

HIGH ION CONDUCTIVE POLYMERS

THIS INVENTION relates to high ion conductive polymers, and in particular to polymers suitable for the formation of proton-exchange membranes.

Ion conductive membranes find application in several fields of technology, for instance in the construction of proton-exchange fuel cells, and in sensors. However, conventional ion conductive membranes suffer from low ion conductivities, and currently available membranes display conductivities ranging from 10^{-2} to 10^{-1} Scm^{-1} . In general, it is desirable for the ion conductivities of such membranes to be as high as possible.

In addition, conventional ion conductive membranes are expensive and technically difficult to produce, leading to high costs for articles containing such membranes.

It is an object of the present invention to provide a polymer suitable for the formation of ion conductive membranes that alleviate at least some of the above drawbacks.

Accordingly, one aspect of the present invention provides a method of producing a polymer, the method comprising the step of copolymerisation of a mixture comprising: about 15% to 50% by weight of water; about 10% to 50% by weight of at least one copolymerisable surfactant; and about 5% to 40% by weight of at least one copolymerisable monomer; whereby the resultant polymer has aqueous domains having sizes smaller than 100nm.

Advantageously, the mixture comprises: about 20% to 25% by weight of water; about 30% to 40% by weight of the at least one copolymerisable surfactant; and about 20% to 25% by weight of the at least one copolymerisable monomer.

Preferably, the mixture further comprises about 0.1% to 0.4% by weight of an initiator.

Conveniently, the initiator is a redox initiator or a photo-initiator.

Advantageously, the mixture is a microemulsion.

Preferably, the at least one copolymerisable monomer is ethylenically-unsaturated.

Conveniently, the at least one copolymerisable surfactant comprises an ionic surfactant.

Advantageously, the ionic surfactant comprises a quaternary ionic group.

Preferably, the at least one copolymerisable surfactant comprises a zwitterionic surfactant.

Conveniently, the zwitterionic surfactant is an imidazole, benzimidazole or piperazine type zwitterionic surfactant.

Advantageously, the at least one copolymerisable surfactant comprises an ionic surfactant.

Preferably, the at least one copolymerisable surfactant comprises a non-ionic surfactant.

Conveniently, the non-ionic surfactant comprises a polyethylene oxide group containing from about 10 to about 110 polyethylene monomers.

Advantageously, the at least one copolymerisable surfactant is copolymerisable with the at least one copolymerisable monomer.

Another aspect of the present invention provides a compound having the structure:



where $6 \leq n \leq 20$, $1 \leq m \leq 10$ and V is (methyl)acrylate or another copolymerisable unsaturated group.

Preferably, the compound is a surfactant.

Conveniently, the compound is a monomer.

A further aspect of the present invention provides a polymer comprising domains containing at least one polar solvent, the domains having sizes smaller than 100nm and the density of the domains being at least about $3 \times 10^3/\mu\text{m}^3$.

Advantageously, the density of the domains is in the range from about $3 \times 10^3/\mu\text{m}^3$ to about $3.5 \times 10^5/\mu\text{m}^3$.

Preferably, the polymer comprises: about 23% water; about 29% AIPSA; about 22% MMA; about 14% SPM; about 8% NAMAP; about 3% A174 and about 1% EGDMA.

Conveniently, the polymer has a conductivity of at least 0.5 Scm^{-1} .

Advantageously, at least some of the domains contain water.

Another aspect of the present invention provides membrane formed from a polymer according to the above.

In order that the present invention may be more readily understood, embodiments thereof will now be described by way of example, in which;

Figure 1 shows a typical ternary phase diagram of a monomer/surfactant/water mixture at 25°C ;

Figure 2 shows a typical conductivity plot indicating an approximate composition region for bicontinuous microemulsions;

Figure 3 shows a typical pore size distribution for a membrane formed from a polymer embodying the present invention; and

Figures 4a and 4b give details of the compositions and ion conductivities of nine membranes formed from polymers embodying the present invention.

The ability of the present invention to provide high ion conductive polymers resides in the technique of copolymerising mixtures comprising about

15% to 50% by weight of water, about 10% to 50% by weight of at least one copolymerisable surfactant and about 5% to 40% by weight of at least one copolymerisable monomer.

Preferably, microemulsions are employed as mixtures for use in methods embodying the present invention (precursor mixtures). A thermodynamically stable microemulsion is a transparent colloidal dispersion of oil and water, stabilised by a surfactant. Depending on the proportion of components and the hydrophile-lipophile value of surfactants used in a microemulsion, the formation of the microemulsion can be in the form of droplets which are swollen with oil but dispersed in water (normal or O/W microemulsion), or swollen with water but dispersed in oil (inverse or W/O microemulsion). In addition, bicontinuous microemulsions exist whose oil and aqueous domains are randomly interconnected to form sponge-like structures.

The above-described technique of polymerisation of organic components in a mixture enables the synthesis of interconnected aqueous channels, which become pores when the finished polymer has been dried. These pores are randomly distributed in the resulting polymer, and when the polymer has been dried the pore sized distribution ranges from around 10nm to 30nm. The nature of these pores (i.e. closed cell or open cell) can be determined by the rate at which the resultant polymer is dried.

Turning to Figure 1, a ternary phase diagram of a monomer/surfactant/water mixture at 25°C is shown. The single-phase microemulsion region of the diagram is represented by a dotted area, and it is preferred to use mixtures falling within this dotted area in methods embodying the present invention. As can be seen from figure 2, the ionic conductivity of the mixture increases substantially in the bicontinuous microemulsion region.

The interconnected aqueous nanostructures in polymerised mixtures embodying the present invention arise from the rapid copolymerisation of substantially all polymerisable organic components present in the precursor mixture. Such rapid copolymerisation is initiated by either redox or photo-initiators at low temperatures, to ensure the nanostructural stability of the mixture during the copolymerisation thereof.

In a preferred embodiment of the invention, the copolymerisable surfactant present in the precursor mixture is anionic, and may, for instance, have the structure:



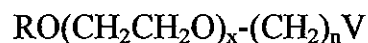
where M is either ammonium or a metal cation, R is either a hydrogen or an alkyl group selected from the group having 1, 2, 3, 4 or 5 carbon atoms, and where $6 \leq n \leq 20$.

Alternatively, the copolymerisable surfactant may be zwitterionic, and may have the structure:



where $6 \leq n \leq 20$, $1 \leq m \leq 10$ and V is (methyl)acrylate or another copolymerisable unsaturated group. This surfactant monomer, which contains a sulphonic acid group, is particularly advantageous in carrying out the present invention.

As a further alternative, the polymerisable surfactant may be non-ionic, and may, for instance, have the structure:



where X is an integer ranging from about 10 to about 110, and where V is p-vinylbenzyl, (methyl)acrylate, or another copolymerisable unsaturated group.

It will be understood that suitable surfactants are not limited to those given above, and many other surfactants may be included in a precursor mixture for use in the method of the present invention.

Ethylenically unsaturated monomers that can be effectively employed in the method of the present invention include methyl methacrylate (MMA), acrylonitrile (AN), butyl acrylate (BA); ethylenically unsaturated monocarboxylic acids such as acrylic acid (AA) and methacrylic acid (MA); the C₁ to C₁₂ alkyl alcohol esters of acrylic as well as methacrylic acid; and other esters of the acids such as sodium salt of 3-sulphopropyl(methyl)acrylic acid (SPM) and glycidyl methacrylate (GMA); substituted methacrylates and acrylates such as 2-hydroxyethyl methacrylate (HEMA) and 2-hydroxyethyl acrylate; vinyl aryl monomers such as styrene and lithium styrene sulphonate, nitriles of ethylenically unsaturated carboxylic acids such as acrylonitrile and methacrylonitrile.

While ethylene glycol dimethacrylate (EGDMA) may be employed as a crosslinking agent in methods embodying the present invention, crosslinking agents such as diethylene glycol dimethacrylate, diethylene glycol diacrylate and γ -methacryloxypropyltrimethoxysilane are also effective.

As mentioned above, for low temperature (e.g. room temperature) polymerisation, a photo-initiator, a redox-initiator or a mixture of both are preferably employed. Examples of effective photo-initiators include 2,2-dimethoxy-2-phenyl acetophenone (DMPA) and dibenzylketone. Examples of effective redox-initiators are ammonium persulphate and N,N,N',N'-tetramethylethylene diamine (TMEDA).

In addition to the above, the water domains of the precursor mixture may optionally include various additives having specific properties. Such additives are selected for conferring a desired property on the resulting polymer, and include fillers, dyes, inorganic electrolytes and pH adjusters.

In carrying out the present invention, it is first necessary to form a precursor mixture by mixing the appropriate components. It is preferred to form a microemulsion and, with appropriate formulations, microemulsions form spontaneously upon mixing the components, with little need for vigorous stirring. However, the mixture may be stirred as much as is necessary to form an appropriate microemulsion.

The polymerisation of the microemulsion may occur readily, however (as mentioned above) at room temperature photo-initiators, redox initiators or both are likely to be required. If relatively large samples of polymer are to be produced, several hours of continuous polymerisation may be required to produce a sample of useful mechanical strength.

Since a major application of polymers embodying the present invention is in the formation of membranes, it is often desirable to form the resultant polymer into a thin sheet. This can be achieved, for instance, by sandwiching the mixture between two glass plates during polymerisation, or by coating the

mixture on other membranes such as papers, glass fibres or other polymer membranes.

Figure 3 shows typical pore size distributions for membranes fabricated using polymers produced by methods embodying the present invention. It will be seen that the vast majority of aqueous domains in the membranes have diameters in the region of 10nm to 30nm. However, the aqueous domains may have diameters of up to 100nm.

The number of aqueous domains per unit volume of a polymer embodying the present invention will vary depending upon the size of the aqueous domains. However, in a preferred embodiment of the present invention, the density of aqueous domains is at least $3 \times 10^3 / \mu\text{m}^3$, and may be as high as $3.5 \times 10^5 / \mu\text{m}^3$.

The existence of numerous aqueous domains randomly distributed throughout polymers formed by methods embodying the present invention facilitates the transport of ions or protons through the polymers, and it will be appreciated that this feature gives the polymers high ion conductivities, thereby improving the performance of membranes comprising these polymers in Applications such as, for example, fuel cells.

The water in the domains can readily be removed by drying, and other polar solvents, such as ethylene carbonate or electrolyte solutions, can be introduced into the vacant domains. It will be appreciated that such polar solvents may confer beneficial properties on the resultant polymer, and the selection of the solvent to be introduced into the vacant domains will depend upon the intended application of the polymer.

In addition to the desirable performance of membranes embodying the present invention, the fact that the method of the present invention effectively involves only a single step (i.e. the co-polymerisation of substantially all of the organic components in the precursor mixture) makes it possible to produce polymers very cheaply using methods embodying the present invention. Indeed, it has been found that membranes can be formed using methods embodying the present invention for around 5% - 10% of the cost of producing conventional ion conductive membranes.

Figures 4a and 4b show tables which give the composition and protonic conductivity of 9 membranes, each of which were synthesised by methods embodying the present invention from bicontinuous microemulsions consisting of polymerisable surfactants, such as AIPSA ($\text{SO}_3^- (\text{CH}_2)_m^+ \text{NCHCHCHN}(\text{CH}_2)_n \text{COOCH}=\text{CH}_2$) or APMPSA ($\text{CH}_2=\text{CH}(\text{CH}_2)_n \text{CONHCHCHCHCHN}^+ \text{CH}_3(\text{CH}_2)_m \text{SO}_3^-$), monomers such as acrylonitrile (AN) and methyl methacrylate (MMA), 2,2,3,3-tetrafluoropropylmethacrylic acid ester (FMA), N-acryloyl-N'-methylpiperazine (NAMAP), 3-sulphopropylmethacrylic acid ester (SPM) Bis-3-sulphopropylitaconic acid ester (SPI) or [(2-methacryloyloxy)ethyl]-dimethyl(3-sulphopropyl) ammonium hydroxide (MDSPA), and N'N methylene bis-acrylamide (MBBA) or ethylene glycol dimethacrylate (EGDMA) or γ -methacryloxypropyltrimethoxysilane (A174) as a crosslinker.

The bicontinuous precursor microemulsions were simply polymerised or impregnated in glass-fibre sheet or filter paper before being subjected to polymerisation at room temperature using either a UV photo-initiator (2,2-dimethoxy-2-phenyl acetophenone (DMPA) and dibenzylketone (DBK)) or a redox initiator comprising an equimolar mixture of ammonium persulphate

(APS) and N,N,N',N'-tetramethylethylene diamine (TMEDA). The membranes were subsequently treated with 0.5M H₂SO₄.

It will be understood from the table displayed in Figure 4 that the protonic conductivities of the 9 membranes listed therein are substantially higher than those of currently available membranes. Indeed, membranes forming from polymers embodying the present invention can display protonic conductivities as high as one order of magnitude above those displayed by conventional membranes.

In summary, it will be appreciated that the present invention provides a method of producing polymers that may be used to form membranes displaying significant advantages over conventional membranes, including increased protonic conductivity and reduced cost.

In the present specification "comprises" means "includes or consists of" and "comprising" means "including or consisting of".

The features disclosed in the foregoing description, or the following claims, or the accompanying drawings, expressed in their specific forms or in terms of a means for performing the disclosed function, or a method or process for attaining the disclosed result, as appropriate, may, separately, or in any combination of such features, be utilised for realising the invention in diverse forms thereof.

CLAIMS:

1. A method of producing a polymer, the method comprising the step of copolymerisation of a mixture comprising:
 - about 15% to 50% by weight of water;
 - about 10% to 50% by weight of at least one copolymerisable surfactant, wherein the at least one copolymerisable surfactant is a zwitterionic surfactant selected from the group consisting of imidazole, benzimidazole or piperazine type zwitterionic surfactants; and
 - about 5% to 40% by weight of at least one copolymerisable monomer;whereby the resultant polymer has aqueous domains having sizes smaller than 100nm.
2. A method according to Claim 1, wherein the mixture comprises:
 - about 20% to 25% by weight of water;
 - about 30% to 40% by weight of the at least one copolymerisable surfactant; and
 - about 20% to 25% by weight of the at least one copolymerisable monomer.
3. A method according to Claim 1 or 2, wherein the mixture further comprises about 0.1% to 0.4% by weight of an initiator.
4. A method according to Claim 3, wherein the initiator is a redox initiator or a photo-initiator.
5. A method according to any preceding claim, wherein the mixture is a microemulsion.

6. A method according to any preceding claim, wherein the at least one copolymerisable monomer is ethylenically-unsaturated.
7. A method according to any preceding claim, wherein the at least one copolymerisable surfactant is copolymerisable with the at least one copolymerisable monomer.
8. A polymer produced according to a method of any one of claims 1 to 7, comprising domains containing at least one polar solvent, the domains having sizes smaller than 100nm and the density of the domains being at least about $3 \times 10^3 / \mu\text{m}^3$.
9. A polymer according to Claim 8, wherein the density of the domains is in the range from about $3 \times 10^3 / \mu\text{m}^3$ to about $3.5 \times 10^5 / \mu\text{m}^3$.
10. A according to any one of Claims 8 or 9, having a conductivity of at least 0.5 Scm^{-1} .
11. A polymer according to any one of Claims 8 to 10, wherein at least some of the domains contain water.
12. A membrane formed from a polymer according to any one of Claims 8 to 11.
13. A polymer substantially as hereinbefore described, with reference to the accompanying drawings.
14. A compound substantially as hereinbefore described, with reference to the accompanying drawings.

15. A method substantially as hereinbefore described, with reference to the accompanying drawings.