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(54) Title: POLYMERIZATION METHOD AND PRODUCT

(57) Abstract: Methods of preparing a polyaniline homopolymer or copolymer comprising at least one carboxylic acid group, and homopolymers or copolymers arising therefrom, the methods comprising: preparing a solution of a polyaniline precursor having at least one aromatic amine group and at least one carboxylic acid group (eg. 2-aminobenzoic acid, 3-aminobenzoic acid or 4-aminobenzoic acid) in a solvent selected from aqueous methanesulfonic acid or aqueous ammonia and optionally one or more additional polyaniline precursors (such as aniline); and oxidatively polymerising the polyaniline precursor or precursors.

TITLE: POLYMERIZATION METHOD AND PRODUCT

TECHNICAL FIELD

The invention relates to processes for preparing polymers that include aminobenzoic acid monomers, and to copolymers and homopolymers prepared by those processes.

BACKGROUND ART

Polymers of aniline and its derivatives are useful as antimicrobial agents and have good antistatic and free radical scavenging properties. These properties make them useful for the manufacture of antimicrobial, antistatic and antioxidant objects, and suitable for use in, for example, the health, food, packaging, water, paint, wood, textile, poultry, glass, paper, rubber, ceramic, seafood, sports, plastic and agricultural industries.

Adding substituents to polyaniline (PANI) is one way in which the various properties of the polymer can be improved. However, the synthesis of substituted PANIs is not always a straightforward matter. Any substituent introduced to the aniline building block needs to be compatible with the reagents used, which is not always possible under the traditionally robust oxidative polymerisation conditions used to form PANIs.

Carboxylated PANIs are one type of PANI derivative of particular interest due to their good antibacterial properties. Carboxylated PANIs can either be homopolymers, which could also be described as a poly(aminobenzoic acid) (poly ABAs) or copolymers, which could be considered as a PANI backbone bearing carboxylic acid groups on some of the aromatic rings. Figure 1 shows the probable structure of poly(2-aminobenzoic acid) and poly(3- aminobenzoic acid). Figure 2 shows the probable structure of copolymers of aniline and 2-aminobenzoic acid or 3-aminobenzoic acid, where X and Y are the numbers of repeat units.

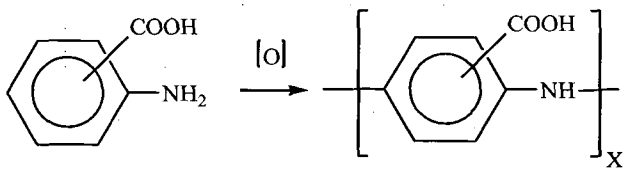


Figure 1

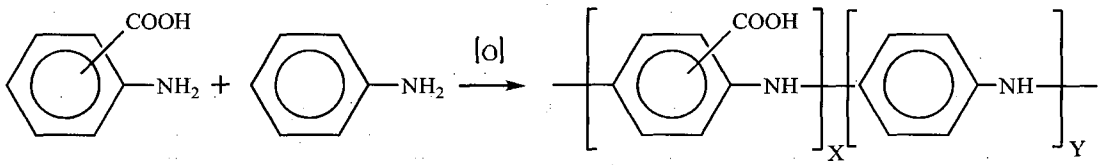


Figure 2

However, producing PANI homopolymers and copolymers from aminobenzoic acid (ABA) monomers in good yield and purity is not a simple procedure. There are significant problems with the solubilities of ABAs. ABAs tend to be solids, unlike aniline itself or many substituted anilines (alkyl anilines like toluidine, alkoxy anilines like anisidine etc) which can be used directly in their liquid form. This low solubility impacts upon the cost of synthesis and the quality of the resultant polymers.

There thus exists a need to produce poly-ABAs (carboxylated PANIs) in high yield and in a cost effective manner, with high conversion of monomer units, short production time and high molecular weights.

It is an object of the present invention to overcome or ameliorate at least one of the disadvantages of the prior art, or to provide a useful alternative.

SUMMARY

In a broad aspect, the invention provides a method of preparing a polyaniline homopolymer or copolymer comprising at least one carboxylic acid group; the method comprising:
preparing a solution of a polyaniline precursor having at least one aromatic amine group and at least one carboxylic acid group in a solvent selected from aqueous methanesulfonic acid or aqueous ammonia and optionally one or more additional polyaniline precursors; and
oxidatively polymerising the polyaniline precursor or precursors.

Unless the context clearly requires otherwise, throughout the description and the claims, the words "comprise", "comprising", and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of "including, but not limited to".

In one aspect, the invention provides a method of preparing a polyaniline homopolymer comprising carboxylic acid groups; the method comprising:
preparing a solution of a polyaniline precursor having at least one aromatic amine group and at least one carboxylic acid group in aqueous methanesulfonic acid; and
oxidatively polymerising the polyaniline precursor having at least one aromatic amine group and at least one carboxylic acid group.

In one aspect, the invention provides a method of preparing a polyaniline homopolymer comprising carboxylic acid groups; the method comprising:
preparing a solution of a polyaniline precursor having at least one aromatic amine group and at least one carboxylic acid group in aqueous ammonia; and
oxidatively polymerising the polyaniline precursor having at least one aromatic amine group and at least one carboxylic acid group.

The polyaniline precursor having at least one aromatic amine group and at least one carboxylic acid group may be any aromatic ring bearing $-NH_2$ and -COOH moieties in any position, with or without other substituents. In certain preferred embodiments,

the substance being polymerised is selected from 2-aminobenzoic acid, 3-aminobenzoic acid or 4-aminobenzoic acid.

Monomers other than amino benzoic acids can be used, for example aniline or pyrrole, or derivatives thereof may be used.

In one aspect, the invention provides a method of preparing a polyaniline copolymer comprising at least one carboxylic acid group; the method comprising: preparing a solution of a polyaniline precursor having at least one aromatic amine group and at least one carboxylic acid group in aqueous methanesulfonic acid and one or more additional polyaniline precursors; and

oxidatively polymerising the polyaniline precursor having at least one aromatic amine group and at least one carboxylic acid group and the one or more additional polyaniline precursors.

In one aspect, the invention provides a method of preparing a polyaniline copolymer comprising at least one carboxylic acid group; the method comprising: preparing a solution of a polyaniline precursor having at least one aromatic amine group and at least one carboxylic acid group in aqueous ammonia and one or more additional polyaniline precursors; and

oxidatively polymerising the polyaniline precursor having at least one aromatic amine group and at least one carboxylic acid group and the one or more additional polyaniline precursors.

The polyaniline precursor having at least one aromatic amine group and at least one carboxylic acid group may be any aromatic ring bearing $-NH_2$ and -COOH moieties in any position, with or without other substituents. In certain preferred embodiments, the substance being polymerised is selected from 2-aminobenzoic acid, 3-aminobenzoic acid or 4-aminobenzoic acid. The one or more additional polyaniline precursors may be any amino substituted aromatic ring, which is in some cases preferably comprises aniline.

Figure 3 shows a possible structure of poly(4-aminobenzoic acid).

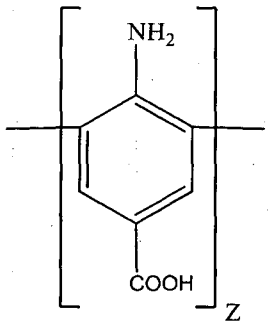


Figure 3

Monomers other than amino benzoic acids can be used, for example aniline and other derivatives thereof or pyrrole and derivatives thereof may be used.

The most preferred copolymers are those formed from mixtures of aniline and 2-aminobenzoic acid, aniline and 3-aminobenzoic acid or aniline and 4-aminobenzoic acid. Figure 4 shows a possible structure of copolymers of aniline and 4-aminobenzoic acid. Y and Z are the numbers of repeat units.

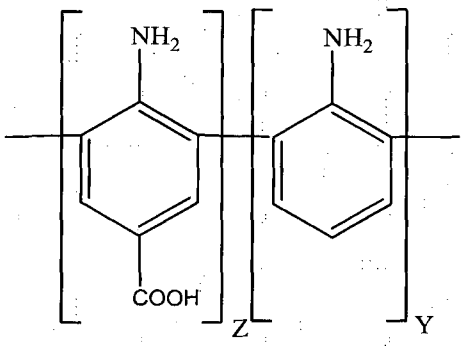


Figure 4

The ratio of the polyaniline precursor having at least one aromatic amine group and at least one carboxylic acid group: the one or more additional polyaniline precursors is from 99:1 to 1:99. Alternatively, ratios in the range 72:25 to 25:75 may be used.

If aqueous methane sulfonic acid is used, it is preferably in a concentration of 0.1 to 10 M in water. It is generally preferred if the ratio of concentration of ABA to methanesulfonic acid is from 2:1 to 1:2. For example, it is preferred to use a solution of methanesulfonic acid of around 1 M and an ABA concentration of around 0.5 M.

The polyaniline precursor having at least one aromatic amine group and at least one carboxylic acid group is preferably dissolved in the aqueous methane sulfonic acid and oxidising agent is added. If a copolymer is desired, additional polyaniline precursors may be added in a suitable compatible solvent, which may include water or aqueous methane sulfonic acid.

If ammonia is used, the polyaniline precursor having at least one aromatic amine group and at least one carboxylic acid group is suspended in water and ammonia is added to dissolve it. The amount and concentration required can be readily determined. Typically, commercial strength ammonia is added to a suspension of the ABA in water until the monomer is dissolved. The pH is readily maintained at around neutral to slightly alkaline pHs, for example around pH 7-8.

The reaction of aminobenzoic acid and/or aniline to synthesize the homopolymer or copolymer is carried out in an acidic or near neutral medium in the presence of an oxidizing agent. Any suitable oxidizing agent may be used. Suitable oxidizing agents include, although are not limited to ammonium persulphate, potassium ferricyanide, potassium iodate, hydrogen peroxide, cerium (IV) sulphate, potassium dichromate and sodium vanadate. For neutral/alkaline based reaction, preferably the oxidizing agent is ammonium persulphate or hydrogen peroxide.

The methods of the present invention will also usually further include the step of collecting the precipitated poly aminobenzoic acid homopolymer or copolymer by filtration.

DESCRIPTION

Aminobenzoic acids have low solubility in water and in common acids used to carry out oxidative polymerization. For example, 3-ABA has only around 5 wt% solubility in 1 M HCl, which is typical for ABAs generally. Even if the aminobenzoic acids can be dissolved to some extent, it is difficult to get them into solution at sufficiently high concentrations to achieve good yields of the resultant polyaniline polymer or copolymer. The present inventors have developed solvent systems based around methanesulfonic acid or ammonia that enable the monomer to be dissolved in MSA or ammonia at high concentration (15% by weight or higher)

The methods of the present invention enable the practical large scale production of PANIs, particularly those starting from amino benzoic acid derivatives, at room temperature. Because of the good solubility of the starting monomers, the reaction yield and starting monomer consumption is high and the reaction time is reduced, resulting in a less wasteful and more economic synthesis. Moreover, the products of the present invention have been found to have high molecular weight and, where copolymers are concerned, high incorporation of n-ABA in the resultant copolymer is observed.

COMPARATIVE EXAMPLES

Oxidative polymerisation of 3-amino benzoic acid to the corresponding polycarboxylated PANI was carried out under standard conditions using 1M HCl as monomer solvent and APS as oxidant.

From 150 ml 1 M HCl solution containing 2.2 g (16 mmol) 3-ABA, 0.0154 g polymer was obtained (0.7% yield*) when the reaction was performed at 10°C for 7 days

From 200 g 1 M HCl solution containing 10 g n-ABA monomer, 1 g polymer was obtained (10% yield*), when the reaction was performed at room temperature for 48 h

*Yield: = 100 × [mass of the polymer]/[mass of the (co)monomer(s)]

INVENTIVE EXAMPLES

METHANE SULFONIC ACID AS SOLVENT

Poly(n-amino benzoic acid) homopolymers, where n=2, 3 or 4 (P(n-ABA)) and poly(n-amino benzoic acid-co-aniline) copolymers (P(n-ABA-co-Ani)) were synthesised in 1 M methane sulfonic acid (MSA) at 25°C (ambient temperature), with ammonium persulfate (APS) as the oxidizing agent. The monomer(s) concentration and the mole ratio of monomer(s) to APS were kept constant at 0.5 M and 1:1.25 respectively. The mole ratio of n-aminobenzoic acid (n-ABA) to aniline (Ani) in the comonomer mixtures was varied from 99:1 to 1:99, or more usually 75:25 to 25:75.

The maximum concentration of n-aminobenzoic acid (n-ABA) in 1 M MSA is about 15%, which may be higher in more concentrated MSA.

HOMOPOLYMERS

Homopolymers of the present invention can be designated as follows:
HpMn: Hp = Homopolymer, M = methane sulfonic acid (MSA), n = position of -COOH functional group (4 or 3 or 2) in n-ABA precursor.
HpAn: Hp = Homopolymer, A = ammonia, n = position of -COOH functional group (4 or 3 or 2) in n-ABA precursor.

Synthesis of PANI homopolymers of aminobenzoic acids P(n-ABA): 13.86 g of 4-ABA was dissolved in 100 mL of 1 M MSA. 28.52 g of APS was dissolved in 100 mL of water and added dropwise to the monomer solution with constant stirring. Polymerisation was continued with stirring for 24 h. The polymeric product that precipitated from the solution was collected by filtration, washed thoroughly with distilled water then (vacuum) dried at 50°C. From this process 7.2 g polymer HpM4 was obtained (52% yield).

The yield can be seen to be significantly better than that obtained from the use of HCl as solvent.

The use of 3-ABA and 2-ABA in an identical manner resulted in the synthesis of a homopolymer of 3-aminobenzoic HpM3 and a homopolymer of 2-aminobenzoic acid HpM2 respectively.

Table 1 shows the properties of HpMn homopolymers synthesised using MSA as solvent. The yields are significantly better than using traditional solvents, such as HCl.

TABLE 1

Material	Monomer	Colour	Yield (%)	Mol wt. (g/mol)	Antimicrobial property (Minimum inhibitory concentration) %		Free radical scavenging (µmol DPPH scavenged/mg of sample) %	Conductivity (S/cm)
					Gram +ve (*S. aureus*)	Gram –ve (*E. coli*)		
HpM4	4ABA	Dark brown	52	19826	0.5	1	64	$<10^{-5}$
HpM3	3ABA	Dark brown	18	12947	1	>2%	60	$<10^{-5}$
HpM2	2ABA	Dark brown	30	22200	0.25	1	61	$<10^{-5}$

COPOLYMERS

Copolymers of the present invention can be designated as follows:

CpMnYZ: Cp = Copolymer, M = methane sulfonic acid (MSA), n = position of -COOH functional group (4 or 3 or 2) in n-ABA precursor, YZ ratio Y:Z of n-ABA:aniline in feed.

CpAnYZ: Cp = Copolymer, A = ammonia, n = position of -COOH functional group (4 or 3 or 2) in n-ABA precursor, YZ ratio Y:Z of n-ABA:aniline in feed.

Synthesis of copolymers of aminobenzoic acids and aniline P(n-ABA-co-Ani): For a typical synthesis of P(n-ABA-co-Ani) (starting from a solution with equimolar proportions of comonomers, for example), 6.94 g of n-ABA was dissolved in 100 mL of 1 M MSA. 4.66 g aniline was added to this solution and stirred for 15 mins. 28.52 g of APS was dissolved in 100 mL of water and added dropwise to the solution of the monomers with constant stirring. Polymerisation was continued with stirring for 24 h. The polymer product that precipitated from the solution was collected by filtration, washed thoroughly with distilled water then (vacuum) dried at 50°C.

Oxidative synthesis of copolymer CpM411: 6.94 g of 4-ABA was dissolved in 100 mL of 1 M MSA. 4.66 g aniline was added to this solution and stirred for 15 mins. 28.52 g of APS was dissolved in 100 mL of water and added dropwise to the solution of the monomers with constant stirring. Polymerisation was continued with stirring for 24 h. The polymer product that precipitated from the solution was collected by filtration, washed thoroughly with distilled water then (vacuum) dried at 50°C. From this process 11.6 g copolymer (CpM411) was obtained (100% yield).

Under similar conditions, copolymers of 4-ABA and aniline, copolymers of 3-ABA and aniline, copolymers of 2-ABA and aniline at various monomer feed ratio (from 99:1 to 1:99) can be synthesized.

Table 2 shows the properties of copolymers (CpMnYZ) synthesised in acidic medium.

TABLE 2

Material	Monomer ratio (n-ABA: Aniline)	Colour	Yield (%)	Antimicrobial property (Minimum inhibitory concentration) %		Free radical scavenging (micromoles of DPPH scavenged/mg of sample) %	Conductivity (S/cm)
				Gram +ve (*S. aureus*)	Gram –ve (*E. coli*)		
CpM431	4ABA: Aniline (3:1)	Dark brown	78	0.25	2	57	$<10^{-5}$
CpM411	4ABA: Aniline (1:1)	Dark brown	100	0.5	>2	59	0.002
CpM413	4ABA: Aniline (1:3)	Dark green	112	0.5	>2	60	1
CpM331	3ABA: Aniline (3:1)	Dark brown	85	0.5	2	57	$<10^{-5}$
CpM311	3ABA: Aniline (1:1)	Dark brown	101	2	>2	54	0.002
CpM313	3ABA: Aniline (1:3)	Dark green	114	>2	>2	46	0.6
CpM231	2ABA: Aniline (3:1)	Dark brown	78	0.5	2	54	$<10^{-5}$
CpM211	2ABA: Aniline (1:1)	Dark brown	81	0.5	>2	47	0.04
CpM213	2ABA: Aniline (1:3)	Dark green	121	0.5	>2	54	2

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AMMONIA AS SOLVENT

HOMOPOLYMERS

Synthesis of HpA4 in non-acidic medium (by neutralizing monomer with ammonia): 13.86 g monomer (4-ABA) was dissolved in 100 mL water by neutralizing with 7.5 mL of 28% ammonia. 28.52 g of APS was dissolved in 92.5 mL of water and added dropwise to the monomer solution with constant stirring. Polymerisation was continued with stirring for 24 h. The polymeric product that precipitated out from the solution was collected by filtration, washed thoroughly with distilled water then (vacuum) dried at 50°C. From this process 11.37 g polymer HpA4 was obtained (82% yield).

Again, the yield can be seen to be significantly better than that obtained from the use of HCl as solvent. Under the same conditions HpA3 and HpA2 can be synthesized in non-acidic medium (by neutralizing monomer with ammonia.)

Figure 5 below shows a possible reaction scheme for synthesis of poly(4-aminobenzoic acid).

Figure 5

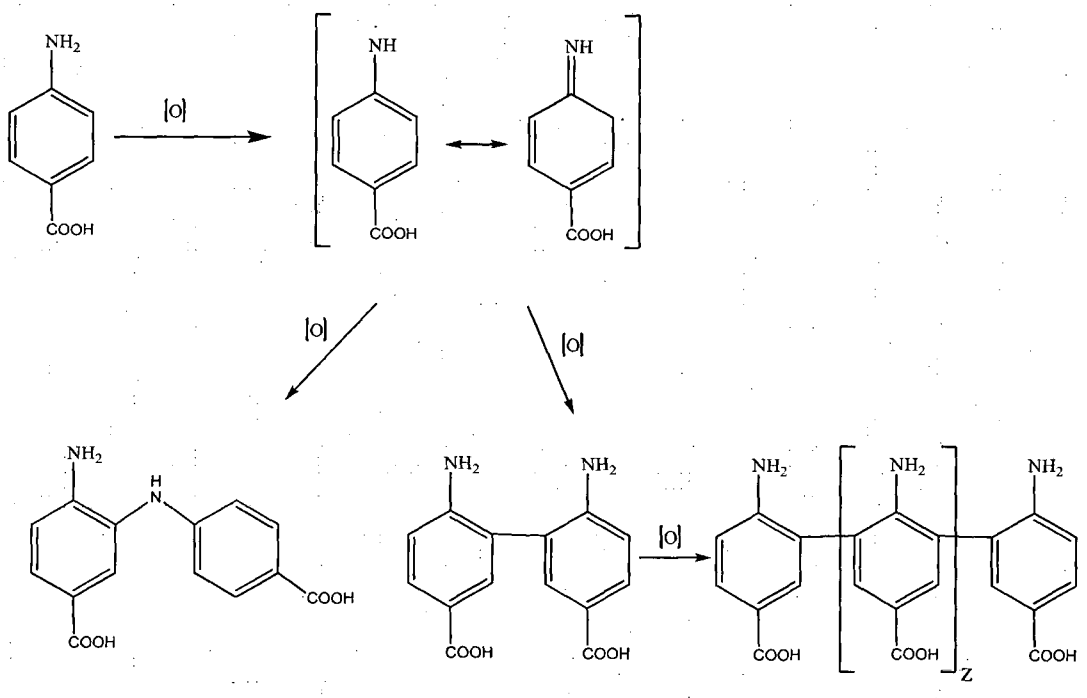


Table 3 shows the properties of HpAn homopolymers synthesised by pre-neutralization with ammonia

TABLE 3

Material	Monomer	Colour	Yield (%)	Mol wt (g/mol)	Antimicrobial property (Minimum inhibitory concentration) %		Free radical scavenging (μmol DPPH scavenged/ mg of sample) %	Conductivity (S/cm)
					Gram +ve (*S. aureus*)	Gram –ve (*E. coli*)		
HPA4	4ABA	Dark brown	82	18362	0.125	>2	55	$<10^{-5}$
HPA3	3ABA	Dark brown	82	62847	1	2	61	$<10^{-5}$
HPA2	2ABA	Dark brown	71	44645	0.5	1	56	$<10^{-5}$

COPOLYMERS

Oxidative synthesis of copolymer CpA411: 6.94 g monomer (4-ABA) was dissolved in 100 mL water by neutralizing with 4 mL of 28% ammonia. 4.66 g aniline was added to this solution and stirred for 15 mins. 28.52 g of APS was dissolved in 96 mL of water and added dropwise to the monomer solution with constant stirring. Polymerisation was continued with stirring for 24 h. The polymeric product that precipitated out from the solution was collected by filtration, washed thoroughly with distilled water then (vacuum) dried at 50°C. From this process 10.2 g copolymer (CpA411) was obtained (88% yield).

Under similar conditions, copolymers of (4-ABA) and aniline, (3-ABA) and aniline, and (2-ABA) and aniline at various monomer feed ratio (can be from 99:1 to 1:99) can be synthesized in acidic medium.

Table 4 shows a property chart of copolymers (CpAnYZ) synthesised by pre-neutralization of monomer n-ABA with ammonia.

TABLE 4

Material	Monomer ratio (n-ABA: Aniline)	Colour	Yield (%)	Antimicrobial property (Minimum inhibitory concentration) %		Free radical scavenging (micromoles of DPPH scavenged/mg of sample) %	Conductivity (S/cm)
				Gram +ve (*S aureus*).	Gram –ve (*E. coli*)		
CpA431	4ABA: Aniline (3:1)	Dark brown	83	0.06%	>2%	60	$<10^{-5}$
CpA411	4ABA: Aniline (1:1)	Dark brown	88	0.13%	>2%	58	$<10^{-5}$
CpA413	4ABA: Aniline (1:3)	Dark green	90	0.25%	>2%	55	0.0003
CpA331	3ABA: Aniline (3:1)	Dark brown	83	0.125	>2	58	$<10^{-5}$
CpA311	3ABA: Aniline (1:1)	Dark brown	87	0.125	>2	61	$<10^{-5}$
CpA313	3ABA: Aniline (1:3)	Dark green	85	0.25	>2	55	0.00005
CpA231	2ABA: Aniline (3:1)	Dark brown	72	0.125	1	53	$<10^{-5}$
CpA211	2ABA: Aniline (1:1)	Dark brown	91	0.125	2	52	$<10^{-5}$
CpA213	2ABA: Aniline (1:3)	Dark green	93	0.25	>2	56	$<10^{-5}$

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A method of preparing a polyaniline homopolymer or copolymer comprising at least one carboxylic acid group; the method comprising:
preparing a solution of a polyaniline precursor having at least one aromatic amine group and at least one carboxylic acid group in a solvent selected from aqueous methanesulfonic acid or aqueous ammonia and optionally one or more additional polyaniline precursors; and
oxidatively polymerising the polyaniline precursor or precursors.

2. A method of preparing a polyaniline homopolymer comprising carboxylic acid groups; the method comprising:
preparing a solution of a polyaniline precursor having at least one aromatic amine group and at least one carboxylic acid group in aqueous methanesulfonic acid; and
oxidatively polymerising the polyaniline precursor having at least one aromatic amine group and at least one carboxylic acid group.

3. A method of preparing a polyaniline homopolymer comprising carboxylic acid groups; the method comprising:
preparing a solution of a polyaniline precursor having at least one aromatic amine group and at least one carboxylic acid group in aqueous ammonia; and
oxidatively polymerising the polyaniline precursor having at least one aromatic amine group and at least one carboxylic acid group.

4. A method according to any one of the preceding claims wherein the polyaniline precursor having at least one aromatic amine group and at least one carboxylic acid group is selected from 2-aminobenzoic acid, 3-aminobenzoic acid or 4-aminobenzoic acid.

5. A method of preparing a polyaniline copolymer comprising at least one carboxylic acid group; the method comprising:

preparing a solution of a polyaniline precursor having at least one aromatic amine group and at least one carboxylic acid group in aqueous methanesulfonic acid and one or more additional polyaniline precursors; and

oxidatively polymerising the polyaniline precursor having at least one aromatic amine group and at least one carboxylic acid group and the one or more additional polyaniline precursors.

6. A method of preparing a polyaniline copolymer comprising at least one carboxylic acid group; the method comprising:

preparing a solution of a polyaniline precursor having at least one aromatic amine group and at least one carboxylic acid group in aqueous ammonia and one or more additional polyaniline precursors; and

oxidatively polymerising the polyaniline precursor having at least one aromatic amine group and at least one carboxylic acid group and the one or more additional polyaniline precursors.

7. A method according to claim 5 or claim 6 wherein the polyaniline precursor having at least one aromatic amine group and at least one carboxylic acid group is selected from 2-aminobenzoic acid, 3-aminobenzoic acid or 4-aminobenzoic acid.

8. A method according to any one of claims 5 to 7 wherein the one or more additional polyaniline precursors comprises aniline.

9. A method according to any one of claims 5 to 8 wherein the ratio of the polyaniline precursor having at least one aromatic amine group and at least one carboxylic acid group: the one or more additional polyaniline precursors is from 99:1 to 1:99

10. A method according to claim1 wherein the polyaniline precursor and methanesulfonic acid are present in a ratio of 2:1 to 1:2.

11. A method according to any one of the preceding claims wherein the polymerisation is carried out by APS.

12. A method according to any one of the preceding claims further including the step of collecting precipitated polyaniline by filtration.

13. A polyaniline random copolymer comprising 4ABA and aniline monomers.

14. A polyaniline random copolymer comprising 4ABA and aniline monomers in a ratio of between 3:1 and 1:3.

15. A polyaniline random copolymer comprising 4ABA and aniline monomers in a ratio of 1:1.

16. A polyaniline random copolymer comprising 2ABA and aniline monomers.

17. A polyaniline random copolymer comprising 2ABA and aniline monomers in a ratio of between 3:1 and 1:3.

18. A polyaniline random copolymer comprising 2ABA and aniline monomers in a ratio of 1:1.

19. A polyaniline random copolymer comprising 3ABA and aniline monomers.

20. A polyaniline random copolymer comprising 3ABA and aniline monomers in a ratio of between 3:1 and 1:3.

21. A polyaniline random copolymer comprising 3ABA and aniline monomers in a ratio of 1:1.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NZ2012/000047

A. CLASSIFICATION OF SUBJECT MATTER

C08G 73/02 (OCT 2005) C08G 73/00 (OCT 2005)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI/EPODOC, STN CAPLUS. Search terms: aniline, polyaniline, aminobenzoic, carboxyaniline, anthranilic, carboxyl, ammonia, methanesulfonic, methylsulfonic and like terms..

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

[X] Further documents are listed in the continuation of Box C [X] See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
15 June 2012	15 June 2012

Name and mailing address of the ISA/AU

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INTERNATIONAL SEARCH REPORT C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		International application No. PCT/NZ2012/000047
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5932144 A (SHIMIZU S. et al) 03 August 1999 See whole of the document but particularly the Abstract, column 10 line 43-54, column 11 line 66 and Example 15	1, 3-4, 6-9, 11-21
X	WO 2009/041837 A1 (AUCKLAND UNISERVICES LIMITED) 02 April 2009 See whole of the document but particularly the Abstract, page 2 line 31 to page 3 line 31, page 9 line 9-14.	13-21
X	Yan H. et al "Novel syntheses of poly(o-aminobenzoic acid) and copolymers of o-aminobenzoic acid and aniline as potential candidates for precursors of polyaniline." Bull. Chem. Soc. Jpn., (1996) Vol. 69, pages 2395-2401. See whole of the document but particularly the Abstract, Table 1, and page 2396, column 1 first paragraph	1, 3-4, 6-9, 11-12 , 16-18
X	US 7374703 B2 (EPSTEIN A. et al) 20 May 2008 See whole of the document but particularly the Abstract, column 3 line 51 to column 4 line 2, column 4 line 18-36, and Example 1.	1-2, 4-5, 7-21

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/NZ2012/000047**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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		US 8038907 B2	18 Oct 2011
		US 2012035353 A1	09 Feb 2012
		WO 2006004653 A2	12 Jan 2006

End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.