tan reported the synthesis of polystyrene-polyacetylene di-block copolymers obtained by thermal elimination of polystyrene-poly(phenyl vinyl sulfoxide) di-block copolymers. Conductivity of the copolymers versus compositions is reported (L. Leung, K Ho Tan, *Macromolecules*, **26**, (1993) pp. 4426). Polyacetylene is a conducting polymer but not a poly(heteroaromatic) polymer.

Goodson and others reported the synthesis of rigid/flexible alternating block copolymers of PPP-PEG (poly(paraphenylene) - poly(ethylene glycol)). The copolymers were characterized by thermogravimetric analysis, differential scanning calorimetry and fluorescence spectroscopy, but no conductivity data were reported (F. Goodson, Z Wagner, T Roenigk, *Macromolecules*, **34**, (2001) 5740-5743). Goodson et al. report the formation of soluble block copolymers when the PPP segment is less than 6 repeat units long. Although PPP forms a conducting polymer, oligomers of 5 repeat units or shorter are non-conducting. Although Goodson and others report the formation of block copolymers of PPP that exhibit fluorescence behavior, they do not report the formation of conducting materials, or materials that can be rendered conducting by doping.

Cao and others reported the synthesis of ABA block copolymers of polyaniline (block A) with poly(ethyleneglycol) (PEG, block B) prepared by oxidative copolymerization of aniline with PEG segments that had previously been reacted with *p*-aminobenzenesulfonyl chloride. The products were reported to be soluble in DMF,

DMSO, and THF in the neutral state, but only slightly soluble in the protonated (doped) state. Conductivity of cast films ranged from 0.62 to 1.7×10^{-4} S/cm (Y. Cao, S. Li, H. Dong, *Synthetic Metals*, **29**, (1989) E329-E336).

5 Zhang and Bi report the synthesis of polyaniline-poly(phenylene-terephthalamide)-polyaniline tri-block copolymers by reacting low molecular weight poly(phenylene-terephthalamide) terminated with two $-\text{COCl}$ groups with low molecular weight polyaniline, previously prepared by oxidative polymerization of aniline in HCl solution (G Zhang, X. Bi, *Synthetic Metals*, **41-43**, (1991) 251-254)

10

Kinlen, Frushour, Ding and Menon reported the synthesis of ABA tri-block copolymers where the A blocks are polyaniline and the B block is a α,ω -diamino terminated poly(ethyleneoxide), poly(propyleneoxide), poly(dimethylsiloxane), or poly(acrylonitrile-co-butadiene). Polymerization was performed in emulsion by oxidative coupling of aniline and the α,ω -diamino terminated B block in the presence of dinonylnaphthalenesulfonic acid. Moderately conducting (10^{-5} S/cm) high molecular weight soluble copolymers were reported (P. Kinlen, B. Frushour, Y. Ding and V. Menon, *Synthetic Metals*, **101**, (1999) 758-761).

20 Kinlen and others (WO99/16084) report the synthesis of diblock AB and triblock ABA copolymers containing intrinsically conducting blocks (A) and a non-conducting block (B) (Figure 1, taken from the published application, illustrates the diblock and triblock copolymers). As shown in Figure 1, diblock copolymers have one non-ICP block and one ICP-block, while triblock copolymers have one non-ICP block and two ICP blocks. The ICP blocks are formed by the polymerization of ICP monomers with the polymerization initiated at a linkage group. The non-ICP blocks have a non-ICP covalently linked with one linkage group (for diblock copolymer) or two linkage groups (for a triblock copolymer) to form a non-ICP precursor. Although the published PCT application mentions the use of ICP monomers including "pyrrole, substituted pyrroles, ... thiophenes and substituted thiophenes, indoles, furans, carbazoles and mixture thereof ...substituted and unsubstituted anilines ..." the only ICP monomer for which copolymer synthesis is reported is aniline and the only block copolymers exemplified are AB di-block and ABA tri-block copolymers of polyaniline

25

30

(where the polyaniline block is A). No methods of preparation are provided in the reference for block copolymers containing blocks of poly(heteroaromatic) polymers such as polypyrrole, polythiophene and their derivatives.

5 There is a significant and continuing need in the art for conducting polymers that exhibit improved processability and mechanical and physical properties. There is a specific need in the art for processable conducting polymers formed from symmetric ICP monomers, such as those containing heteroaromatic monomers.

SUMMARY OF THE INVENTION

10 The present invention provides block copolymers containing at least one block of a poly(heteroaromatic) polymer and at least two blocks of a non-conjugated polymer. The chemically different blocks of the copolymer are covalently bonded to each other in an alternating fashion through an appropriate linkage group. The poly(heteroaromatic) block may exist in its neutral or oxidized form, and when in the
15 oxidized form, it associates with organic or inorganic counter-anions to balance the charge. The poly(heteroaromatic) polymer is an intrinsically conducting polymer (ICP), and when in the oxidized form it is electrically conducting. When the ICP block or blocks of the block copolymer are in the doped form, the block copolymer is electrically conducting. Preferably the conducting block copolymers have
20 conductivities in the range 10^{-6} - 10^3 S/cm. More preferably the conducting block copolymers have conductivities greater than about 10^{-3} S/cm. Conducting block copolymers of this invention include those having conductivities in the range of 10^{-3} to about 10^2 S/cm. The block copolymers of this invention are soluble or dispersible in water, one or more organic solvents, or in a mixture thereof at a level of at least
25 about 0.1g/liter. More preferable soluble block copolymers of this invention are soluble in water, one or more organic solvents, or in a mixture thereof at a level sufficient to form a solution of concentration of about 1.0% weight/volume or more. More preferable dispersible block copolymers of this invention are dispersible in water, one or more organic solvents, or in a mixture thereof at a level sufficient to
30 form a dispersion containing about 1.0% weight/volume or more of block copolymer..

The block copolymers described in this invention combine the electrical and optical properties of the ICP block with the properties of the non-conducting block, including,

but not limited to solubility, processability, adhesion, substrate bonding, biodegradability, bioactivity, mechanical properties, toughness, flexibility, non-linear optical properties, ionic conductivity, compatibility with other components, fillers or substrates, among others.

5

The conducting blocks of the block copolymers of this invention must be of sufficient length to be conducting and must be present in sufficiently high concentration to allow bulk conducting percolation in the solid state. In preferred embodiments the block copolymers of this invention contain conducting blocks
10 having 3 or more monomers, particularly 3 or more heteroaromatic monomers. In a more preferred embodiment the conducting blocks contain at least 8 heteroaromatic units.

The present invention also provides block copolymers formed by at least one
15 block of a poly(heteroaromatic) polymer and at least two blocks of a non-conjugated polymer in which the non-conjugated polymer contains one or more latent polymerizable groups that undergo polymerization under selected conditions, during or after the formation of the block copolymer, to cross-link the block copolymer into a polymeric network.

20

The present invention also provides a method for the preparation of such block copolymers comprising a first step in which a non-conducting block of appropriate molecular weight is modified with one or two linkage groups that undergo oxidative polymerization, and a second step in which the modified non-conducting
25 block is copolymerized with a heteroaromatic monomer under oxidative conditions to form a tri- or a multi-block copolymer. Tri-block copolymers are formed using non-conducting blocks that have one linkage group, while multi-block copolymers are formed using non-conducting blocks that have two linkage groups. Tri-block copolymers are BAB type, while multi-block copolymers contain a minimum of 4
30 blocks (e.g. ABAB).

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 illustrates the structure of di-block and tri-block copolymers from Kinlen et al. WO99/16084.

5 Figure 2 illustrates head-to-tail polymerization of aniline and other asymmetric monomers to forms only AB and ABA block copolymers

Figure 3 illustrates the polymerization of pyrrole, thiophene, and their derivatives by random coupling of radical cations to form multi-block ABABAB .
10

Figure. 4 illustrates synthesis of ABABABA multi-block, BAB tri-block, and capped BABAB multi-block copolymers (where A is the ICP block and B is the non-ICP block),
15

DETAILED DESCRIPTION OF THE INVENTION

A important concept of the present invention is that continuous conjugation along the molecular backbone is not required to have macroscopic electrical conductivity, rather the conducting blocks must be of sufficient length to be
20 conducting and must be present in sufficiently high concentration to allow bulk conducting percolation of the dry material. It has been demonstrated that the conductivity of composite materials containing a conducting component and a non-conducting component is not linear with the volume fraction of the conducting component but follows a sigmoidal function. This has been explained in terms of
25 percolation theory (Wessling B.; "Dispersion as the key to Processing Conducting Polymers", in *Handbook of Conducting Polymers, 2nd Ed.*, Ed. T.A. Skotheim, RL Elsenbauer, J.R. Reynolds, (1998), Marcel Dekker, New York, p-471-473). Below a critical concentration (percolation threshold) of the conducting component, the composite material is an insulator. Around the critical concentration, a small
30 increase in the conducting component's concentration increases the conductivity by several orders of magnitude. Above the critical concentration, the addition of conducting material brings only a slight further increase in conductivity.

This invention provides block copolymers containing conducting and non-conducting blocks, which combine the desired conductivity with significantly improved processability and mechanical properties. The block copolymers of this invention are prepared by polymerization of ICP blocks having heteroaromatic monomers and non-conducting blocks of various chemical structures.

There are major differences among ICP monomers in their mechanisms of polymerization. Aniline is an asymmetric monomer that polymerizes head-to-tail (i.e. the NH_2 group reacts with the carbon in the para position to the benzene ring of another molecule). This implies that the polyaniline block, once it has started to grow (polymerize) at the linkage group on the non-ICP block, can grow only in one direction until all the monomer is consumed. No coupling of growing segments can occur because this would require the reaction of a NH_2 group with another NH_2 (as shown in Figure 2). In contrast, pyrrole, thiophene, furan, other five member heteroaromatic monomers, and their derivatives are symmetric monomers. Polymerization occurs with these ICP monomers by random coupling of radical cations that form by oxidation of neutral precursor species, including the ICP monomer, its dimer, its trimer, a section of the ICP polymer or a growing ICP segment on the non-ICP block. Because of this random coupling of species, multi-block copolymers of the type ABABABAB are obtained from non-ICP blocks with two linkage groups, and tri-block copolymers of the type BAB are obtained from non-ICP blocks terminated with a single linkage group (where A is the conducting block, and B is the non-ICP block, as shown in Figure 3 and Figure 4).

Because of the substantial difference in the polymerization of asymmetric monomers such as aniline and symmetric heteroaromatic monomers such as pyrrole and thiophene, methods previously exemplified (Kinlen (WO99/16084) for the polymerization of asymmetric monomers are not applicable to polymerization of the symmetric heteroaromatic monomers of the present invention.

The differences in formation of block copolymers of symmetric and asymmetric ICP are illustrated in Figs. 4A, 4B and 4C:

5 a) when starting from a non-ICP block (B) with two linkage groups a triblock copolymer of the type ABA is formed if using aniline or another asymmetric monomer that polymerizes head-to tail by the method described by Kinlen, but a multiblock copolymer of the type ABABABAB is obtained when following the method of the present invention with a symmetric heteroaromatic monomer (Fig. 4A);

10 b) when starting from a non-ICP block (B) with one linkage group a diblock copolymer of the type AB is formed if using aniline or another asymmetric monomer that polymerize head-to tail by the method described by Kinlen, but a triblock copolymer of the type BAB is obtained when following the method of the present invention with a symmetric heteroaromatic monomer (Figure 4B).

15 c) when using a mixture of mono and difunctional non-ICP blocks, a capped multiblock copolymer of definite molecular weight can be prepared using the present invention (Fig. 4C).

20 Therefore, the block copolymers of this invention contain two or more non-ICP block, while the copolymers described by Kinlen always contain only one non-ICP block. Kinlen's copolymers are prepared from monomers that polymerize head to-tail while copolymers of this invention are prepared from symmetric heteroaromatic monomers.

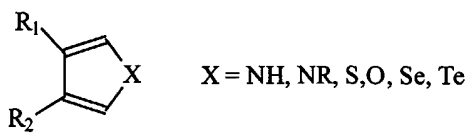
25 DEFINITIONS

A heteroaromatic monomer is an aromatic compound containing a heteroatom in the conjugated ring system and is isoelectronic with the original aromatic hydrocarbon (F. Carey, R. Sundberg, *Advanced Organic Chemistry, Third Ed., Part A*, Plenum Press, New York (1990) p. 531). Atoms other than a carbon (heteroatoms) include nitrogen, sulfur, oxygen, selenium and tellurium. Heteroaromatic monomers comprise pyrroles, thiophenes, selenophenes, tellurophenes, furans, indoles, isoinoles, isothianaphthalenes, pyridines, pyrimidines, pyrazines, triazines, thiazoles, imidazoles, quinolines, isoquinolines, benzimidazoles,

thiazoles, triazoles, oxidiazoles, benzopyrrolines, dithienobenzene, thianaphthene, carbazoles, benzothiophenes, isobenzothiophenes, benzofurans, isobenzofurans, isoindolines, isobenzoselenophenes, isobenzotellurophenes, their substituted derivatives, or mixtures thereof.

5

Some heteroaromatic monomers of this invention are illustrated in Formula 2.



Formula 2. Heteroaromatic monomers.

where R, R₁ or R₂ are selected independently of one another and may be the same or different groups including hydrogen, deuterium, halogens, alkyl, fluoroalkyl, halogenated alkyl, alkenyl, alkoxy, carboxylate, alkylcarbonyl, acanoyl, alkylthio, mercapto, cycloalkoxy, alkenyldioxy, aryl, alkylaryl, arylalkyl, aryloxy, amino, alkylamino, dialkylamino, alkylcarbonylamino, alkylsulfinyl, aryloxyalkyl, alkoxyalkyl, polyetheralkyl, phosphate, phosphite, phosphine, hydroxyl, cyano, sulfonate, alkylsulfonate, arylsulfonate, alkylsulfate, arylsulfate, nitro, alkylsilane, arylsilane, or

10 R₁ and R₂ together form an alkylene, alkenylene, alkenyloxy, alkenyldioxy, alkynyloxy, alkynyldioxy chain that completes a 3,4,5,6,7 or 8 membered alicyclic or aromatic ring which can optionally include one or more heteroatom including nitrogen, oxygen, sulfur, phosphorous, selenium, tellurium, or silicon. R, R₁ or R₂ can also be an oligomeric or polymeric chain made by repeating one of more

20 monomers, including among others glycols, ethers, fluoroethers, olefins, fluoroolefins, acrylates and methacrylates, vinyl compounds, alkynes, esters, amino acids, lactones and lactams, polyols, urethanes, epoxies, hydroxyacids, dienes, polyenes, chloroolefins, diols, diamines, and polyamines.

25 The poly(heteroaromatic) blocks comprise polymers made by polymerization of one or more heteroaromatic monomers listed above. The conducting sections of the conducting block copolymers of this invention preferably have 3 or more

polymerized monomers ($n = 3$ or more in certain formulas herein). In more preferred embodiments, the conducting sections have 8 or more repeating units (i.e., monomer units). Block copolymers of this invention also include those having from 5 to about 500 monomers, those having 5 to about 100 monomer units and those having 5 to about 50 monomer units. In each case the conducting sections can contain one or more different monomer units (as in Figs. 6 and 6A), but preferred block copolymers have conduction sections in which all of the monomers are the same. Conducting blocks containing one or more selected heteroaromatic monomers can be combined by the methods herein to form block copolymers with conducting blocks that contain one or more different selected heteroaromatic monomer.

The non-conducting sections of the block copolymers of this invention include, among others, polyethers, poly(fluoroethers), polyglycols, polyactals, polyolefins, polystyrene and its copolymers, polyfluoroolefins, polyoxides, polychloroolefins, polychlorofluoroolefins, polysiloxanes, polyesters, polybromoesters, natural and synthetic rubbers (vulcanized or un-vulcanized), polyacids, polycarbonates, polyanhydrides, polysulfides, polyamides, polyamines, polyimides, vinyl polymers and polymers derived from the polymerization of unsaturated monomers, polyacrylates and polymethacrylates, polyacrylonitriles and its copolymers, polybutadiene and its copolymers, alkyds, polyalcohols, polyurethanes, epoxies, cellulose and its derivatives, starch and its derivatives, other natural occurring polymers, polypeptides, and other biomolecules and combinations and copolymers thereof.

The molecular weight of the block copolymer preferably ranges from 40 Daltons to about 1 million Daltons. In more preferred embodiments the non-conducting blocks (B) of the block copolymers of this invention contain 1 to about 100 repeating units and the conducting block/s (A) contain 3 to about 500 repeating units.

The non-conducting block is modified at one end or at both ends with a linkage group (L1 and L2 in Formulas 3-9) that undergoes oxidation under the conditions used to polymerize the heteroaromatic monomer. Linkage groups include

among others aliphatic acids, aromatic amino groups, phenols, substituted thiophenes, pyrroles, furan species and their derivatives, carbonyl compounds, quinones, halogenated compounds, acetylenes, phosphorous containing compounds, thiols, and other species that undergo oxidation.

5

The linkage group is bonded to the non-conducting polymer during the first step of the synthesis, preferably through a covalent bond. The covalent bond between the non-conducting block and the linkage group may be an ester, thioester, amide, ether, thioether, amino, carbon-carbon, sulfonic ester, sulfonamide, phosphate ester, anhydride, urea, urethane, carbonate, imine, imide, thiocarbonate, thiourethane or thiourea linkage.

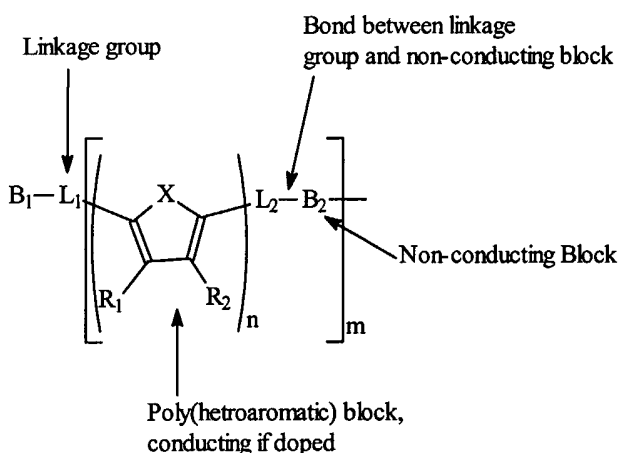
The modified non-conducting block (with one or more terminal linkage groups) is then copolymerized with one or more heteroaromatic monomers (second step of the synthesis). Copolymerization occurs by chemical or electrochemical oxidation of the monomers.

Preferred block copolymers of this invention are soluble or dispersible in selected solvent to facilitate processing of the copolymers. A material is soluble in a solvent or solvent mixture if it substantially dissolves in that solvent or solvent mixture at a level of at least about 0.1 g/L at room temperature. As used herein the term soluble encompasses materials where small amounts of the material may not dissolve in the selected solvent, but wherein the amount of material that does not dissolve does not significantly interfere with processability of the material or the use or application of the solution. A fully dispersible material is a material that forms a stable suspension of droplets, micelles, or colloidal particles in a liquid medium such as water, an organic solvent or a mixture thereof at a concentration of at least 0.1 g/L. The droplets, micelles or colloidal particles are stable under the force of gravity and the dispersed material does not precipitate or separate out of the liquid medium over a time period that significantly interferes with the use of the dispersed material. Preferably the material does not precipitate or separate out of the liquid medium within a one-month period after the dispersion is formed. . A material is dispersible in a liquid medium if it substantially disperses. As used herein -the term "dispersible"

encompasses materials where small amounts of the material may not disperse in the selected liquid medium, but wherein the amount of material that does not disperse does not significantly interfere with processability of the material or the use or application of the dispersion.

5

In specific embodiments the block copolymers of this invention have the structures in Formulas 3-6:



Formula 3

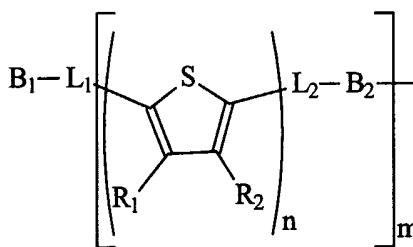
10

where variables are defined above, B₁ and B₂ are the non-conducting blocks and can be the same or different and are independently described by B above, and L₁ and L₂ which may be the same or different are optional suitable linkage groups linked with a suitable covalent bond to the non conducting blocks B₁ and B₂, and n ≥ 3 and m ≥ 1.

15

In particular, the block copolymer includes the structures shown in Formulas 4, 5 and 6:

20



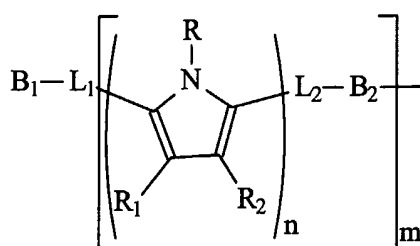
Formula 4

30

35

5

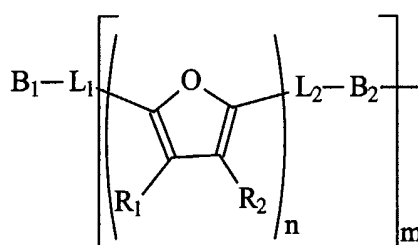
10



15

Formual 5

20



Formula 6

where variables are as defined above.

25

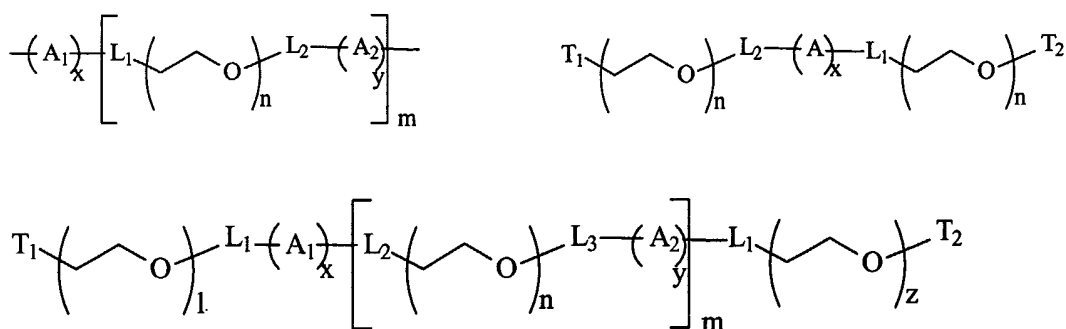
Suitable linkage groups are illustrated in the examples herein and include among others pyrrole and thiophene derivatives. Suitable bonds between the linkage groups and the non-conducting block include single bonds, e.g., $-\text{CO}-$, $-\text{CO}_2-$, $-\text{CO}_2-\text{CH}_2-$, $-\text{NH}-$, and $-\text{CONH}-$ groups among others.

30

Block copolymers of this invention also include those having the formulas 7, 8 and 9) where A, A1 and A2 can be the same or different heteroaromatic monomers as defined above for A, L1 and L2 are optional linkage groups which may be the same or different and l, n, m, x, and y are integers that represent the number of repeating monomer units in the block, T1 and T2 represent a end-cap of the non

35

conducting block that does not undergo oxidation:



Formulas 7, 8 and 9, respectively

- 5 Chemical polymerization can be performed in the presence of an oxidizing agent comprising one or more of the following: hydrogen peroxide; organic or inorganic peroxides; persulfates; peracids; peroxyacids; hypobromite; bromates; hypochlorite; chlorates; perchlorates; periodates; organic or inorganic salts of iron (III), chromium (IV), chromium (VI), manganese (VII), manganese (V), manganese (IV), vanadium (V), osmium (VIII), ruthenium (IV), mercury (II), copper (II), lead (IV),
- 10 (IV), vanadium (V), osmium (VIII), ruthenium (IV), mercury (II), copper (II), lead (IV), molybdenum (VI); gasses such as oxygen, ozone, chlorine, bromine, SO₂, SO₃, NO₂; organic oxidants such as formic acid, oxalic acid, oxalyl chloride, acetic anhydride, trifluoroacetic anhydride, and substituted or unsubstituted quinones. The polymerization reaction is carried out in a solvent or mixture of solvents which can
- 15 include water, alcohols, glycols, alkoxyalcohols, ketones, esters, linear and cyclic ethers, alkoxyethers, chlorinated solvents, carbonates, nitriles, amides, sulfoxides, hydrocarbon and aromatic solvents and mixtures thereof. The polymerization is typically carried out at a temperature between -80°C and the boiling point of the solvent used. Polymerization conditions can be controlled to control the size of
- 20 polymers formed as is known in the art. Polymerization may be carried out in the presence of an organic or inorganic acid or salts, thereof.

Preferred heteroaromatic monomers are pyrrole and thiophene and derivatives thereof, particularly those derivatives carrying substituents in position 3 or

25 in positions 3 and 4 on the aromatic ring. Substituents have been defined above. Especially preferred heteroaromatic monomers are pyrrole, N-methylpyrrole, N-alkylpyrrole, 3-methylpyrrole, 3-methoxypyrrole, thiophene, 3-methylthiophene, 3-hexylthiophene, 3-octylthiophene, 3-methoxythiophene, 3,4-ethylenedioxythiophene,

3,4-propylenedioxythiophene, 3,4-butylenedioxythiophene, 3,4-ethylenedioxy pyrrole, and 3,4-propylenedioxy pyrrole.

Preferred non-conducting blocks are poly(ethylene glycol)s, poly(propylene glycol)s, acrylonitrile-butadiene copolymers, poly(dimethylsiloxane)s, polyesters, other polyols, and polyalcohols. Preferred molecular weight of the non-conducting block ranges from 100 to 3000 Daltons. Preferred linkage groups are pyrrole, thiophene, and 3,4-ethylenedioxythiophene. These linkage groups are preferably bonded to the non-conducting block in position 2 through an ester, amide, sulfonamide, sulfonic esters, ether, or carbon-carbon bond.

The non-conducting B blocks of the block copolymers of this invention may contain one or more latent polymerizable groups for further reaction or crosslinking. Latent polymerizable groups include acrylates, methacrylates, vinyl esters, vinyl ethers, olefins, and substituted olefins, isocyanates, thioisocyanates, nitriles, epoxy groups, alkids, alkoxy silanes, vinyl silanes, amino, hydroxyl, thiol, carboxy, anhydrides, phenols, aldehydes, furans, melamine, unsaturated polyesters, cyanate esters, cyano acrylates, acetylenes, esters, amides, lactones and lactams.

In preferred embodiments, block copolymers containing latent polymerizable groups are of the type BAB where the latent polymerizable group is at the free or distal end of the B block. Preferred polymerizable groups include acrylates and methacrylates that can be cross-linked by radical polymerization in the presence of radical initiators such as redox initiators, peroxides, azo compounds or photoinitiators.

Preferred chemistries for the first step of the synthesis (functionalization of the non-conducting block with a linkage group that undergoes oxidation) are:

- 1) Formation of an ester bond by reacting a hydroxy-terminated non-conducting segment with 2-thiophenecarbonyl chloride or N-methyl-2-pyrrolecarbonyl chloride (see Examples 1-7 and 10-14).
- 2) Formation of an ether bond between a thienylmethanol unit and the non-conducting block following the Williamson reaction, Vogel A. I. "Textbook of

Practical Organic Chemistry" 5th Ed., 1998 reprint Longman, Singapore p. 583-585; Freedman H.H. and R.A. Dubois (1975) *Tetrahedron Letters*, 3251).

- 5 3) Formation of a carbon-carbon bond by reacting an organometallic reagent such as thienyllithium with a di-chloro or di-bromo terminated non-ICP block or a diglycidyl-terminated non-ICP block (Example # 9 A, Vogel A. I. "Textbook of Practical Organic Chemistry" 5th Ed., 1998 reprint Longman, Singapore, p. 557-559). An EDOT-terminated macromonomer can be prepared following the same method: 3,4-ethylenedioxythiophene is first lithiated with butyl lithium or methyl lithium (Rajappa S. (1984) "Thiophenes and Their Benzoderivatives: (ii) Reactivity" in *Comprehensive Heterocyclic Chemistry*, C Bird, and G. Cheeseman Editors, Pergamon Press, Oxford, p. 771), and then reacted with the di-chloride of the soft segment or with a poly(ethylene glycol) diglycidyl ether (Example 17).
- 10 4) Formation of sulphonamides and sulfonate esters by reacting thienylsulphonyl chloride with a diol or a diamine (Examples 8).
- 15 5) Reductive amination of thiophene carboxyaldehyde, pyrrole carboxyaldehyde, or EDOT carboxyaldehyde (Examples 15, 18, and 19).

The copolymerization reaction (step two of the synthesis) is preferably carried out with molecular oxygen, ozone, a peroxide, hydrogen peroxide, a persulfate or an iron(III) salt. Preferably an organic acid or its salt is present during the polymerization. Preferred organic acids include *para*-toluenesulfonic acid, dodecylbenzenesulfonic acid, poly(styrenesulfonic acid), di-nonylnaphthalenesulfonic acid, and mono- and dialkyl sulfosuccinates. Preferred solvents for the copolymerization are water, butanol, pentanol, ethoxyethanol, butoxyethanol, THF, acetone, methylethylketone, nitromethane, and mixture thereof. Preferred reaction temperature is between -20 °C and 80°C.

20

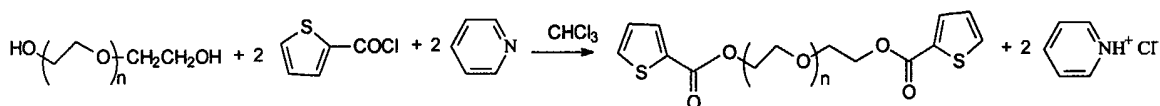
25

EXAMPLES**Example 1: Synthesis of poly(EDOT-*block*-EG 400) (ABAB multi-block or larger)**

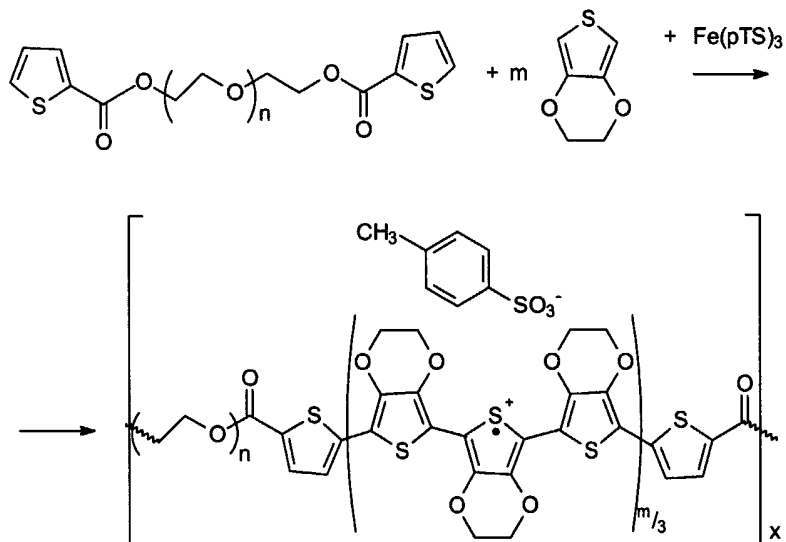
5 Poly(EDOT-*block*-EG 400) (a multi-block copolymer of ethylenedioxythiophene (EDOT) and ethylene glycol (EG) having poly(ethylene glycol) (PEG) segments of MW= 400) was prepared in a two-step synthesis following the strategy illustrated below: a PEG segment having average molecular weight of

10 poly(ethylene glycol)dithiophene (PEGdTh, step A), then the PEGdTh was copolymerized with EDOT in the presence of iron (III) *para*-toluenesulfonate (Fe(pTS)₃) (step B).

Step A:



Step B:



Step A: Synthesis of Thiophene-capped PEG blocks (PEGdTh)

2-Thiophenecarbonyl-chloride (7.06 mL, 66 mmol = 2.2 eq.) was added at 0 °C to PEG (400) (Aldrich, 12 g = 30 mmol = 1eq.) and pyridine (5.73 mL, 70 mmol) in CH₂Cl₂. Pyridinium hydrochloride formed as the solution was warmed to room
5 temperature. After cooling, the pyridinium hydrochloride was removed by filtration and the filtrate was washed 3 times with dilute HCl (to remove excess pyridine) and NaHCO₃ (to remove excess 2-thiophene carbonyl chloride and/or its hydrolysis product, 2-thiophene carboxylic acid). A ¹H NMR spectrum of this material indicated that the major species was the desired product. The yield of the reaction was
10 calculated by comparing the peak integrals of the thiophenic protons with the peak integrals of the α CH₂ of the PEG. The yield was near quantitative on the PEG used.

Step B: Synthesis of poly(EDOT-*block*-EG 400)

15 PEGdTh (400) (0.64 mmol) was dissolved in *n*-butanol (0.5 ml), mixed with 32.4g of Baytron® C from Bayer (50%wt. Fe(*p*TS)₃ in butanol, = 23 mmol of iron), and heated under stirring to 80 °C. Freshly distilled ethylenedioxythiophene (EDOT from Bayer; 1.6 g = 11.3 mmol) was dissolved in 120 ml of *n*-butanol (final concentration of 10⁻² M) and slowly added to the hot mixture of PEGdTh and Baytron
20 ® C over a 1.5 hr period under stirring. After the addition was completed, the reaction was kept at 80 °C for 1.5 hr, then cooled to room temperature and stored overnight. The following day the solution was dark blue and no precipitate was present.

25 The crude mixture was filtered and extracted two times with water. The water phase was yellow in color and had a pH of 1-2. The dark blue butanol phase containing the conducting copolymer had a pH of 2-3 and was used to prepare thin films on polycarbonate. This solution was analyzed by gel permeation chromatography (GPC) and its residue after evaporation of the butanol was
30 characterized by elemental analysis. GPC experiments were conducted using a Phenogel 00H-3259-K0 column connected to a Waters HPLC system. Tetrahydrofuran was used as the mobile phase at an operating flow rate of 1 ml /

min. The copolymers were injected as solution in butanol and a UV-Vis detector was used to monitor their presence in the eluent at a wavelength of 330 nm, which is above the absorbance of both butanol and THF. Poly(EDOT-*block*-EG 400) has a very broad molecular weight distribution that is centered between 10,000 and 20,000 daltons. Elemental analysis of a dry sample was performed at Huffman Laboratories in Golden, CO and the results are shown in Table 1. A thin film of poly(EDOT-*block*-EG 400) coated on polycarbonate sheets from the butanol solution is optically clear. The electrical bulk conductivity of this thin film measured by the "four-point conductivity method" (P. Chandrasekhar, *Conducting Polymers, Fundamental and Applications*, Kluwer Academic Publishers, Boston, 1999) was 480 S/cm ($\pm 50\%$).

Table 1: Elemental Analysis of Poly (EDOT-*block*-EG 400)

Element	Weight %
C	45.56
H	4.71
O	28.69
S	16.04
Fe	5.53
Total	100.5

15 Alternative Step B: Synthesis of poly(EDOT-*block*-EG 400)

In a glass flask 0.5 ml of butanol, 0.233 g of PEGdTh (400) and 32.48 g Baytron® C (50% butanol, 50% Iron (III) *paratoluenesulfonate*) are mixed together and heated to 80° C. Using an addition funnel, a solution of 10 ml butanol and 1.6 g distilled Baytron® M (EDOT) was added drop-wise over a three-hour period. The reaction was allowed to proceed for 24 hours at 80° C. A dark thick blue solution formed together with some precipitate. The product was then filtered and the filtrate extracted over water in a separatory funnel two times with water and two times with brine. Films were cast on glass plates with this solution were green/blue after drying and poorly conducting.

25

Example 2: Synthesis of poly(EDOT-*block*-EG 600) and poly(EDOT-*block*-EG 1500) (ABAB multi-block or larger)

Poly(EDOT-*block*-EG 600) and poly(EDOT-*block*-EG 1500) were synthesized following the strategy in Example # 1 from PEG oligomers with molecular weights of 5 600 or 1500. 2-Thiophenecarbonyl-chloride (8.8 mL, 82 mmol = 2.2 eq.) was added to PEG (600) or PEG (1500) (1eq.) and pyridine in dry CHCl₃ and refluxed overnight. The solvent was removed by vacuum distillation using a rotary evaporator and the residue was re-dissolved in hot CH₂Cl₂. After cooling, the pyridinium hydrochloride precipitated and it was removed by filtration. The filtrate was washed 3 times with 10 dilute HCl to remove excess pyridine, and with NaHCO₃ to remove pyridinium hydrochloride and any potential 2-thiophene carbonyl chloride and/or its hydrolysis product, 2-thiophenecarboxylic acid. Positive confirmation of the formation of the desired product PEGdTh was obtained by ¹H NMR and FT-IR analysis. The yield of each reaction was obtained by comparing the intensity of the thiophenic protons with 15 the intensity of the α and β methylene protons of the PEG section. The ¹H NMR of the PEGdThs (600) showed complete conversion and no impurity was present in the product. The ¹H NMR of the PEGdThs (1500) showed the presence of an impurity in the aromatic region. It was purified by recrystallization from hot ethanol to a white amorphous solid that gels slightly when warmed to room temperature.

20

The copolymerization of PEGdTh (600) with EDOT was performed as follows: PEGdTh (600) (0.46 g = 0.64 mmol) was dissolved in *n*-butanol (0.5 ml), mixed with 32.4g of Baytron® C (50%wt. Fe(*p*TS)₃ in butanol, = 23 mmol of iron), and heated under stirring to 80 °C. In an addition funnel freshly distilled EDOT (1.6 g = 11.3 mmol) was dissolved in 120 ml of *n*-butanol (final concentration of 10⁻² M). The EDOT solution was slowly added to the hot mixture of PEGdTh and Baytron® C over a 3 hr period under stirring, and turned dark blue in color. After the addition was completed the reaction was cooled to room temperature and stored overnight. The following day the solution was dark blue and no precipitate was present. The crude mixture was filtered and extracted two times with water. The water phase was

Table 2: Elemental Analysis of Poly(EDOT-*block*-EG)s (Weight %).

	Poly(EDOT- <i>block</i> -EG 600)	Poly(EDOT- <i>block</i> -EG 1500)
C	44.74	45.96
H	5.74	5.08
O	30.97	29.29
S	14.14	14.78
Fe	5.52	5.66
Total	101.2	100.8

yellow in color and had a pH of 1-2. The dark blue butanol phase had a pH of 2-3 and was used to prepare thin films on polycarbonate.

A similar copolymerization was performed starting from PEGdTh (1500). A dark blue solution with no precipitate was obtained. This solution was used to coat polycarbonate sheets.

Both films of poly(EDOT-*block*-EG 600) and poly(EDOT-*block*-EG 1500) were optically clear and electrically conducting. The electrical bulk conductivity of a thin film of poly(EDOT-*block*-EG 600) measured by the "four-point conductivity method"

was 2.2 S/cm (± 1 S/cm), while the conductivity of a thin film of poly(EDOT-*block*-EG 1500) was 0.5 S/cm (± 0.2 S/cm). The elemental analysis of these two copolymers is shown in Table 2.

5 Alternative Step B: Synthesis of poly(EDOT-*block*-EG 1500)

In a 100 mL round-bottom flask, a mixture of PEGdTh (1500) (0.116g) and Baytron C (16.21 g) were heated to 80°C with stirring. To the heated mixture, a solution of 0.805 g of Baytron M in 5 mL of *n*-butanol was added dropwise over 35 minutes. After the addition, the heater was switched off and the reaction mixture
10 was left stirring at room temperature for 7 days. A thick blue-green solution was obtained. The solution was then filtered but no residue was collected. The sample was then extracted with an excess (10 times the organic phase) of water. Because water did not separate from the butanol phase, NaCl was added. The extracted deep-blue organic phase was used to coat a polycarbonate sheet with a hand
15 coater. The resulting coating was conductive. No precipitate was present after storing the deep-blue solution for two months. A portion of the solution was gently dried at r.t. in a vented chamber. A pressed pellet made from the dry powder had a conductivity of 0.1 S/cm as determined with a Jandel four-point conductivity probe.

20 Alternative step B: Synthesis of poly(EDOT-*block*-EG 1500)

PEG₁₅₀₀dTh (1.25g, 0.343mmol = 1/40eq) was mixed with para-toluene sulfonic acid (7.59g, 39.1mmol = 1.35eq), dodecylbenzene sulfonic acid (18.34g, 39.1mmol = 1.35eq), ammonium sulfate (6.78g, 29.1mmol = 1eq), and iron(III) sulfate (0.047g, 0.092mmol = 0.003eq) in 100mL of DI water. EDOT (3.10mL,
25 29.1mmol = 1eq) was mixed with 200mL of 1-butanol and added dropwise to the PEG1500dTH solution. The addition took approximately 4 hours. Upon the addition of EDOT/butanol, the solution went from clear yellow to cloudy gray then finally black. The resulting solution was stirred at room temperature for approximately 24hours before work-up. After 24 hours, the organic layer was washed with water 3
30 times, then 2 times with concentrated sodium chloride solution, and 2 more times with DI water. The volume of water or sodium chloride solution used were 1/3 of the volume of the organic layer present. A portion of the organic solution was gently

dried in a vented oven and pressed to form a pellet that had conductivity of 2.3×10^{-3} S/cm.

Example 3: PEG(550)monothiophene – co- EDOT (BAB tri-block copolymer)

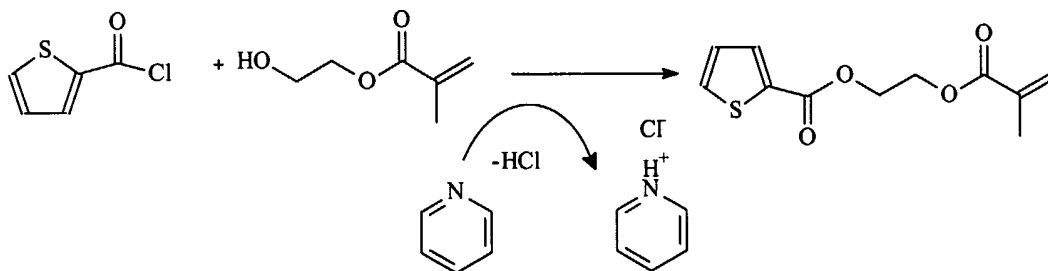
5 Polyethylene glycol (550) monomethyl ether was reacted with 2-thiophenecarbonyl-chloride following the recipe in Example # 1 to form a mono-methoxy mono-thiophene poly(ethylene glycol). This compound was copolymerized with 3,4-ethylenedioxythiophene to form a BAB tri-block copolymer.

10 In a round bottomed flask, 0.37g of PEG(550)mono-methoxy mono-thiophene (0.563 mmol), 0.5 mL butanol and 32.48g Baytron C (50 wt% solution of iron(III) tosylate in butanol) were combined and heated to 80 °C. A solution of 1.6 g of EDOT (11.26 mmol) and 112 mL n-butanol was added drop-wise. The solution was held at 80 °C under constant stirring for 3 hours and cooled overnight. After 24 hours the
15 solution was washed twice over water. Gel Permeation Chromatography confirmed the formation of compounds with molecular weights from 2,000 to 10,000 daltons.

Example 4: Methacrylated BAB tri-block copolymer

Step A: Synthesis of thiophene / methacrylate compound.

20 This molecule is used as the "B" block to make a BAB type block copolymer and it contains a latent polymerizable group (the methacrylate) for further reaction or cross-linking.



25 10 mL of anhydrous CH₂Cl₂ plus 5 mL 2-thiophenecarbonyl chloride (2-TCC) (46.8 mmol, 4.7 M solution) was added drop-wise to 100 mL of anhydrous CH₂Cl₂ (distilled, dried over molecular sieves, and de-gassed before use) plus 5.15 mL 2-

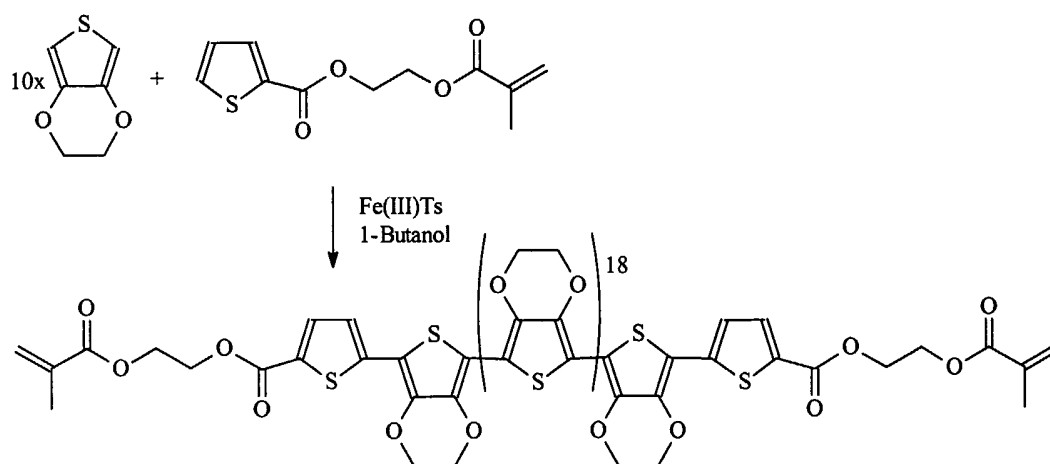
hydroxyethyl methacrylate (HEMA, 5.53g, 42.5 mmol, 0.425 M soln.) plus 4.05 mL pyridine (50 mmol) at 0°C (under constant stirring). The solution was allowed to warm to room temperature by allowing the ice bath to melt and warm under ambient conditions. The formation of pyridinium chloride precipitate confirmed the reaction.

5 The solution sat 40 hours and was filtered (to remove the pyridinium chloride), washed 3 times with dilute HCl (to remove pyridine) and washed 1 times with dilute NaHCO₃ to remove 2-TCC. The solvent was removed *in vacuo* and the organic phase was dried with molecular sieves.

10 The product was characterized by FTIR and NMR. FTIR confirmed that the majority of the primary alcohol groups of HEMA were consumed. The methacrylate C=C was still present as evidenced by the peak at 1636 cm⁻¹. The peak at 1716 cm⁻¹ is the C=O for both the methacrylate ester and the thionyl ester. The peak at 1523 cm⁻¹ was assigned to the thiophene ring. NMR also confirmed that the desired
15 product was formed. The starting material HEMA has an NMR spectrum with peaks at 1.95 ppm (CH₃), 3 ppm (OH), 3.85 and 4.28 ppm (CH₂), and 5.6 and 6.15 ppm (=CH₂). Protons from the methacrylate group were found in the synthesis product along with the aliphatic protons of the HEMA tail. However, the original hydroxyl proton is not present (at a chemical shift of 3 ppm), indicating the reaction of the
20 alcohol to the acid chloride proceeded as desired. Additionally, the spectrum for the synthesis product contains the thiophene protons in the 3,4,5 positions.

25

30

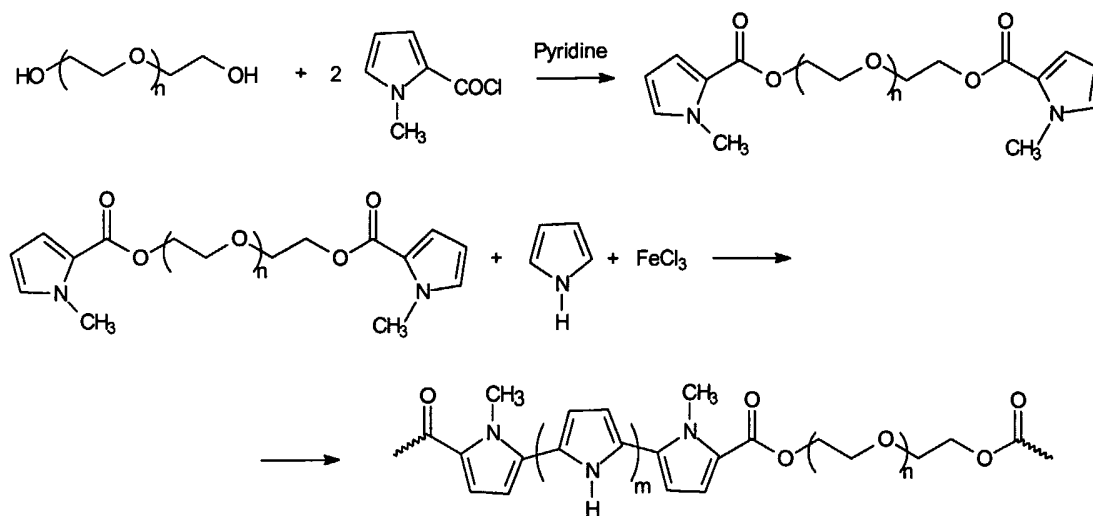
Step B: Synthesis of BAB block copolymer

Theoretical doping level of 1:3, Ts : thiophene

In a round bottom flask the reactants were combined: 100 mL butanol, 0.25g
 5 (1.04 mmol) HEMA-2-TCC synthesis product (as described in Step A), 29.5 g (20:1
 wt ratio based on EDOT) Baytron C® (which is a 50 wt% solution of iron(III) tosylate
 in butanol), and 1.48 g (10.4 mmol) EDOT (dist.) added drop-wise. This mixture was
 stirred at room temperature.

10 After 12 total days of stirring at room temperature, the product was purified.
 The mixture was washed twice with a large excess volume of water (to remove the
 iron salt). The organic phase was blue and the water phase yellow. The organic
 phase was de-watered *in vacuo* followed by drying with molecular sieves. The cast
 films were blue/opaque, conductive and re-dissolvable in butanol.

15 The FTIR spectrum of the product shows a sloped baseline that is typical of
 conducting polymers. The peak at 1715 cm^{-1} confirms the presence of C=O from the
 methacrylate and thiophene-HEMA connection, the peak at 1522 cm^{-1} confirms the
 thiophene rings, and the peaks at 1652 and 814 cm^{-1} confirm that the methacrylate
 20 C=C double bond survived during the oxidative polymerization of the EDOT
 monomer.

Example 5: Synthesis of Poly(Py-*block*-EG) (ABAB multi-block or larger)

Block copolymers of pyrrole with ethylene glycol (poly(Py-*block*-EG)) were synthesized from pyrrole and a low molecular weight polyethyleneglycol (PEG) following the two-step synthesis below. PEG (for example MW = 600) was reacted

5 with *N*-methyl-2-pyrrole carbonyl chloride in the presence of pyridine to form the di-pyrrole derivative macromonomer PEGdPy. This macromonomer was then copolymerized with pyrrole in the presence of iron chloride and *para*-toluenesulfonic acid. For example, a solution of the PEGdPy ($2 \cdot 10^{-1}$ M) in water was mixed with a solution of iron (III) chloride ($2 \cdot 10^{-1}$ M) and *para*-toluenesulfonic acid ($2 \cdot 10^{-1}$ M) in

10 water. To this mixture a diluted solution of pyrrole in methoxyethanol (10^{-2} M) was added with a dropping funnel over a three-hour period at -20°C and under strong stirring. The product was filtered to eliminate the homopolymer that eventually formed and then was extracted to eliminate unreacted reagents and the iron(II) chloride byproduct. In an alternative copolymerization method molecular oxygen

15 was bubbled through an iced solution containing PEGdPy (10^{-2} M), pyrrole (10^{-1} M), alkylnaphthalenesulfonate ($2 \cdot 10^{-1}$ M), and a catalytic amount of Fe(III).

For simplicity, the synthetic scheme above represents the PPy segments in the neutral, non-conducting form. PPy segments are, however, in the oxidized,

20 conducting form, and the counterions *paratoluenesulfate* or

alkylnaphthalenesulfonate are present inside the conducting domains to balance the charges.

Example 6: Synthesis of Poly(EDOT-*block*-PG) (ABAB multi-block or larger)

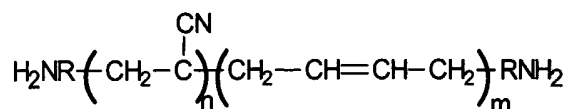
5 Block copolymers of EDOT with poly(propylene glycol) Poly(EDOT-*block*-PG) were synthesized from EDOT and a low molecular weight poly(propylene glycol) (PPG) oligomer following a two-step method in Example 1. PPG (MW = 1500) was reacted with 2-thiophene carbonyl chloride in the presence of pyridine to form a di-thiophene derivative macromonomer PPGdTh. This macromonomer was then
10 copolymerized with ethylenedioxythiophene (EDOT) in the presence of an oxidizing agent and a suitable counterion. This second step was preferably conducted in diffusion-controlled conditions to avoid the homopolymerization of thiophene; for example, a solution of the PPGdTh (2×10^{-1} M) in 1-pentanol was mixed with a solution of sodium persulfate (2×10^{-1} M) and poly(*para*-styrenesulfonate) in water.
15 To this mixture a diluted solution of EDOT in 1-pentanol (10^{-2} M) was added dropwise under strong stirring at 80°C. The product was filtered to eliminate the homopolymer and then extracted with water to eliminate unreacted monomer and byproducts.

20 **Example 7: Synthesis of Poly(Th-*block*-PG) (ABAB multi-block or larger)**

 Block copolymers of thiophene (Th) with propylene glycol (poly(Th-*block*-PG)) were synthesized from thiophene and a low molecular weight poly(propylene glycol) (PPG) following a two-step method of Example #1. PPG (MW = 600) was reacted with 2-thiophene carbonyl chloride in the presence of pyridine to form a di-thiophene
25 derivative macromonomer PPGdTh. This macromonomer was then copolymerized with thiophene in the presence of an oxidizing agent and an opportune counterion. For example, a solution of the PPGdTh (2×10^{-1} M) in acetonitrile was mixed with a solution of thiophene in acetonitrile (10^{-2} M). To this mixture a solution of iron (III) chloride (2×10^{-1} M) and *para*-toluenesulfonate (2×10^{-1} M) in water was added with a
30 dropping funnel over a three-hour period at 40 °C. The product was filtered to eliminate the homopolymer that eventually formed and extracted to eliminate unreacted reagents and the byproduct iron (II) chloride.

Example 8: Synthesis of Poly(EDOT-*block*-NBR) (ABAB multi-block or larger)

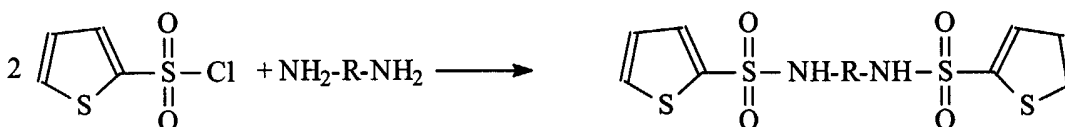
Block copolymers containing segments of PEDOT and segments of nitrile-butadiene rubber (poly(EDOT-*block*-NBR)) were synthesized from EDOT and a low molecular weight amino-terminated nitrile-butadiene rubber.



Amino-terminated nitrile-butadiene rubber

5

The amino-terminated nitrile-butadiene rubber (Hycar ATBN from Noveon) was first reacted with thiophene sulfonylchloride shown below to form a dithiophene-terminated macromonomer (NBRdTh). This macromonomer was then copolymerized with EDOT under diffusion-controlled conditions. For example a solution of NBRdTh (2 X 10⁻¹ M) in methylethyl ketone (MEK) was mixed with a solution of sodium persulfate (2 X 10⁻¹ M) and poly(*para*-styreneulfonate) in water. To this mixture a solution of EDOT in MEK (10⁻¹ M) was added drop wise under stirring at 80°C. The product was filtered to eliminate the homopolymer and extracted with water to eliminate the unreacted reagents and byproducts.



. Synthesis of di-thiophene terminated macromonomer from thienyl-sulfonyl chloride.

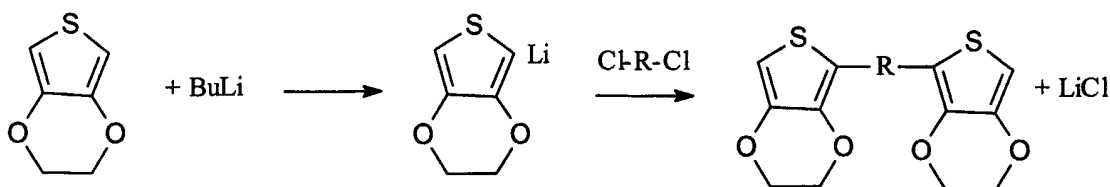
15

Example 9: Alternative synthesis of Poly(EDOT-*block*-EG) (ABAB multi-block or larger)

Poly(EDOT-*block*-EG) was synthesized from a di-EDOT terminated macromonomer (PEGdEDOT) prepared by reacting a di-chloro terminated PEG oligomer with an EDOT that has been lithiated in position 2, as illustrated below. The di-EDOT terminated macromonomer was then copolymerized with EDOT. For example, a solution containing 1 mmol of PEGdEDOT, and 10 mmol of EDOT in

20

butanol was heated at 80°C. To this solution, a solution of Na₂S₂O₈ in water was added drop wise over the course of several hours. After completion of the reaction the product was filtered and extracted.



Synthesis of di-EDOT terminated macromonomer.

5 **Example 10: polyethylene glycol monomethacrylate / thiophene – co – EDOT (BAB tri-block copolymer)**

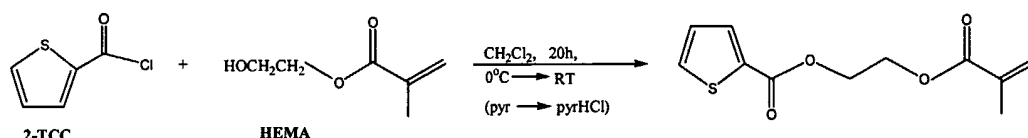
Mono-thiophene terminated poly(ethylene glycol) mono-methacrylate was prepared from poly(ethylene glycol) mono-methacrylate of molecular weight of 200, 400, or 1000 Daltons with the strategy outlined in Example 4. 2-Thiophenecarbonyl chloride (1 eq) was added to poly(ethylene glycol) monomethacrylate (1 eq) and pyridine (1.2 eq) in dry CHCl₃ and refluxed overnight. The solvent is removed *in vacuo* and the residue is redissolved in hot CH₂Cl₂. After cooling, the pyridine hydrochloride precipitated and was removed by filtration. The filtrate was washed 3 times with dilute HCl to remove excess pyridine, and with NaHCO₃ to remove pyridine hydrochloride and any potential 2-thiophene carbonyl chloride and/or its hydrolysis product, 2-thiophene carboxylic acid.

BAB block copolymers were formed by the strategy outlined in Example #4. In a round bottom flask we mixed 100 mL butanol, 1.0 mmol mono-thiophene terminated poly(ethylene glycol) monomethacrylate, and 29.5 g Baytron C® by Bayer (a 50 wt% solution of iron(III) tosylate in butanol). Then 1.48 g (10.4 mmol) EDOT (dist.) was added drop-wise. This mixture was stirred 2 hours at 80 °C and one week at room temperature. The mixture was then washed twice with a large excess volume of water and the organic phase was dried with molecular sieves.

Example 11: Synthesis of HEMA / thiophene -co- 3-hexylthiophene (BAB tri-block copolymer (Exp 1))

Step A: synthesis of end-capped precursors

A methacrylated end-capped monomer was synthesized from hydroxyethyl methacrylate (HEMA) and 2-thiophenecarbonyl chloride. This molecule was later used as the "B" end-cap of BAB tri-block copolymers of 3-hexylthiophene conducting oligomers.



10

10 mL of anhydrous CH_2Cl_2 plus 5 mL 2-thiophenecarbonyl chloride (2-TCC) (46.8 mmol, 4.7 M solution) was added drop-wise to 100 mL of anhydrous CH_2Cl_2 plus 5.15 mL HEMA (5.53g, 42.5 mmol, 0.425 M soln.) plus 4.05 mL pyridine (50 mmol) at 0°C (under constant stirring). The solution was allowed to warm to room temperature by allowing the ice bath to melt and warm under ambient conditions. The formation of pyridinium chloride precipitate confirmed the reaction. The solution sat overnight and was filtered the following day (to remove the pyridinium chloride), washed 3 times with dilute HCl (to remove pyridine) and washed 1 time with dilute NaHCO_3 to remove 2-TCC. The organic phase was dried with excess MgSO_4 (anhydrous) to remove H_2O . The CH_2Cl_2 was removed under vacuum and the product was characterized by Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy. FTIR spectroscopy confirmed that the majority of the primary alcohol groups of HEMA were consumed. The methacrylate $\text{C}=\text{C}$ was still present as evidenced by the peak at 1636 cm^{-1} . The peak at 1716 cm^{-1} was the $\text{C}=\text{O}$ for both the methacrylate ester and the thionyl ester. The peak at 1523 cm^{-1} is associated with the thiophene ring.

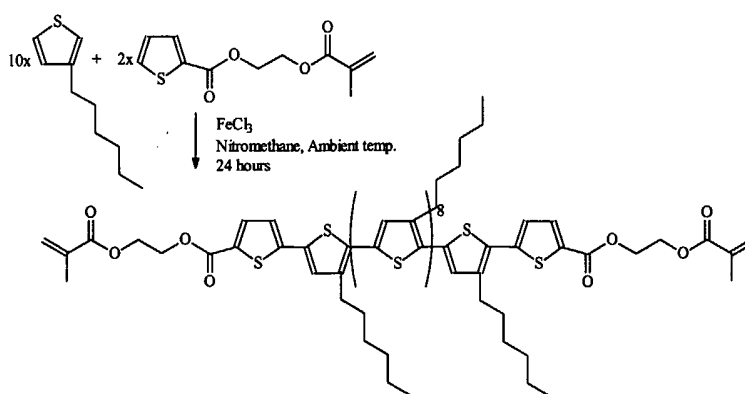
NMR spectroscopy also confirmed that the desired product was formed. The starting material HEMA has an NMR spectrum with peaks at 1.95 ppm (CH_3), 3 ppm (OH), 3.85 and 4.28 ppm (CH_2), and 5.6 and 6.15 ppm ($=\text{CH}_2$). Protons from the methacrylate group were found in the synthesis product as well as the aliphatic

30

protons of the HEMA tail, however, the original hydroxyl proton is not present (at a chemical shift of 3 ppm) indicating the reaction of the alcohol to the acid chloride proceeded as desired. Additionally, the spectrum for the synthesis product contains the thiophene protons in the 3,4,5 positions. This product was found to be stable at

5 80 °C for 14 hours under dark conditions.

Step B: Synthesis of the BAB tri-block copolymer



10

4.37g of FeCl₃ was dissolved in 75ml CH₃NO₂ and poured into a round bottom flask. 0.48g 2-TCC/HEMA (precursor from Step A) and 1.51g 3-hexylthiophene were combined in 10ml CH₃NO₂ and added to FeCl₃ solution dropwise. The color

15 immediately changed from red to dark green. Initially there was no precipitate. The mixture was stirred at room temperature in air for 24 hours. The dark green solution was then filtered to recover a blue/black solid. The solid was washed twice with 10ml CH₃NO₂ to remove FeCl₃ and FeCl₂ (spent oxidizing agent), leaving 1.66g of a blue solid. A small amount of a non-soluble material was filtered with a glass wool.

20 The product was soluble in CHCl₃ and THF. The product yield was 68-72%, of a blue soluble solid that had a conductivity of 1.4E-02 S/cm.

Step C: photo-crosslinking of the tri-block copolymer

The product from Example 11 Step B was dissolved in CHCl₃ and 0.5 wt. % of

25 2,2-dimethoxy-2-phenyl acetophenone (DMPA, an initiator of radical polymerization) was added to the solution. The solution was cast on a glass substrate and the

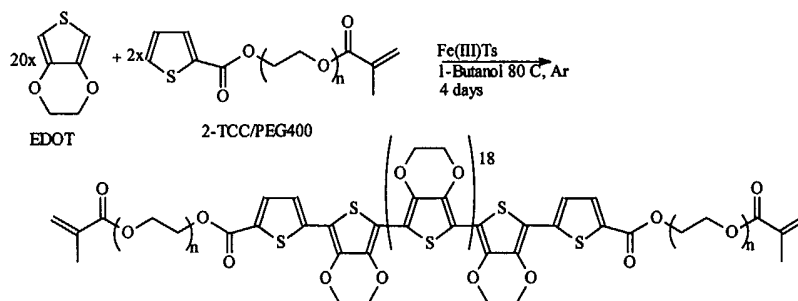
content of the flask was filtered and the blue/black solid collected on the frit was washed twice with 15ml CH_3NO_2 to remove FeCl_3 and FeCl_2 . The blue solid remaining on the frit was extracted with a total of 200ml CHCl_3 , and the CHCl_3 extract was dried *in vacuo*, yielding a total of 0.959g blue, hard and elastomeric solid. The yield was 49-51 % and the product was soluble in CHCl_3 . Films made of the product had a conductivity of $3.3\text{E}-03$ S/cm. The film containing a photo-initiator were photo-crosslinked to form non-soluble conducting films by a similar method to Example 11 Step C.

10 **Example 13: Synthesis of PEG400 methacrylate / thiophene -co- EDOT (BAB tri-block copolymer)**

Step A: synthesis of end-capped precursor

A methacrylate end-capped precursor was synthesized from poly(ethylene glycol) mono-methacrylate (MW=400) and 2-thiophenecarbonyl chloride as described in Example 12, Step A.

Step B: Synthesis of BAB tri-block copolymer



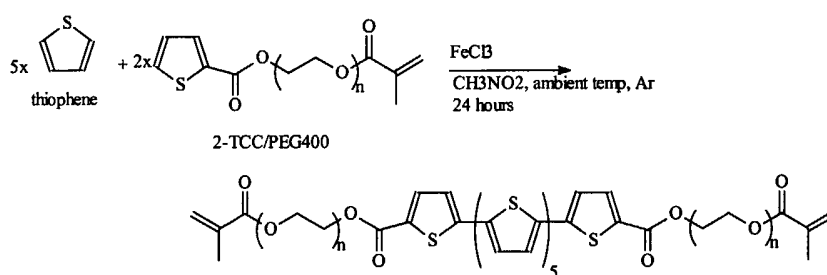
20 In a round bottomed flask 0.452 g 2-TCC/PEG 400 mono-methacrylate (1.14 mmol, precursor from Example 12 part A), 34.738 g of Baytron C, and 100 mL n-butanol were heated to 80 °C with stirring. 1.628 g EDOT (11.8 mmol) were added dropwise over 4 hours, The reaction mixture was cooled to r.t. and stirred for 4 days. The dark blue/green solution was filtered and extracted with water. The solution was cast onto a polycarbonate sheet to form a conducting film that can be partially re-dissolved in butanol.

Example 14: Synthesis of PEG400 methacrylate / thiophene – co – thiophene (BAB tri-block copolymer)

Step A: Synthesis of End-capped precursors

A methacrylate end-capped precursor was synthesized from poly(ethylene glycol) mono-methacrylate (MW=400) and 2-thiophenecarbonyl chloride as described in Example #12 Step A.

Step B: Synthesis of tri-block copolymer



10

Thiophene (0.524 g, 6.2 mmol), PEG400 mono-methacrylate / mono-thiophene (1.31 g, 2.6 mmol), FeCl₃ (2.74 g, 16.9 mmol), and CH₃NO₂ (100 mL) were mixed in a flask and stirred for 24 hours at ambient temperature under argon. The product solution was poured into 150 mL of 50:50 (v:v) mixture of Et₂O:HCl, conc. A solid precipitated and the liquid layers separated. The upper organic phase was separated and washed first with conc. HCl and then with water (5 times). Thin films made from this solution were conducting. The dry film could be re-dissolved completely in nitromethane and partially in butanol.

15

20 Example 15: Synthesis of di-ol BAB tri-block copolymers and conducting polyurethane coatings

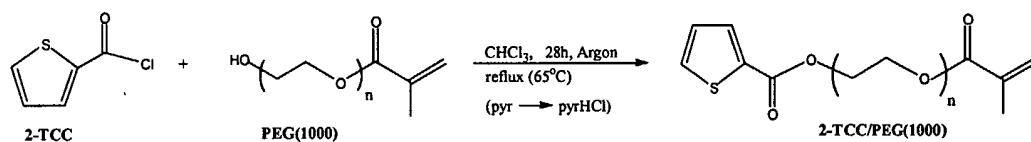
A di-ol triblock copolymer, of the structure HO-BAB-OH, was synthesized from 3,4-ethylenedioxythiophene and a precursor that contained a hydroxyl group at one end and an EDOT group at the other end. This precursor was prepared by reacting a mono-amino mono-hydroxyl terminated poly(ethylene glycol) oligomer with 3,4-ethylenedioxythiophene-2-carboxaldehyde under the conditions described in Example #18, Part A. 3,4-Ethylenedioxythiophene-2-carboxaldehyde was prepared

25

according to Mohanakrishnan method in high yield (Mohanakrishnan et al., *Tetrahedron*, **55**, 11745-11754 (1999)). The tri-block copolymers were made as follows: 2 mmol of PEGmonoEDOT with average molecular weight of 1500 Dalton and 170 mmol EDOT were mixed in butanol and heated at 80°C. To this solution, a solution of Baytron C from Bayer (50% iron p-toluenesulfonate in butanol) was added drop-wise over 30 minutes. The reaction was stirred at room temperature for 6 days then the product was filtered and extracted with copious amount of water. Butyl acetate (150 mL) was added under stirring and the butanol was removed by fractional distillation. The resulting butyl acetate suspension was mixed with a trimer of hexamethylene diisocyanate at a ratio NCO/OH of 1.2 (Bayhydrur XP 7007 from Bayer). This mixture was used to cast coatings on primed iron panels. The resulting polyurethane coatings had a conductivity of $1 \cdot 10^{-4}$ S/cm.

Example 16: Synthesis of poly(EDOT-*block*-EG 1500) with PEG 1000 endcaps
(endcapB'-ABABA-B'endcap multi-block copolymer):

Step A: Synthesis of end-groups

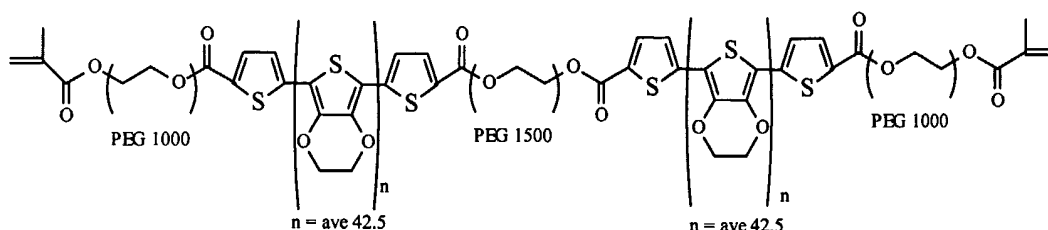


20

This reaction was conducted under argon using standard Schlenk techniques. 0.98g of pyridine and 11.40g PEG mono-methacrylate (MW=1000) were premixed in 130ml CHCl₃. 1.2ml 2-TCC was added dropwise with a syringe. The mixture was refluxed for 28h, then cooled to room temperature. No precipitate, (i.e., pyridine hydrochloride) was noted even after several hours. The solution was extracted with 5% HCl (aq.) then 5% NaHCO₃. CHCl₃ from the organic portion was removed by vacuum distillation leaving approximately 8g of a yellow liquid. The NMR spectrum was consistent with the desired product.

30 Step B: synthesis of PEG (1500) di-thiophene segments

PEGdTh (1500) was synthesized by the method in Example 2, Step A.

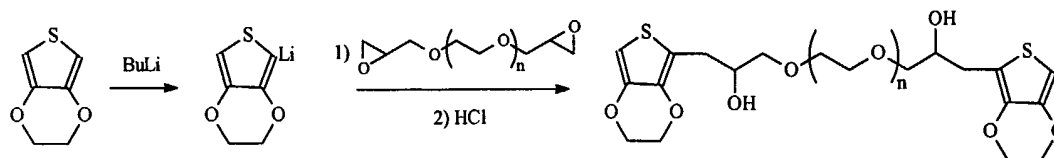
Step C: Synthesis of end-capped multi-block copolymer

- 5 In a 100 mL round-bottom flask, a mixture of PEGdTh (1500) (0.116g, 0.067 mmol), PEG1000monomethacrylate thiophene (153 g, 0.134 mmol) and Baytron C (16.59 g) were heated to 80°C with stirring. To the heated mixture, a solution of 0.805 g (5.7 mmol) of EDOT (Baytron M from Bayer) in 5 mL of *n*-butanol was added dropwise over 35 minutes. After the addition, the heater was switched off and the
- 10 reaction mixture was left stirring at room temperature for 7 days. A thick green-bluish solution was obtained. A fraction of this solution was tested for conductivity giving positive results. The solution was then filtered but no residue was collected. The sample was then extracted with an excess (10 times the organic phase) of water. Because water did not separate from the butanol phase, NaCl was added.
- 15 The extracted deep-blue organic phase was used to coat a polycarbonate sheet with a hand coater. The resulting coating was conductive. No precipitate was present after storing the deep-blue solution for two months.

Example 17: Synthesis of poly(EDOT-*block*-EG1098)20 STEP A: Synthesis of PEG(1098)dEDOT

A di-EDOT terminated poly(ethylene glycol) segment was synthesized by alkylation of a Poly(ethylene glycol) diglycidyl ether with lithiated EDOT (Keegstra, M.A.; T.A. Peters; L. Brandsma; (1992) "Copper (I) Catalysed Synthesis of Alkyl Aryl and AlkylHeteroaryl ethers," *Tetrahedron*, **48**, 3633-3652)

25



A solution of EDOT (5.408 g = 38.0 mmol, Bayer) in dry THF (20 ml) under argon was cooled to -80 C with an acetone/liquid nitrogen slurry. A 1.4 M solution of methyl lithium in diethyl ether (26.5 ml = 37.1 mmol, Aldrich) was added with stirring over the course of about one minute. Poly(ethylene glycol) diglycidyl ether with average molecular weight of 1098 Daltons (10.5 g = 9.56 mmol, Denacol EX 861 by Nagase America Corporation) diluted in 25 ml of dry THF was transferred to reaction flask. Upon addition, a thick cream-colored solid formed (the lithium alkoxide salt of the product). After addition, the flask was removed from the cold acetone bath and allowed to warm to room temperature. Two hours after the addition, approximately 50 ml of 5% HCl was added to the reaction flask, making the aqueous phase to pH ~ 1 . After 16 hours, the product was extracted with CH_2Cl_2 , washed with water (2x50 ml) and evaporated at reduced pressure and $\sim 35\text{ C}$ for 6 hours.

$^1\text{H-NMR}$ analysis showed that the crude contained the desired product and unreacted EDOT in a molar ratio of 1 : 2.6. Therefore the yield of the di-substituted product over the poly(ethylene glycol) diglycidyl ether is 64% and the yield over the EDOT (including the recovered unreacted materials) is 74%.

Step B: Synthesis of poly(EDOT-*block*-EG1098)

Para-toluenesulfonic acid (14.17g, 73.3mmol = 1.35eq), dodecylbenzenesulfonic acid (22.80g, 48.9mmol = 1.35eq), ammonium sulfate (8.36g, 36.2mmol = 1eq), and iron(III) sulfate (0.058g, 0.11mmol = 0.003eq) were mixed in 100mL of DI water. EDOT (5.18g, 36.2mmol = 1eq) was mixed with $\text{PEG}_{1098}\text{dEDOT}$ (1.27g, 0.904mmol = 1/40eq) in 200mL of 1-butanol and added dropwise to the aqueous solution over 4 hours. The resulting solution was stirred at room temperature for 24 hours. The organic layer was washed with water 3 times, then 2 times with concentrated sodium chloride solution, and 2 more times with DI water. A portion of the deep blue organic phase was dried in a vented oven and pressed to form a pellet with conductivity of $2.3 \cdot 10^{-3}\text{ S/cm}$.

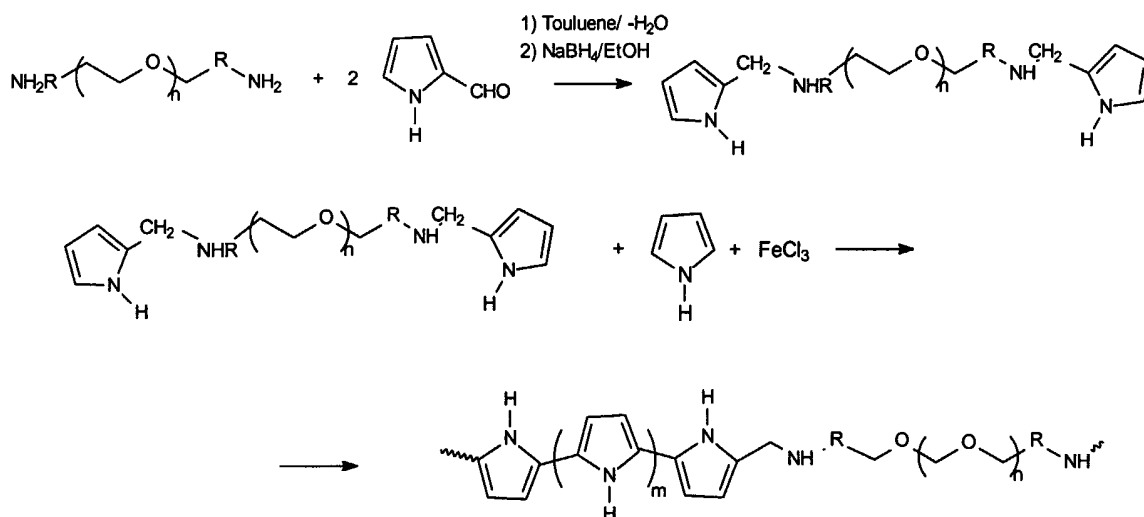
Alternative Step B: Synthesis of poly(EDOT-*block*-EG 1098)

In a 100 mL round-bottomed flask placed dEDOT PEG_{1098} (0.228 g, $1.655 \cdot 10^{-4}$ mole) was mixed with Baytron C from Bayer (45 g) and heated to 80°C . A solution

of EDOT (2 g, 0.014 mole) in 4 mL 1-butanol was added dropwise. At the end of the addition, the reaction mixture was removed from the oil bath and stirred at room temperature for 7 days. The blue fine dispersion was diluted with 15 mL of fresh 1-butanol and washed with 200 mL DI-water (x3). The organic phase was stored in a first vial. The combined aqueous fractions were extracted with 20 mL of fresh 1-butanol and this was stored in a second vial. Both samples were dried in a vented oven and tested for conductivity with a Jandel four point conductivity probe. The sample from the first vial had a conductivity of 3.4×10^{-2} S/cm, the sample from the second vial had a conductivity of 0.14 S/cm.

10

Example 18: Synthesis of Poly(pyrrole-block-ethylene glycol)



15 Step A: Synthesis of pyrrole end-capped poly(ethylene glycol) Jeffamine XTJ-500

In a 1000 mL three-necked round-bottomed flask equipped with a Dean Stark trap and a condenser, a diamino-terminated poly(ethylene glycol) having average molecular weight of 600 Daltons (Jeffamine XTJ-500 from Huntsman, 50 g, 0.083 mole) was dissolved in dry toluene (~250 mL) under argon atmosphere. The solution was heated to 70°C, pyrrole-2-carboxaldehyde (16.01 g, 0.167 mole) was added drop-wise, and the mixture refluxed at 80°C 3 hours under Ar. The brown solution was taken to dryness by rotavap and the residue was dissolved in ~ 250 mL of dry ethanol. The stirred solution was treated with NaBH₄ (6.38 g, 0.167 mole) at room temperature for one hour and acidified to a pH value of 2 with concentrated HCl. The precipitate was collected by filtration and discarded. Removal of the

25

solvent gave a thick, brown, oily residue that was dissolved in ~200 mL DI-water. The aqueous solution was washed with ~250 mL CH₂Cl₂ (2 times), and the pH was raised to 11 with a saturated solution of NaOH. An oil-like residue was extracted with fresh CH₂Cl₂ and the organic fraction was dried over MgSO₄ for 20 minutes.

5 Removal of the solvent gave the desired product (pyrrole end-capped XTJ-500 (dPyXTJ-500)) as dark brown, thick oil in 50% yield. ¹H-NMR (CDCl₃): δ (ppm) 6.697 (m, pyrrole), 6.071 (m, pyrrole), 5.988 (m, pyrrole), 3.804 (m, -CH₂-NH-), 3.602 (m, -CH₂-O-), 1.038 (m, -CH(CH₃)-O-).

10 Step B: Copolymerization of Pyrrole and Pyrrole end-capped XTJ-500

The synthesis of a block copolymer with a molar ratio of 40:1 between pyrrole and the pyrrole end-capped XTJ-500 (dPyXTJ-500) was carried out with ammonium persulfate as the oxidizing agent and dodecylbenzenesulfonic acid (DBSA) as counterion.

15

Pyrrole (35.4 g, 0.527 mole) was added to dPyXTJ-500 (10 g, 0.0132 mole) that has been diluted with 111.14 g DI-water and a two-phase system formed. Dodecylbenzenesulfonic acid (125.93 g, 0.27 mole) was then added to the mixture under stirring and the mixture formed an homogeneous brown solution. The solution
20 was diluted with 71.94 g of water, cooled to 0°C and an aqueous solution of ammonium persulfate (25.17 g in 100 g H₂O) was added dropwise over 15~20 minutes. The reaction mixture was stirred at 0°C for 48 hours and a suspension of blue/black polymer particles of medium size in a cloudy white solution was obtained.

25 A portion of this mixture (260 g) was diluted with 256.37 g of CHCl₃ and shaken to form an emulsion with no phase separation. The mixture was centrifuged at 9000 rpm for 3 to 5 minutes. After centrifugation, three bands formed: Top clear layer, an emulsion and the organic layer containing the majority of the product. The bottom organic band was separated and collected as a homogeneous thick black solution
30 with a copolymer concentration of 21 wt.%. . An aliquot was dried for conductivity. Conductivity of a pressed pellet was 4 10⁻³ S/cm as determined by the four point method. The dry polymer re-dispersed in chloroform and N-methylpyrrolidone very

rapidly. Residues, from chloroform and N-methylpyrrolidone solutions respectively were conductive.

5 **Example 19: Synthesis of block copolymer of polypyrrole containing ester linkages**

The synthesis of block copolymers of polypyrrole containing hydrolyzable (biodegradable) ester linkages was carried out in three steps: first 2-pyrrolecarboxyaldehyde was reacted with an excess of hexamethylene diamine, then
10 the pyrrole mono-end capped hexamethylene diamine was reacted by Michael addition with a diacrylate-terminate poly(ethylene glycol) segment. The product of this reaction was then copolymerized with pyrrole in the presence of ammonium persulfate and dodecylbenzenesulfonic acid. The product of this synthesis has uses in biomedical applications

15

Step A: Synthesis of pyrrole mono-end capped hexamethylenediamine

A 500 mL two-necked round-bottomed flask equipped with a Dean Stark trap and a condenser was placed in an oil bath and purged with argon. Hexamethylenediamine
20 (100 g, 0.843 mole) was added to 50 mL of dry toluene and the sample was heated to 100°C, then a solution of pyrrole-2-carboxaldehyde (3.21 g, 0.034 mole) in dry toluene (30 mL) was added dropwise. The reaction mixture was refluxed 3 hours at 140°C. The sample was partially cooled and the solvent and the excess hexamethylenediamine were removed under vacuum. The oily brown residue was
25 dissolved in dry ethanol (100 mL) and then treated with NaBH₄ (1.4 g, 0.037 mole) for one hour at room temperature. The mixture was acidified to pH 2 with concentrated HCl. The precipitate was removed and the filtrate was taken to dryness to give a thin brown oily residue. The solid precipitate was re-dissolved in 100 mL DI-water and washed with an excess of CH₂Cl₂. The aqueous phase was
30 brought to pH 11 with NaOH and extracted with fresh CH₂Cl₂. The organic fraction was dried over MgSO₄, filtered and taken to dryness to give the product as a redish brown oily residue with a yield of 65%. ¹H-NMR (CDCl₃): δ (ppm) 9.38 (s, -NH₂);

6.64, 6.06, 5.97 (m, 3H, Pyrrole Hs); 3.707 (s, 2H, pyrrole-CH₂-); 2.589 (m, 2H, -CH₂-NH₂); 1.338 (m, -CH₂-).

Step B: Michael Addition Reaction between Pyrrole mono-capped Hexamethylenediamine and Diacrylated PEG₆₀₀

5 A solution of pyrrole mono-capped hexamethylenediamine (1g, $5.12 \cdot 10^{-3}$ mole) in 12 mL acetone was placed in a 100 mL two-necked round-bottomed flask purged with Ar. The solution was heated to 40°C and slowly reacted with a solution of diacrylated polyethyleneglycol having average molecular weight of 742 Dalton (SR-610 from Sartomer, 1.9 g, $2.56 \cdot 10^{-3}$ mole) in 8 mL acetone. The reaction mixture
10 was diluted with 4 mL fresh acetone, refluxed for 5 hours and further stirred at room temperature overnight. The solvent was removed to give the desired product in quantitative yield as a brown thin oil-like residue. ¹H-NMR (CDCl₃): δ (ppm) 6.734, 6.086, 5.978 (Pyrrole Hs), 4.252 (m, 4H, -COO-CH₂-), 3.751 (m, 4H, -CH₂-pyrrole),
15 3.655 (-CH₂-O-), 2.771 (m, 4H, -CH₂-NH-pyrrole), 2.467 (m, 12H, -CH₂-NH-R), 1.414-1.267 (m, 16H, -CH₂- hexamethylenediamine).

Step C: Synthesis of Block Copolymer of Pyrrole and Michael Addition Product

20 A solution of the Michael addition product from Step B (2.0 g, $1.76 \cdot 10^{-3}$ mole) in 30 mL of DI-water was placed in a 100 mL Erlenmeyer flask. Pyrrole (4.73 g, $7.05 \cdot 10^{-2}$ mole) and dodecylbenzenesulfonic acid (DBSA, 16.9g, $7.21 \cdot 10^{-2}$ mole) were added to the solution under stirring. The sample was cooled to 0°C and slowly reacted with a solution of ammonium persulfate (3.29g, $1.44 \cdot 10^{-2}$ mole) in 30 mL water. The
25 reaction mixture was stirred at 0°C for 48 hours to obtain a thick, paste-like dark brown suspension. The raw material was extracted with CHCl₃ forming an excellent suspension that gels with time. A fraction of this suspension was taken to dryness at room temperature and the residue was pressed in a pellet for conductivity measurements. The conductivity measured with a four-point linear probe was $3.68 \cdot 10^{-2}$ S cm⁻¹.
30

Those of ordinary skill in the art will appreciate that starting materials, procedures, reactants, solvents, reaction conditions (temperature, solvent, reagent

and reactant concentrations, etc.) other than those specifically exemplified can be employed in the practice of this invention without resort to undue experimentation. The skilled artisan will further be aware of materials, methods and procedures which are functional equivalents of the materials, methods and procedures specifically exemplified herein. All such art-known functional equivalents are intended to be encompassed by this invention.

All references cited herein are incorporated by reference herein to the extent that they are not inconsistent with the teachings herein.

We claim:

1. A block copolymer which comprises at least one block of a poly(heteroaromatic) polymer and at least two blocks of a non-conjugated polymer.
5
2. The block copolymer of claim 1 which is an electrically conductive polymer when the poly(heteroaromatic) blocks are doped.
3. The block copolymer of claim 2 which, when doped, exhibits conductivity
10 between about 10^{-6} - 10^3 S/cm.
4. The block copolymer of claim 2 which, when doped, exhibits conductivity between about 10^{-3} - 10^2 S/cm.
- 15 5. The block copolymer of claim 2 which, when doped, exhibits conductivity greater than about 10^{-3} S/cm.
6. The block copolymer of claim 1 which, when doped, is soluble or dispersible in water, an organic solvent or in a mixture thereof at a concentration of at least
20 about 0.1g/liter.
7. The block copolymer of claim 1 which, when doped, is soluble or dispersible in water, an organic solvent or in a mixture thereof at a concentration of at least about 1.0% (weight/volume)
25
8. The block copolymer of claim 1 wherein the conducting poly(heteroaromatic) polymer blocks have molecular weight between about 70 to about 300,000 daltons.
9. The block copolymer of claim 1 wherein the non-conducting polymer blocks
30 have molecular weight between 40 to about 1×10^6 daltons.
10. The block copolymer of claim 1 wherein the non-conducting blocks are the same polymer.

11. The block copolymer of claim 1 wherein the non-conducting blocks are different polymers.
12. The block copolymer of claim 1 wherein the poly(heteroaromatic)polymer
5 block is made by polymerization of one or more heteroaromatic monomers selected from the group consisting of pyrroles, thiophenes, selenophenes tellurophenes, furans, indoles, isoinoles, isothianaphthalenes, pyridines, pyrimidines, pyrazines, triazines, thiazoles, imidazoles, quinolines, isoquinolines, benzimidazoles, thiazoles, triazoles, oxidiazoles, benzopyrrolines, dithienobenzene, thianaphtene, carbazoles,
10 benzothiophenes, isobenzothiophenes, benzofurans, isobenzofurans, isoindolines, isobenzoselenophenes, isobenzotellurophenes, and their substituted derivatives, and mixture thereof.
13. The block copolymer of claim 12 wherein the poly(heteroaromatic)polymer is
15 selected from the group consisting of polymers of pyrroles, thiophenes, and their substituted derivatives.
14. The block copolymer of claim 12 wherein the poly(heteroaromatic)polymer is made by oxidative copolymerization of 3,4-ethylenedioxythiophene and a non-
20 conducting block that is selected from the group of di-thiophene terminated polymer, di-(3,4-ethylenedioxythiophene)-terminated polymer, di-pyrrole terminated polymer, mono-thiophene terminated polymer, mono-pyrrole terminated polymer, and a mono-(3,4-ethylenedioxythiophene)-terminated polymer.
- 25 15. The block copolymer of claim 12 wherein the poly(heteroaromatic)polymer is made by oxidative polymerization of pyrrole and a non-conducting block that is selected from the group of di-pyrrole terminated polymer and mono-pyrrole terminated polymer.
- 30 16. A method for making a conducting polymer which comprises the steps:
modifying a non-conducting block with one or more linkage groups that undergo oxidative polymerization, and

copolymerizing the modified non-conducting block with a heteroaromatic monomer under oxidative conditions to form a tri- or a multi-block copolymer.

5 17. The method of claim 16 wherein the heteroaromatic monomer is selected from the group consisting of pyrroles, thiophenes, selenophenes tellurophenes, furans, indoles, isoinoles, isothianaphthalenes, pyridines, pyrimidines, pyrazines, triazines, thiazoles, imidazoles, quinolines, isoquinolines, benzimidazoles, thiazoles, triazoles, oxidiazoles, benzopyrrolines, dithienobenzene, thianaphthene, carbazoles,
10 benzothiophenes, isobenzothiophenes, benzofurans, isobenzofurans, isoindolines, isobenzoselenophenes isobenzotellurophenes, and their substituted derivatives.

18. The method of claim 16 wherein the heteroaromatic monomer is a pyrrole, a thiophene or their substituted derivatives.

15

19. The method of claim 16 wherein the copolymerization step is a free radical polymerization.

20. A block copolymer which comprises at least one block of a poly(heteroaromatic) polymer and at least two blocks of a non-conjugated polymer wherein the non-conducting blocks contain functional groups that can undergo further polymerization reactions.

21. The block copolymer of claim 20 which is a conductive polymer when the poly(heteroaromatic) blocks are doped.
25

22. The block copolymer of claim 20 wherein the polymerizable groups are selected from the group consisting of acrylates, methacrylates, hydroxyl groups, epoxy groups, isocyanates, dienes, vinyl groups, and vinyl ethers.

30

23. The block copolymer of claim 20 wherein where polymerizable groups are selected from acrylates and methacrylates.

24. Polymerized or cross-linked materials made by polymerization of the compounds in claim 20
25. Polymerized or cross-linked materials of claim 24 made by by free radical
5 polymerization.
26. A non-conducting polymer containing one or two terminal groups that undergo oxidative polymerization and are selected from the group of 2-pyrrolyl-, 2-(N-methyl)pyrrolyl-, 2-(3-alkyl)pyrrolyl-, 2-(4-alkyl)pyrrolyl-, 2-(3-alkoxy)pyrrolyl-, 2-(4-
10 alkoxy)pyrrolyl-, 2-(3-phenyl)pyrrolyl-, 2-(4-phenyl)pyrrolyl-, 2-(3,4-ethylenedioxy)pyrrolyl-, 2-thienyl-, 2-(3-alkyl)thienyl-, 2-(4-alkyl)thienyl-, 2-(3-alkoxy)thienyl-, 2-(4-alkoxy)thienyl-, 2-(3-phenyl)thienyl-, 2-(4-phenyl)thienyl-, 2-(3,4-alkylenedioxy)thienyl-, 2-(3,4-ethylenedioxy)thienyl-, and 2-isothianaphthalenyl-.

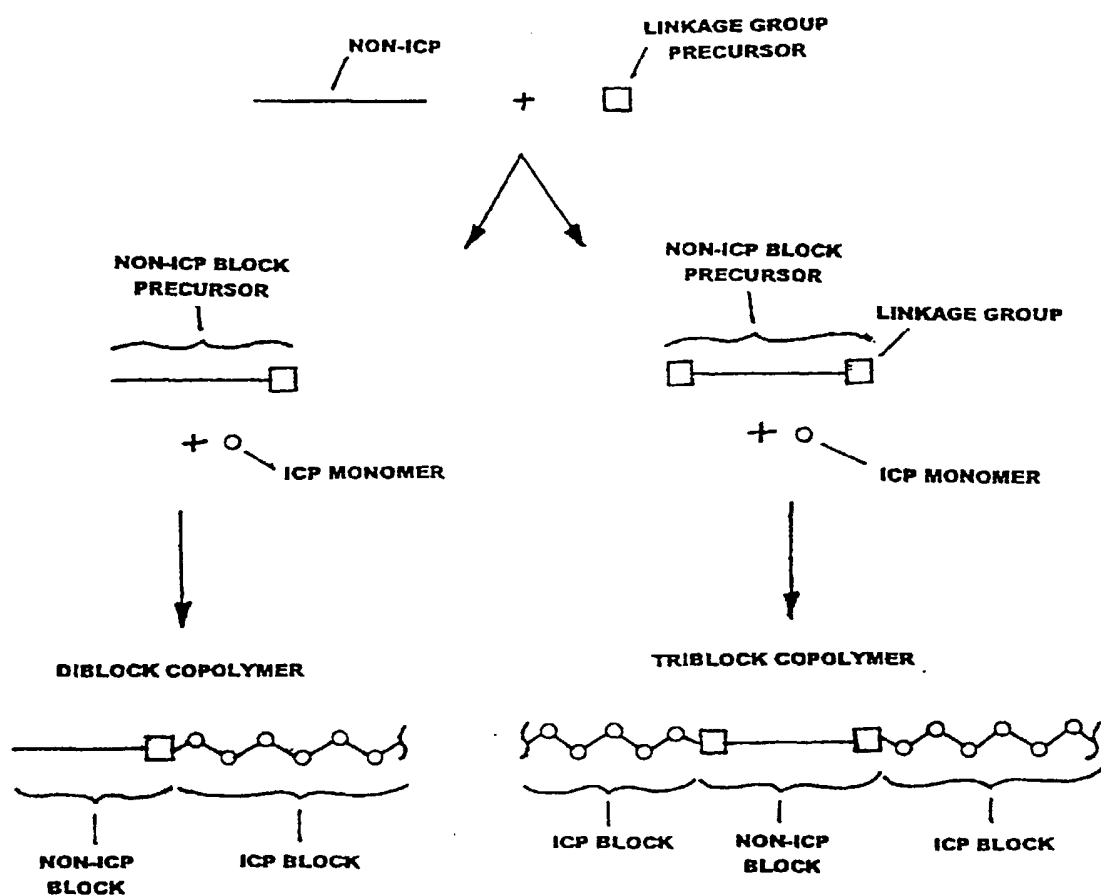
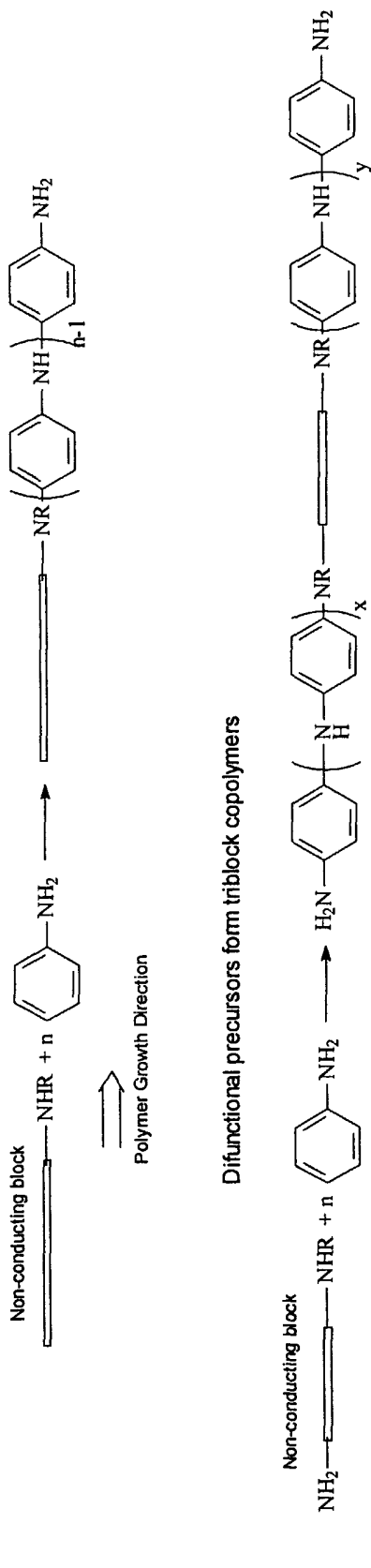


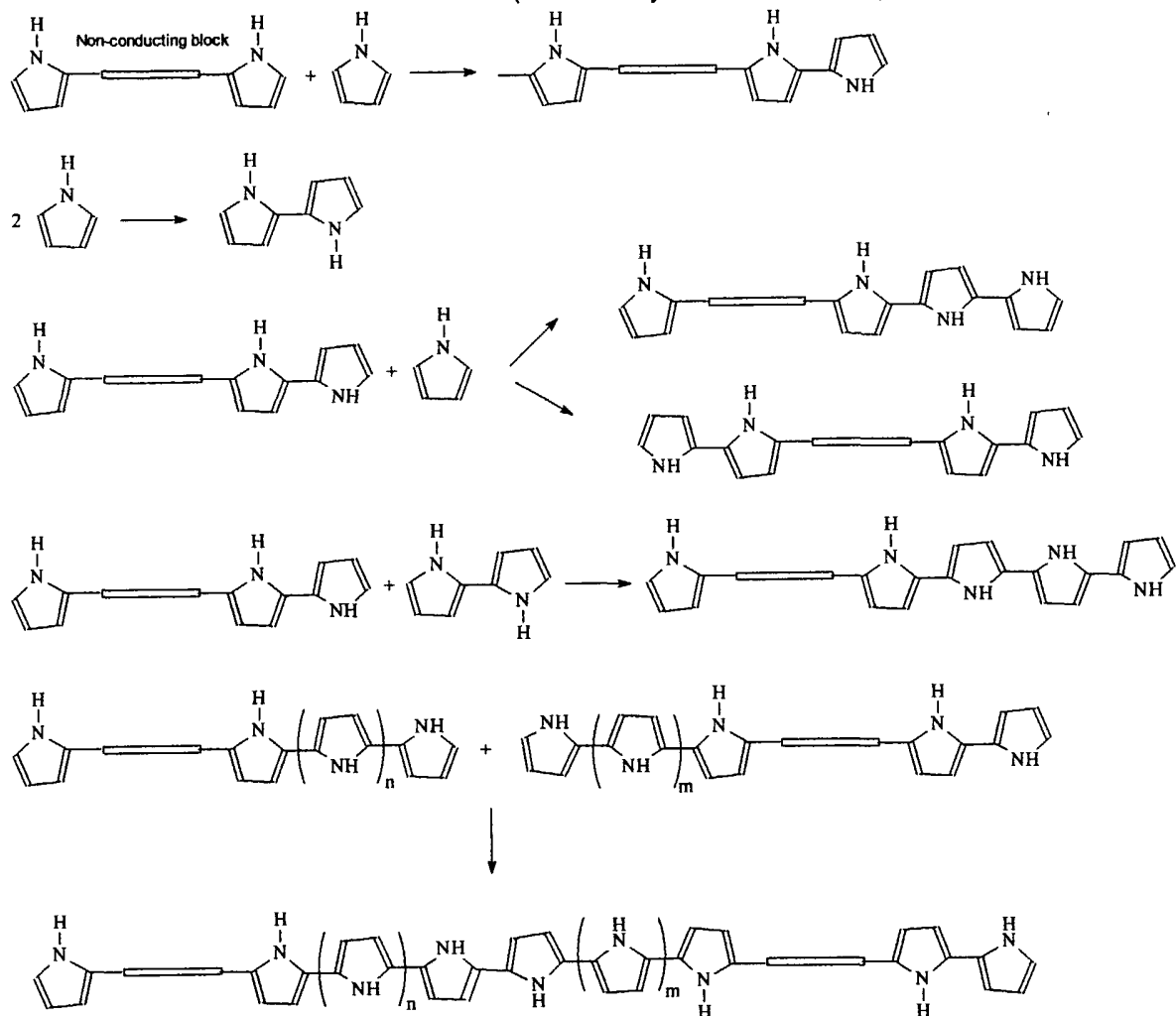
Fig. 1



Head-to-tail polymerization of aniline and other asymmetric monomers forms only ABA block copolymers

Fig. 2

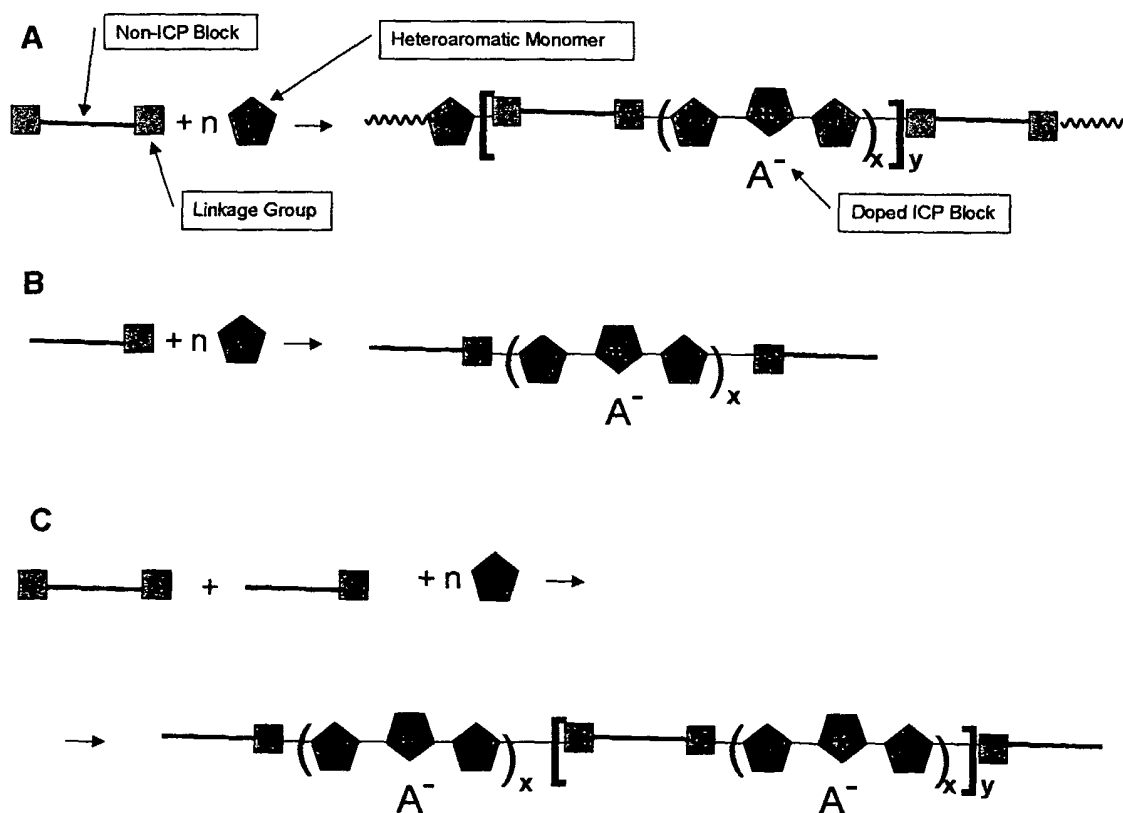
Polymerization of EDOT, Pyrrole, and Thiophene by statistical coupling of growing segments in solution (and other symmetric monomers)



Formation of Multiblock copolymers

The polymerization of pyrrole, thiophene, and their derivatives occurs because random coupling of radical cations: multi-block ABABAB are formed.

Fig. 3




Synthesis of ABABABA multi-block, BAB tri-block, and capped BABAB multi-block copolymers where A is the ICP block and B is the non-ICP block

Fig. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US02/28064

<p>A. CLASSIFICATION OF SUBJECT MATTER IPC(7) :C08F 126/06, 26/06, 234/04 US CL :525/256, 259, 261; 526/256, 258, 251, 263; 528/380 According to International Patent Classification (IPC) or to both national classification and IPC</p>														
<p>B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) U.S. : 525/256, 259, 261; 526/256, 258, 251, 263; 528/380</p> <p>Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched</p> <p>Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WEST, search terms: heteroaromatic polymer or heteroaromatic copolymer or heteroaromatic block copolymer, electrically conductive, doped</p>														
<p>C. DOCUMENTS CONSIDERED TO BE RELEVANT</p> <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X</td> <td>US 4,900,782 A (HAN et al) 13 FEBRUARY 1990</td> <td>1-2, 11-13, 15-26</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	US 4,900,782 A (HAN et al) 13 FEBRUARY 1990	1-2, 11-13, 15-26						
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.												
X	US 4,900,782 A (HAN et al) 13 FEBRUARY 1990	1-2, 11-13, 15-26												
<p><input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.</p>														
<table border="0"> <tr> <td>* Special categories of cited documents:</td> <td>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td> </tr> <tr> <td>"A" document defining the general state of the art which is not considered to be of particular relevance</td> <td>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td> </tr> <tr> <td>"E" earlier document published on or after the international filing date</td> <td>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td> </tr> <tr> <td>"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td> <td>"G" document member of the same patent family</td> </tr> <tr> <td>"O" document referring to an oral disclosure, use, exhibition or other means</td> <td></td> </tr> <tr> <td>"P" document published prior to the international filing date but later than the priority date claimed</td> <td></td> </tr> </table>			* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"G" document member of the same patent family	"O" document referring to an oral disclosure, use, exhibition or other means		"P" document published prior to the international filing date but later than the priority date claimed	
* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention													
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone													
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art													
"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"G" document member of the same patent family													
"O" document referring to an oral disclosure, use, exhibition or other means														
"P" document published prior to the international filing date but later than the priority date claimed														
Date of the actual completion of the international search 24 OCTOBER 2002		Date of mailing of the international search report 18 DEC 2002												
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer JAMES SEIDLECK Telephone No. (703) 308-0661 Jean Prost Parisien 												

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US02/28064

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- The additional search fees were accompanied by the applicant's protest.
 No protest accompanied the payment of additional search fees.