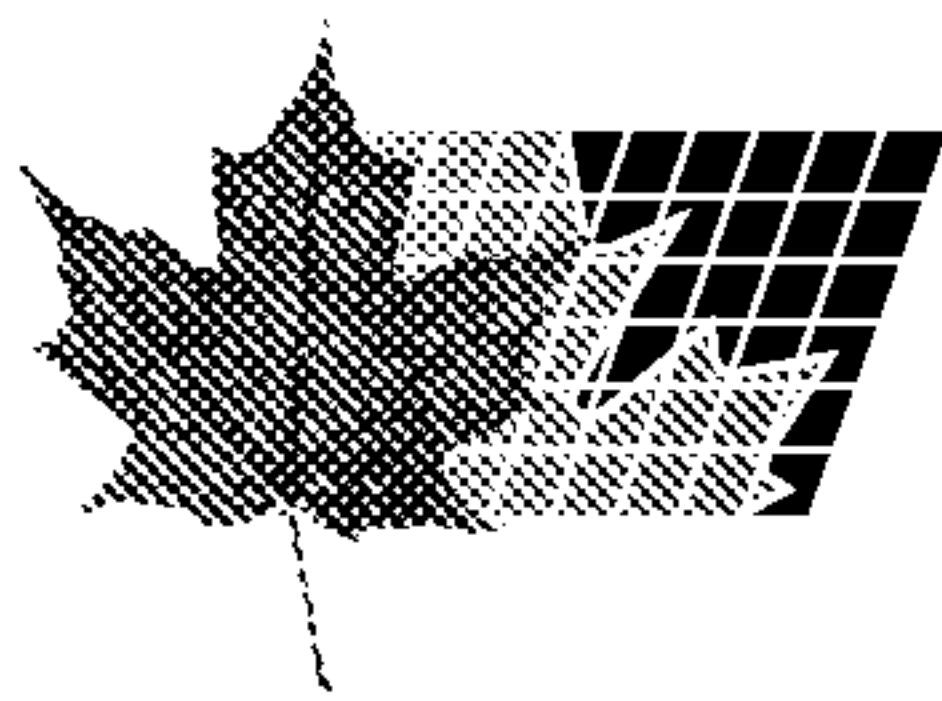




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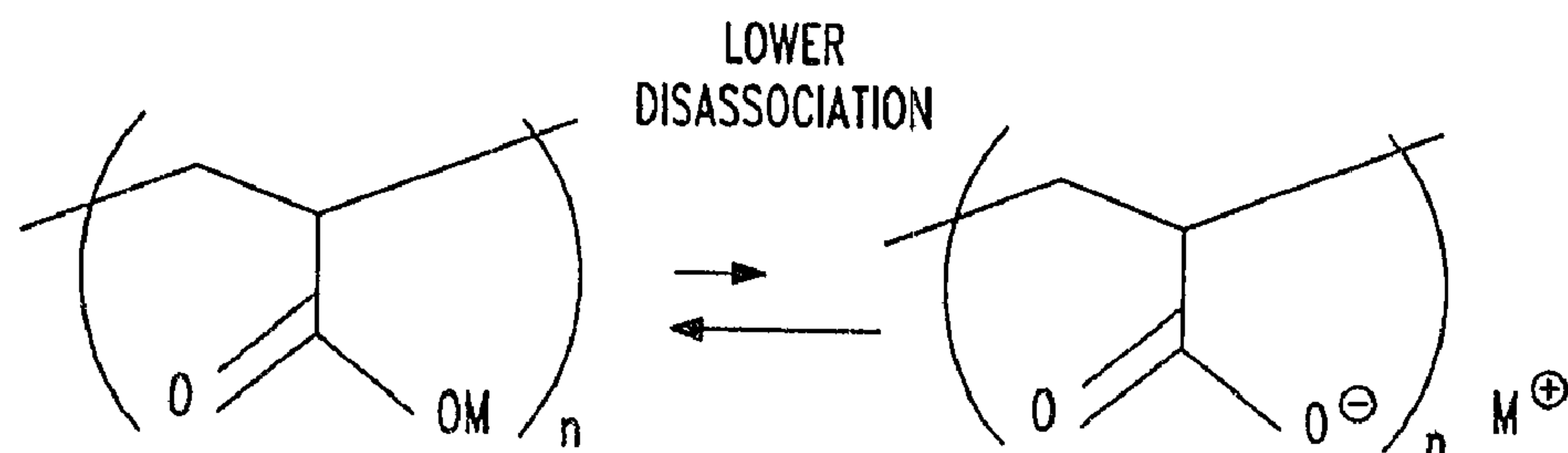
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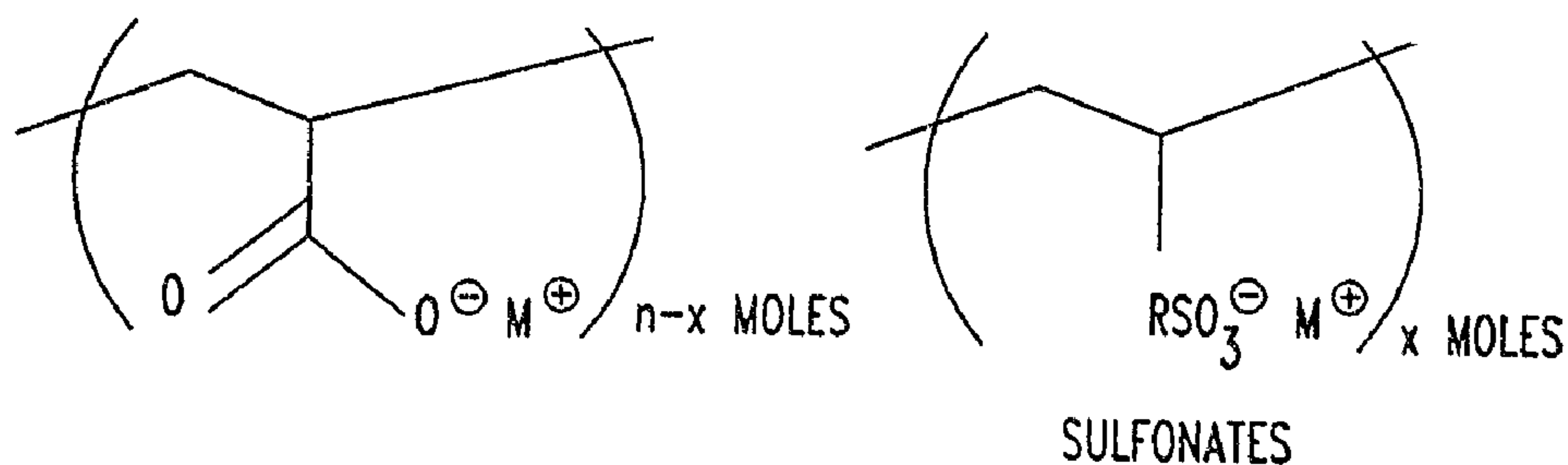
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(54) **MATERIAUX POLYMERES SUPERABSORBANTS
INSENSIBLES A LA TEMPERATURE ET AUX SELS, ET
CABLES COMPORTANT CES MATERIAUX**

(54) **SUPERABSORBENT POLYMERIC MATERIALS WHICH ARE
TEMPERATURE AND SALT TOLERANT AND CABLES
WHICH INCLUDE SAME**



WHERE COUNTER ION $M^{\oplus} = NH_4^{\oplus}$,
AMMONIUM CARBOXYLATE HAS LESS IONIC PROPERTY
DUE TO LOWER DISASSOCIATION CONSTANT



(57) A cable (20) includes a waterblocking member (29) which includes a superabsorbent polymer. The superabsorbent polymer includes an ionic constituent which is characterized in that its solubility product is substantially higher than that of carboxylate and in that it has a lower reaction rate for forming an anhydride than does carboxylate. The ionic constituent may be selected from the group consisting of sulfate, sulfonate and phosphate and also includes a counter ion. Other constituents may include a carboxylate and a non-ionic group constituent. The superabsorbent polymer is such that the amount of crosslinking is sufficient to avoid the polymer going into solution, but is not so much as to affect adversely the water absorbency of the waterblocking member. Further, the superabsorbent polymer is much more salt tolerant and temperature tolerant than are prior art superabsorbent polymers.

SUPERABSORBENT POLYMERIC
MATERIALS WHICH ARE TEMPERATURE AND SALT TOLERANT
AND CABLES WHICH INCLUDE SAME

Abstract

5 A cable (20) includes a waterblocking member (29) which
includes a superabsorbent polymer. The superabsorbent polymer includes
an ionic constituent which is characterized in that its solubility product is
substantially higher than that of carboxylate and in that it has a lower
reaction rate for forming an anhydride than does carboxylate. The ionic
10 constituent may be selected from the group consisting of sulfate, sulfonate
and phosphate and also includes a counter ion. Other constituents may
include a carboxylate and a non-ionic group constituent. The
superabsorbent polymer is such that the amount of crosslinking is sufficient
to avoid the polymer going into solution, but is not so much as to affect
15 adversely the water absorbency of the waterblocking member. Further, the
superabsorbent polymer is much more salt tolerant and temperature
tolerant than are prior art superabsorbent polymers.

**SUPERABSORBENT POLYMERIC
MATERIALS WHICH ARE TEMPERATURE AND SALT TOLERANT
AND CABLES WHICH INCLUDE SAME**

Technical Field

5 This invention relates to superabsorbent polymeric materials that are temperature and salt tolerant and to cables which include same.

Background of the Invention

10 In the cable industry, it is well known that changes in ambient conditions lead to differences in vapor pressure between the inside and the outside of a plastic cable jacket. This generally operates to diffuse moisture in a unidirectional manner from the outside of the cable to the inside of the cable. Eventually, this will lead to an undesirably high moisture level inside the cable, especially if a plastic jacket is the only barrier to the ingress of the moisture. High moisture levels inside a cable sheath system may have a
15 detrimental effect on the transmission characteristics of the cable. Furthermore, water may enter the cable because of damage to the cable which compromises its integrity. Although the presence of water itself within an optical fiber cable is not detrimental to its performance, passage of the water along the cable interior to connection points, terminals or
20 associated equipment may cause problems and should be prevented.

 Presently, many commercially available cables also include a water-swappable tape to prevent the ingress of water through the sheath system of a cable and into the core. The tape is used to prevent the travel of water through the sheath system and into the core as well as its travel
25 longitudinally along the cable. Such a tape generally is laminated, including a water-swappable powder which is trapped between two polyester tapes. The water-swappable powder comprises a superabsorbent polymer (SAP).

 Superabsorbent polymer materials generally are made in several ways which result in crosslinked polyacrylates, the major functional groups
30 of which are carboxylate groups. Superabsorbent polymers may be made through a process of a crosslinking water-soluble polymers. Crosslinking renders the polymers insoluble in water and forms a matrix in which water is absorbed and retained. The amount of crosslinking is important and must be maintained at an optimum level depending on the application, such
35 as the rate of water absorption and the total amount of water absorbed, for example. The amount of crosslinking determines the space in the network

(matrix) of the superabsorbent polymer and thus the total volume of superabsorbent polymer, which in turn influences the density of functional groups in the network.

5 The mechanism by which a superabsorbent polymer absorbs and retains water can be described in two ways, physical and chemical. On the physical level, aqueous fluid wets the surface of the superabsorbent polymer and is physically distributed into and throughout the network of the superabsorbent polymer.

10 Chemical absorbency occurs on the molecular level. The aqueous fluid interacts with polymer chains. A carboxylate group will absorb water through a mechanism which is referred to as hydrogen bonding. The bulk of fluid chemically bonded to the superabsorbent polymer does not easily escape out of the network of the superabsorbent polymer.

15 Currently used superabsorbent polymers are not effective in a physiologically saline solution of about 0.9% NaCl or sea water due to the molecular structure of presently used superabsorbent polymers which have predominately carboxylate groups. For example, water absorbency drops from about 900 ml/g to 70 ml/g in a 0.9% NaCl solution and to 8 ml/g in a synthetic sea water solution.

20 The reasons why prior art superabsorbent polymers will not work well in a sea water environment, for example, are twofold. Carboxylates are sensitive to sodium chloride or other electrolytes. As a result, the water absorbing capability of prior art superabsorbent polymers decreases substantially when the polymers are exposed to salt.

25 The reason for such decrease may be explained in terms of a parameter termed osmotic pressure. Osmotic pressure is one of the mechanisms by which superabsorbent polymers absorb water because superabsorbent polymers are polyelectrolytes. An osmotic pressure gradient between the network of superabsorbent polymer and the surrounding
30 aqueous solution determines the absorbency of the superabsorbent polymer. The osmotic pressure gradient between the network of the superabsorbent polymer and the surrounding aqueous fluid drives water into the network of the superabsorbent polymer.

35 The reduced water absorbing capability when the polymers are exposed to salt occurs because of a drop in the osmotic pressure gradient between the network of superabsorbent polymers and the external salt

solution. When the surrounding aqueous solution changes from distilled water (zero concentration in functional groups or electrolytes) to 0.9% NaCl and then to sea water (about 3% in various electrolytes), the concentration gradient decreases, thus causing the osmotic pressure gradient to decrease.

- 5 The decrease in osmotic pressure gradient results in a decrease in absorbency of the superabsorbent polymer. Another reason for the reduction in water absorbing capability is an effect referred to as the common ion effect which also decreases the osmotic pressure.

- Another reason for the substantial decrease in absorbency by
10 prior art superabsorbent polymers in salt solutions is multivalent ion complexation. In a multivalent ion environment, the multivalent ion will complex with the carboxylates and limit polymer chain extension and charge repulsion between the carboxylate ions which in turn reduces water absorbency. A well known phenomena in water soluble polymer chemistry
15 is referred to as salting-out. A carboxylate-containing water soluble polymer solution can be turned easily into a precipitation of polymer separated from aqueous solution by the addition of a multivalent ion such as calcium. Calcium and other multivalent ions exist in sea water in low concentrations. The multivalent charges on the calcium ion will attract and
20 complex with carboxylates in polymer chains. In effect, the complexation of these polymer chains increase the molecular weight of the polymer which becomes insoluble in water and precipitates out of solution.

- In the case of a carboxylate-containing superabsorbent polymer, the net effect of complexation of multivalent ions with carboxylates is
25 crosslinking. The addition of such complexation or crosslinking upsets the optimum level of crosslinking introduced when superabsorbent polymers are made. Therefore, the absorbency of the superabsorbent polymer is altered accordingly. This occurs in addition to the aforementioned drop in osmotic pressure gradient when superabsorbent polymers are exposed to any salt
30 solution, not necessarily multivalent salts.

- Another property of superabsorbent polymers is the temperature tolerancy thereof. The repetitive application of heat energy to carboxylate groups, whether in highly humid or dry conditions, will form anhydrides. The formation of an anhydride from two carboxylate groups, in
35 effect, is a crosslinking of polymer chains which, as mentioned hereinabove, can reduce the water absorbency of the superabsorbent polymer. In some

cases, high temperature and/or high humidity will destroy the crosslinking of polymer chains, thus reducing the water absorbency of the superabsorbent polymers. In either case, the optimum level of crosslinking can no longer be maintained and, accordingly, the water absorbing property of the superabsorbent polymer is changed.

What is sought after and what seemingly is not available is a cable that includes a superabsorbent polymer which is effective notwithstanding exposure to salt solutions such as, for example, in cables which are deployed in sea water environments or in hygienic and agricultural products which are exposed to saline environments. Further, the sought after superabsorbent polymer which may be included in cables should be one which is substantially temperature insensitive.

Summary of the Invention

The foregoing problems of the prior art have been overcome with superabsorbent polymers which are characterized by (1) an ionic constituent which is characterized in that its solubility product is substantially higher than that of carboxylate and in that it has a slower reaction rate for forming an anhydride than does carboxylate, and (2) a monovalent counter ion wherein the concentration of the ionic constituents and the counter ion are substantially equal and which are salt tolerant (ST) and temperature tolerant (TT). A cable which includes such a superabsorbent polymer is set forth.

Brief Description of the Drawing

FIG. 1 is a perspective view of a cable which includes a superabsorbent polymer material;

FIG. 2 is a schematic view which depicts hydrogen bonding;

FIG. 3 is a schematic view which depicts hydrodynamic volume increase as a result of charge repulsion;

FIG. 4 is a schematic view which shows that a multivalent ion reduces the water absorbency of prior art superabsorbent polymers;

FIG. 5 is a schematic view which shows anhydride formation of superabsorbent polymers as a result of absorption and drying cycles; and

FIG. 6 is a schematic view which depicts superabsorbent polymers of this invention.

Detailed Description

Referring now to FIG. 1, there is shown an optical fiber cable which is designated generally by the numeral 20. The cable 20 includes a core comprising one or more optical fibers 22-22 which are disposed within a longitudinally
5 extending tubular member 24 made of a plastic material and which commonly is referred to as a core tube. A plastic jacket 26 is disposed about the core tube with longitudinally extending strength

members (not shown) disposed outside the core tube. Interposed between the core tube and the jacket is a layer 29 comprising a waterblocking member. The waterblocking member which functions to prevent substantially the longitudinal flow of water includes a superabsorbent
5 polymeric material.

The superabsorbent polymer of the cable of this invention includes an ionic group or derivatives thereof and a counter ion. The ionic group includes an ionic constituent which is characterized by a solubility product, K_{sp} , that is substantially higher than that of carboxylate and in
10 that it has a lower reaction rate for forming an anhydride than does carboxylate. In the preferred embodiment, the ionic constituent is selected from the group consisting of sulfonate, sulfate or phosphate. As a function, the ionic group absorbs water and is less sensitive to a salt solution as compared to a carboxyl group which typically has been used.

15 Included in the preferred embodiment is a primary ionic group selected from sulfonate, sulfate and phosphate, a counter ion, another or secondary ionic group which preferably is carboxylate and a non-ionic constituent. The non-ionic constituent may be hydroxyl, amide or nitrile or any of their derivatives. The carboxylate which also is sensitive to salt
20 solutions may be included to absorb water because of its high hydrogen bonding ability. On the other hand, the non-ionic group is immune to salt solutions because it is non-ionic. One or all of the non-ionic grouping may be included to reduce sensitivity to salt concentration. The composition of each group will depend upon the desired sensitivity of the resulting
25 superabsorbent polymer to a salt solution.

As mentioned hereinabove, it has been determined that a sulfonate, sulfate or phosphate constituent is suitable as the primary ionic constituent. This constituent of the superabsorbent polymer is characterized by a multivalent sensitivity which is less than that of
30 carboxylates, which has less tendency to form an anhydride and which has less tendency to crosslink during the use of the superabsorbent polymer.

Also there is a substantial difference in the solubility product between carboxylate and members of the ionic group, such as sulfonate, for example. Some examples of solubility product, K_{sp} , of constituents are as
35 follows:

Calcium carbonate	CaCO_3	2.8×10^{-9}
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Calcium sulfate	CaSO_4	9.1×10^{-6}
Magnesium carbonate	MgCO_3	3.5×10^{-8}
Magnesium sulfonate	MgSO_3	3.2×10^{-3}

As is shown above, there is a substantial difference between the
 5 solubility product of carbonate, sulfate and sulfonate. Although the
 solubility product of carboxylate is not given, it is similar to that of
 carbonate. The smaller its solubility product, the easier it is for a
 constituent to come out of solution and precipitate. Similarly, when a
 superabsorbent polymer with predominating carboxylate groups encounters
 10 calcium or magnesium ions (such as in sea water), the complexation of
 carboxylates and the calcium and magnesium ions occurs readily due to the
 low solubility products of calcium or magnesium polyacrylates
 (carboxylates). This occurs less readily in the case of superabsorbent
 polymers with predominating sulfonate, sulfate or phosphate groups because
 15 of their higher solubility products.

In order to diminish salt sensitivity and to increase the rate of
 water absorbency of the superabsorbent polymer of this invention, a counter
 ion is included in the superabsorbent polymer. The function of the counter
 ion is to counter the negative charge of the primary ionic group hereinbefore
 20 described. Accordingly, in the preferred superabsorbent polymer of this
 invention, the concentrations of the ionic group and the counter ion are
 substantially equal. For example, if one mole of the ionic group is included,
 then the superabsorbent polymer includes one mole of a counter ion.

In the preferred embodiment, ammonium, potassium, lithium or
 25 cesium, rather than sodium is used as the counter ion. Whenever one of the
 hereinbefore - identified ionic groups is used, a counter ion is needed and
 that counter ion preferably should not be sodium in order to avoid the
 common ion effect present in sea water and in physiological saline solutions.
 What is not desired is an ion, e.g., sodium, which is present in sea water and
 30 in physiological saline solutions common to the environment in which
 superabsorbent polymers are used. Diapers, personal hygiene pads and
 incontinent products, where superabsorbent polymers may be used,
 encounter a physiological saline solution, while agricultural and cable
 applications of superabsorbent polymers may involve exposure to salt water,
 35 even sea water. A counter ion such as ammonium is preferred because it is
 characterized as less ionic than the sodium, potassium or cesium, and will

be less sensitive towards salt solutions. Furthermore, when ammonium, for example, is used, surface wettability is increased. Counter ions other than those identified hereinbefore may be used.

Also, the combination of carboxylate groups with sulfate or
5 sulfonate groups (e.g. vinyl sulfonate or, 2 acryl-amido-2 - methyl propane sulfonate) will decrease the sensitivity of the superabsorbent polymer to salts while maintaining suitable water absorbency. This is a result of the difference between the disassociation constants of sulfonic or sulfate acids and carboxylic acids, and the difference between the solubility products of
10 sulfonic acid salts and of carboxylic acid salts.

Further, the primary ionic constituent of the superabsorbent polymer composition advantageously is capable of forming hydrogen bonds. Going now to FIG. 2 there is shown a schematic view of the mechanism of hydrogen bonding. Between different molecules, intermolecular hydrogen
15 bonding occurs whereas within the same molecule, intramolecular hydrogen bonding occurs.

Using the water soluble polymer, polyacrylamide, as an example, polyacrylamide polymer chains once dissolved in water will exhibit two types of hydrogen bonding, intra- and intermolecular. Intramolecular
20 hydrogen bonding tends to cause each individual polymer chain to become folded and curled. The molecular volume of such a polymer in water is small. The volume which the polymer chains occupy in aqueous solution may be called the hydrodynamic volume. The smaller the hydrodynamic volume, the closer the viscosity of the polymer solution approaches that of
25 water. In other words, the polymer's influence on the water is small if the hydrodynamic volume of that polymer is small. In the case of polyacrylamide, for example, intermolecular hydrogen bonding pulls the polymer chains together. In summary, polymer chains not only curl by themselves, via intramolecular hydrogen bonding, they also bundle together
30 via intermolecular hydrogen bonding. The effective hydrodynamic volume of polyacrylamide is therefore low, resulting in low viscosity.

It is well known that an amide can be hydrolyzed to a carboxylate. If the amide groups in polyacrylamide were hydrolyzed to carboxylate groups (i.e., the same functional groups in polyacrylates, or
35 superabsorbent polymer), intermolecular as well as intramolecular charge repulsion exists between polymer chains. These repulsions extend the

hydrodynamic volume of polyacrylates and result in a much higher viscosity and higher water absorbency. In fact, some low molecular weight polyacrylates are used as thickeners. Carboxylates also have a higher ability than amides in polyacrylamides to form hydrogen bonding with water molecules. Having numerous hydrogen bonding with water molecules, the superabsorbent polymer absorbs water into its network and retains it.

If hydrolysis of amides occurs as shown in FIG. 3, the molecules extend between polymer chains due to charge repulsion between newly created carboxylates. The polymer with carboxylates now occupies more volume in water solution which results in a higher viscosity. As a result, there are more polymer chains to occupy space and absorb water. On the other hand, with amides, there is a tendency to curl up and polymer chains are not extended to occupy more volume, resulting in a lower viscosity.

In a superabsorbent polymer, it is desired to have an ionic group occupy as much hydrodynamic volume as possible. The problem with a carboxylate type of superabsorbent polymer is that although it has a high volume and charge repulsion, in salt solutions, its water absorbency drops from about 900 ml/g to 70 ml/g in a 0.9% NaCl solution and to 8 ml/g in a synthetic sea water solution. See Table I.

TABLE I

WATER ABSORBENCY OF
TYPICAL PRIOR ART SUPERABSORBENT POLYMER

5		NaCl	MgCl ₂	CaCl ₂	Na ₂ SO ₄	Water Absorbency	Rate of Absorption
10	Unit	grams/liter				ml/gram	sec
	Distilled H ₂ O					900	45 - 60
	0.9%NaCl	9				70	100 - 120
15	Synthetic (ASTM D1141)						
20	Sea Water (2.5% NaCl)	24.53	5.2	1.16	4.09	8	

Shown in FIG. 4 is a typical property of carboxylate. Upon the addition of "multivalent salt" such as calcium chloride, a carboxylate-containing water soluble polymer will be crosslinked and precipitated to the bottom of a container because of the low disassociation constant of calcium carboxylate. As a result, its ability to absorb water will be decreased substantially. With carboxylate-containing superabsorbent polymers, complexation of the multivalent ion causes crosslinking. Such complexation and crosslinking of the carboxylate by a multivalent salt upsets the optimum cross-linking needed in superabsorbent polymers, and the water absorbency is altered accordingly. An optimum amount of crosslinking is desired so that there is optimum space within the polymer matrix. Optimum space allows water to be taken in, so that the polymer is not soluble in water, and so that the matrix of the polymer will retain a maximum amount of water. The change in crosslinking occurs in addition to the drop in osmotic pressure gradient when superabsorbent polymers are exposed to any salt solution, not necessarily multivalent salts.

The second problem which is solved by the superabsorbent polymer of this invention is that of temperature sensitivity. After heating and drying (see FIG. 5), the water absorbency of some prior art superabsorbent polymers decreases. It decreases because of the relatively

large amount of carboxylates which are present in prior art superabsorbent polymers and which form anhydrides and thus crosslink. Too much crosslinking results in a decrease in water absorbency. The crosslinking of the superabsorbent polymer of this invention is controlled in order to achieve optimum water absorbency.

5 It is desired to use as little carboxylate as possible. In the superabsorbent polymer of the invention, a substantial portion of a carboxylate constituent so common in prior art superabsorbent polymers has been replaced with an ionic group selected from sulfate, sulfonate or phosphate. Of course, the superabsorbent polymer may include all three. However, carboxylate is not excluded altogether because it has excellent water absorbing
10 capability via hydrogen bonding. Instead of a relatively large amount of carboxylate, a group such as sulfonate which forms sulfonic anhydride much less readily is used. As a result, the optimum level of crosslinking achieved during the making of the polymer is maintained. Water absorbency of such superabsorbent polymers will not be affected by temperature - induced crosslinking or decrosslinking. Sulfonic anhydride is formed much less readily
15 because the acid disassociation constant is higher. Thus, the superabsorbent polymer may include a sulfite group, a phosphate group, an amide group, and a carboxylate group.

 Referring now to FIG. 6, the top portion illustrates the ionic property of counter ions. The less ionic, the less the sensitivity towards salt solutions of superabsorbent polymer. Where the counter ion is ammonium, ammonium carboxylate is characterized as less ionic
20 because of a lower disassociation constant. The lower portion of FIG. 6 illustrates the combination of sulfonates with carboxylates in a superabsorbent polymer of the invention.

Claims:

1. A superabsorbent polymer which retains substantially its superabsorbent capability notwithstanding exposure to solutions having a relatively high salt concentration and/or relatively high temperatures, said superabsorbent polymer
5 being characterized by (1) an ionic constituent which is characterized in that its solubility product is substantially higher than that of carboxylate and in that it has a slower reaction rate for forming an anhydride than does carboxylate, and (2) a monovalent counter ion wherein the concentrations of the ionic constituent and the counter ion are substantially equal.
- 10 2. The superabsorbent polymer of claim 1, wherein said ionic constituent is selected from the group consisting of sulfonate, sulfate and phosphate.
3. The superabsorbent polymer of claim 1, wherein said superabsorbent polymer also includes an ion selected from the group consisting of ammonium, potassium, lithium and cesium.
- 15 4. The superabsorbent polymer of claim 3, which also includes a non-ionic group.
5. The superabsorbent of claim 4, wherein said superabsorbent polymer includes amide and carboxylate groups.
6. The superabsorbent polymer of claim 3, which also includes a
20 carboxylate group.
7. The superabsorbent polymer of claim 6, which also includes a constituent selected from the group consisting of a nitrile group, a hydroxyl group and an amide group.

8. The superabsorbent polymer of claim 1, wherein said superabsorbent polymer includes a sulfate group, a phosphate group and a carboxylate group.

9. The superabsorbent polymer of claim 1, which includes a sulfate group, a phosphate group, an amide group and a carboxylate group.

5 10. A cable, which includes a core comprising at least one communication transmitting medium, and a sheath system in which is disposed said core, said cable including at least one waterblocking member which comprises a superabsorbent polymer as set forth in claim 1.

FIG. 1

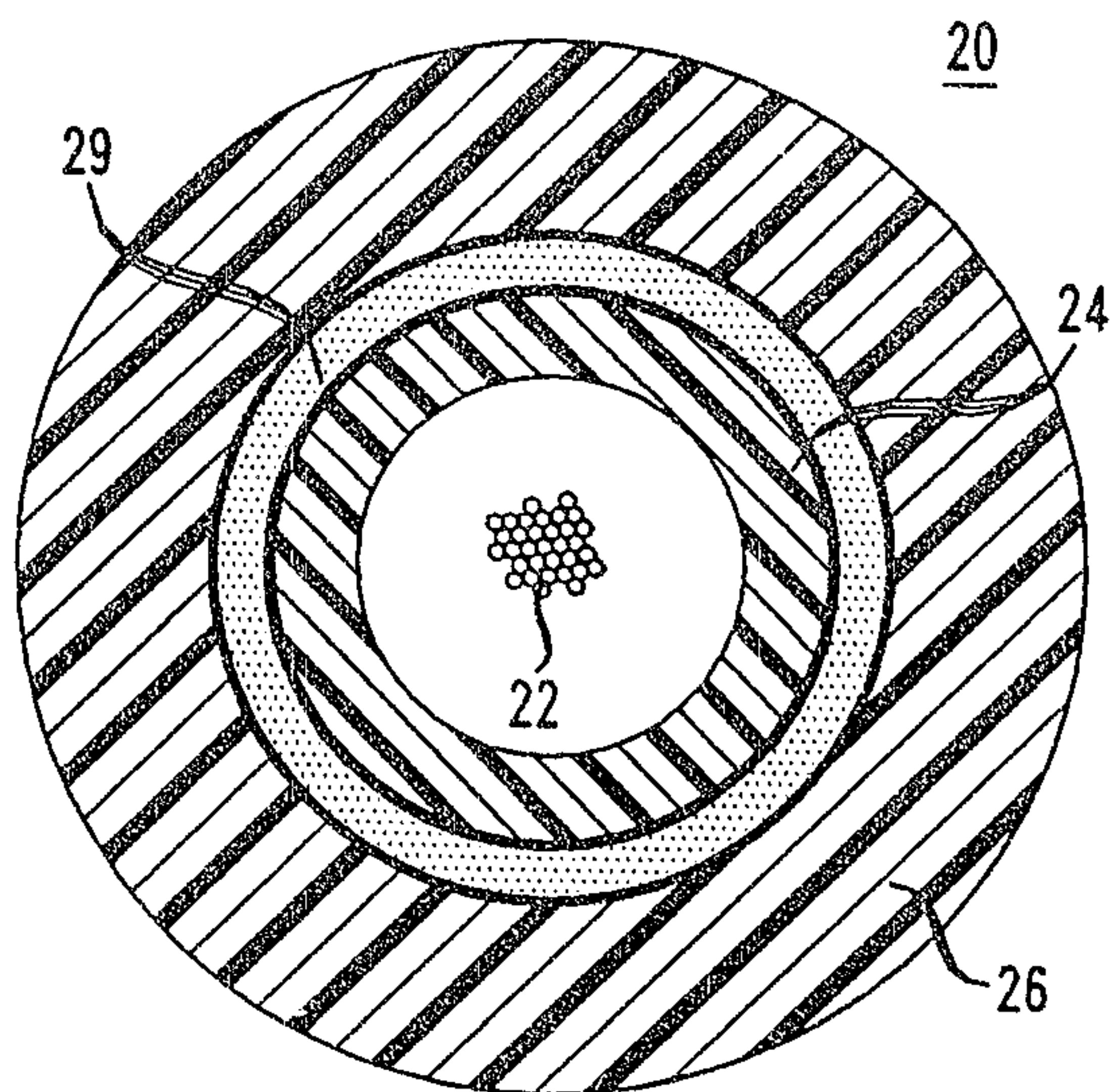
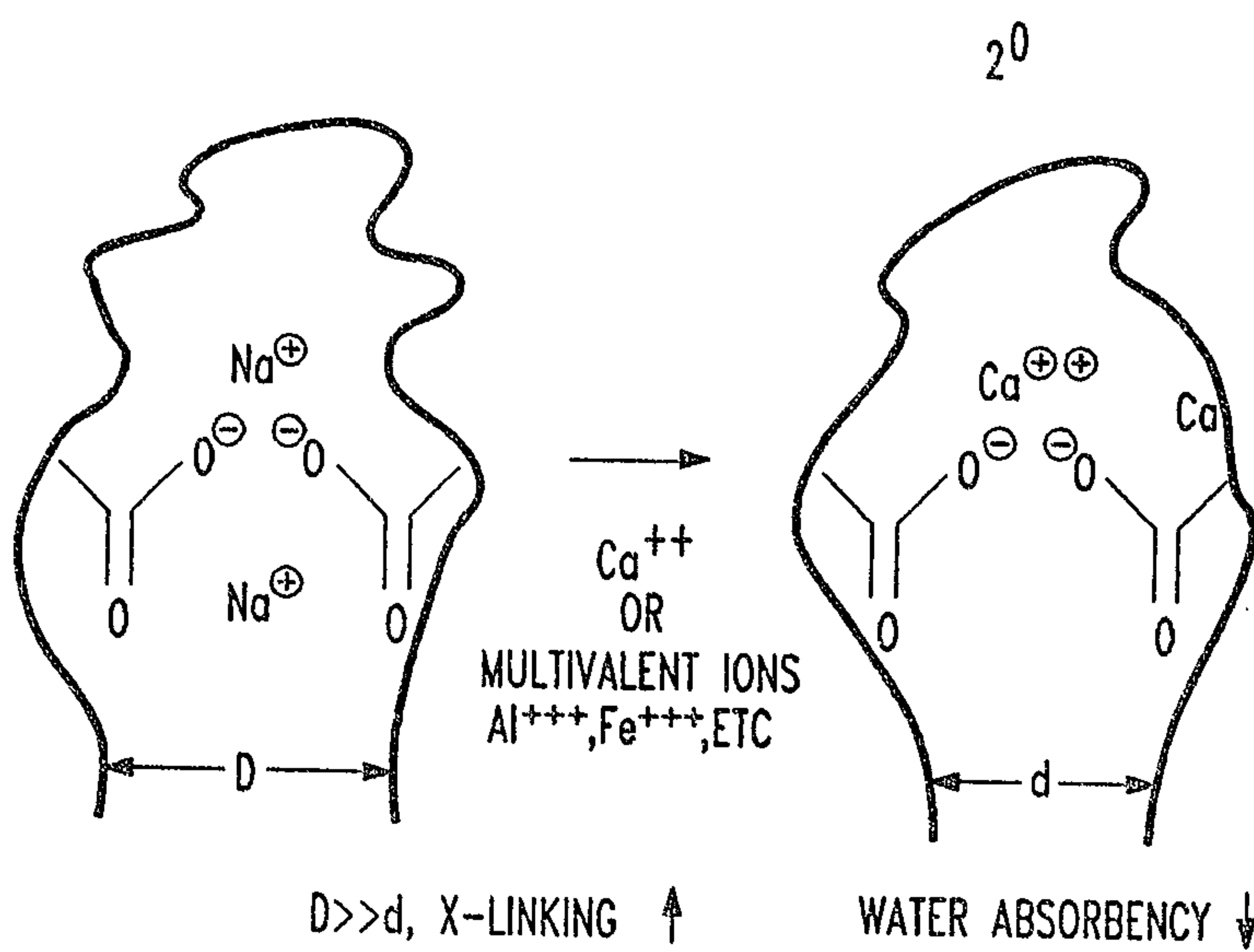


FIG. 4



**Kirby, Eades, Gale,
Baker & Potvin**

FIG. 2

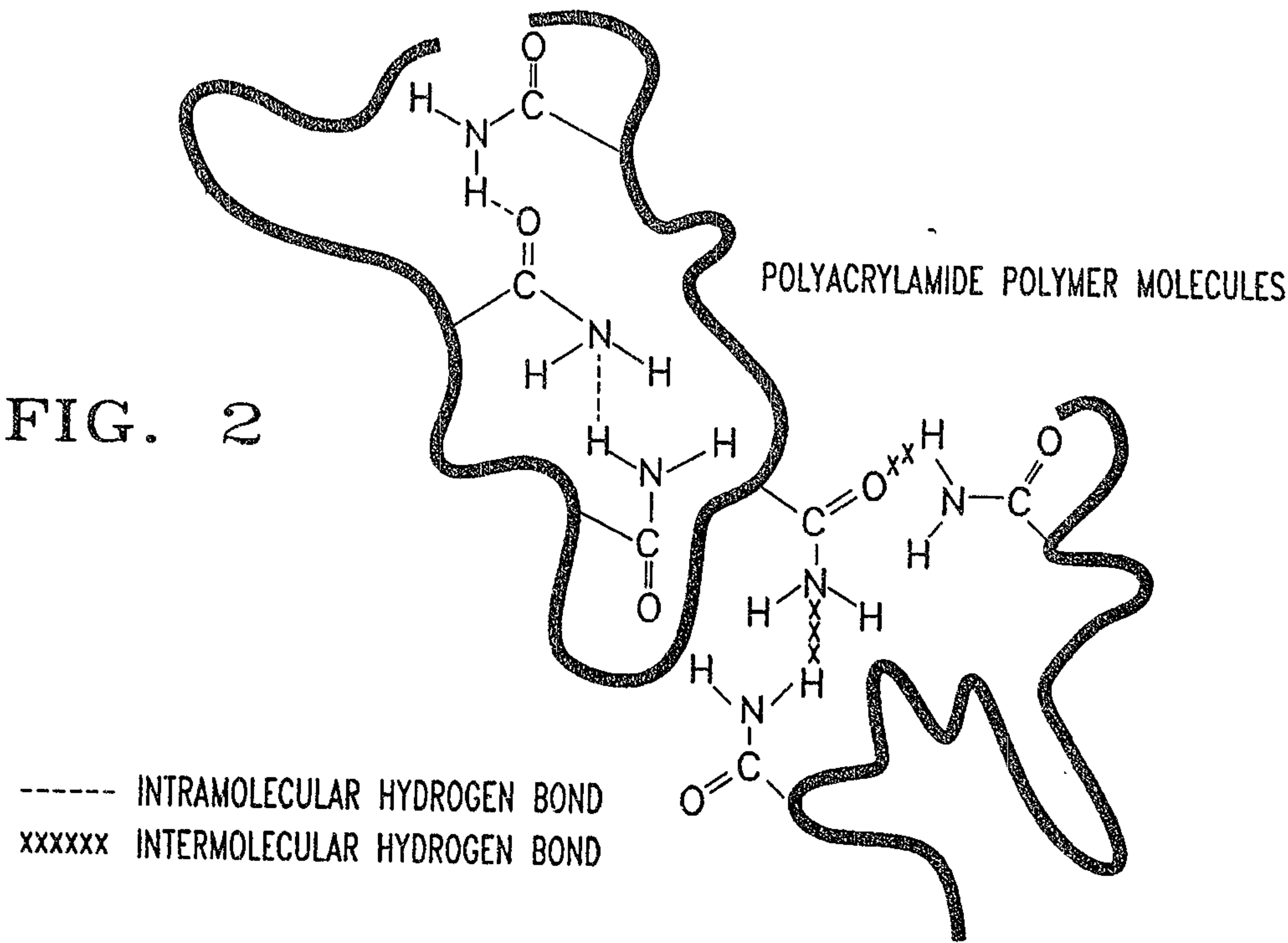
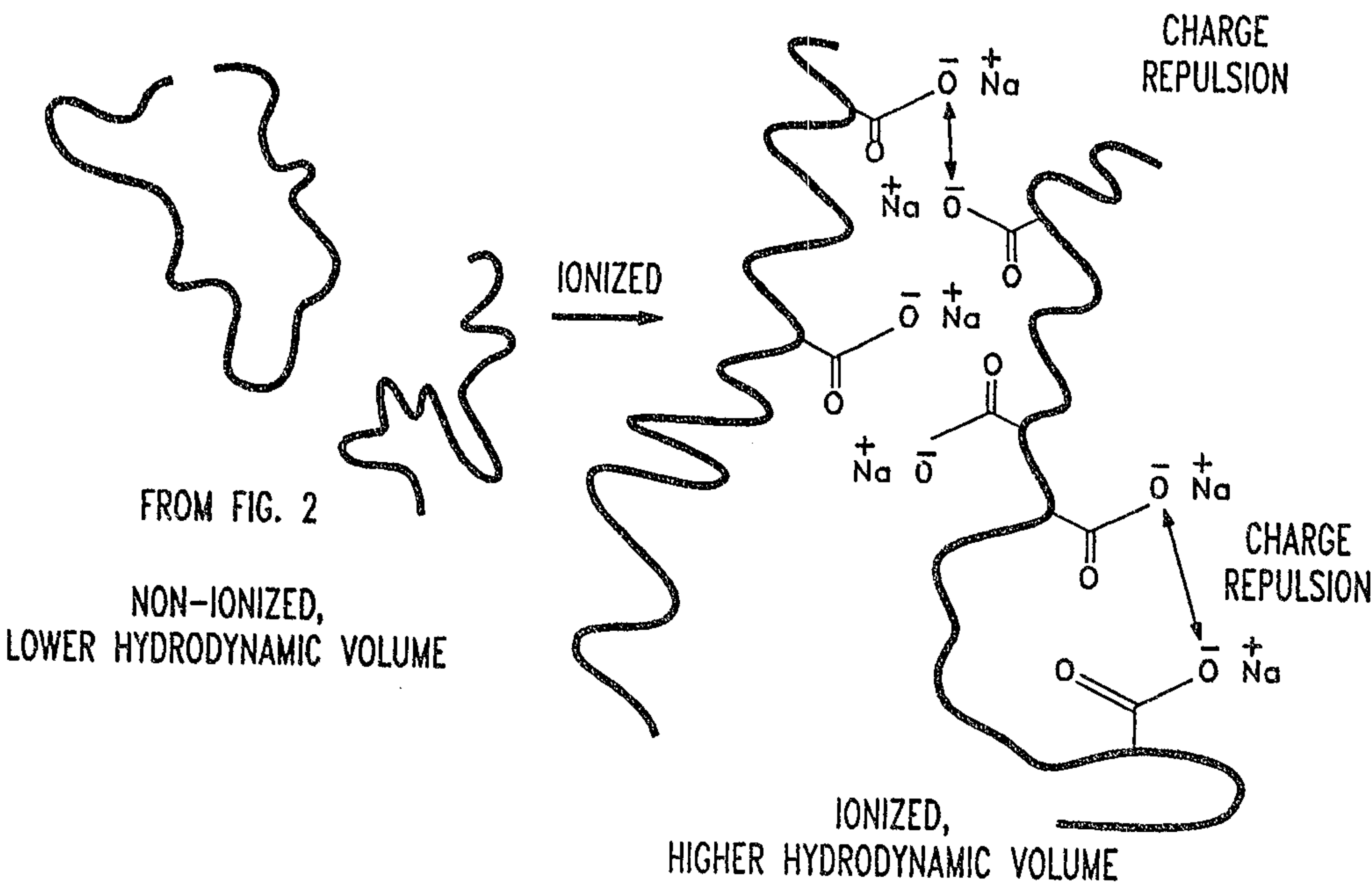


FIG. 3



Kirby, Eades, Gale,
Baker & Porvin

FIG. 5

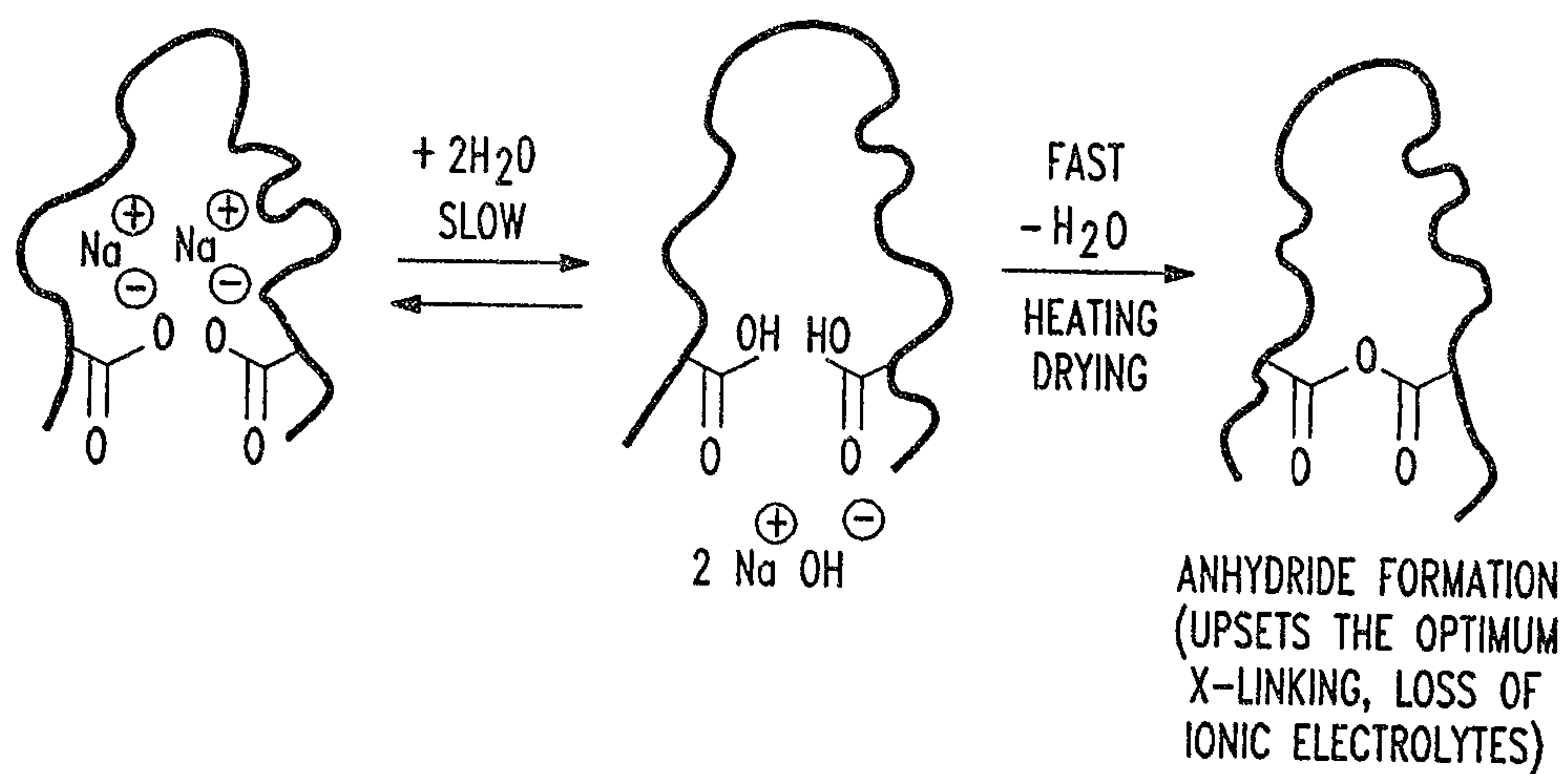
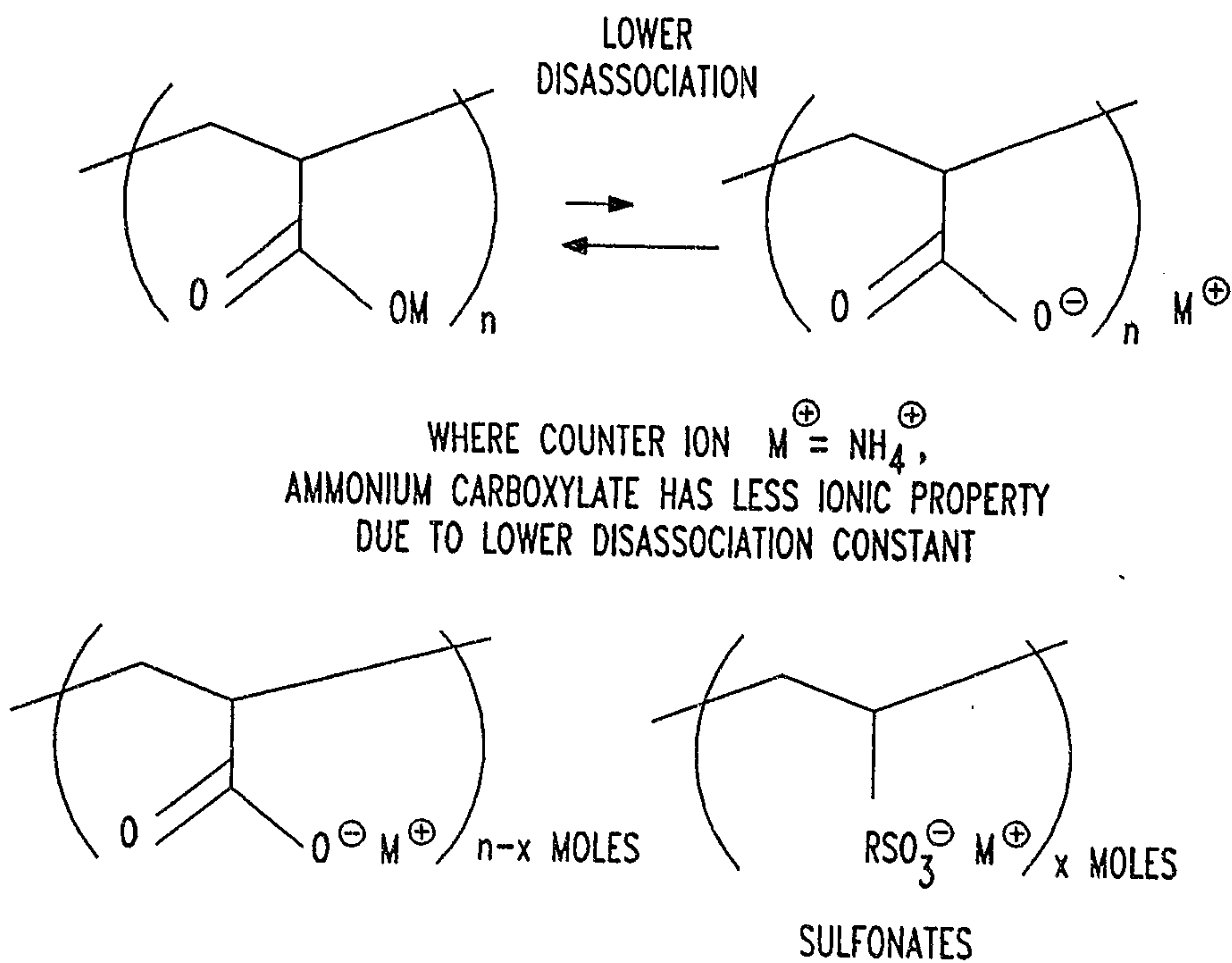
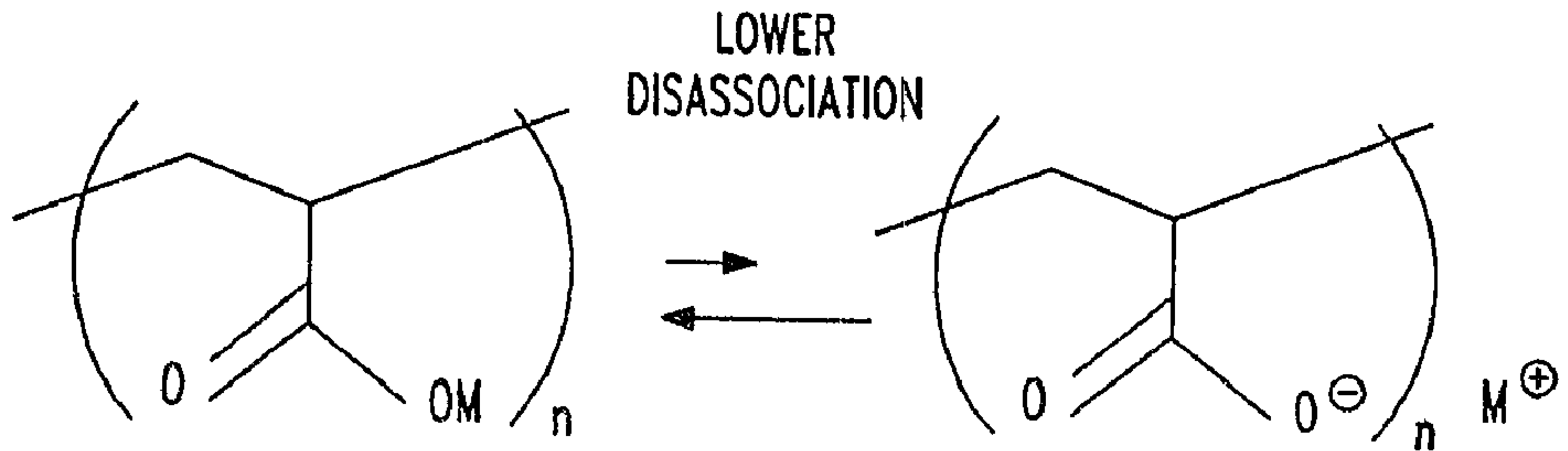


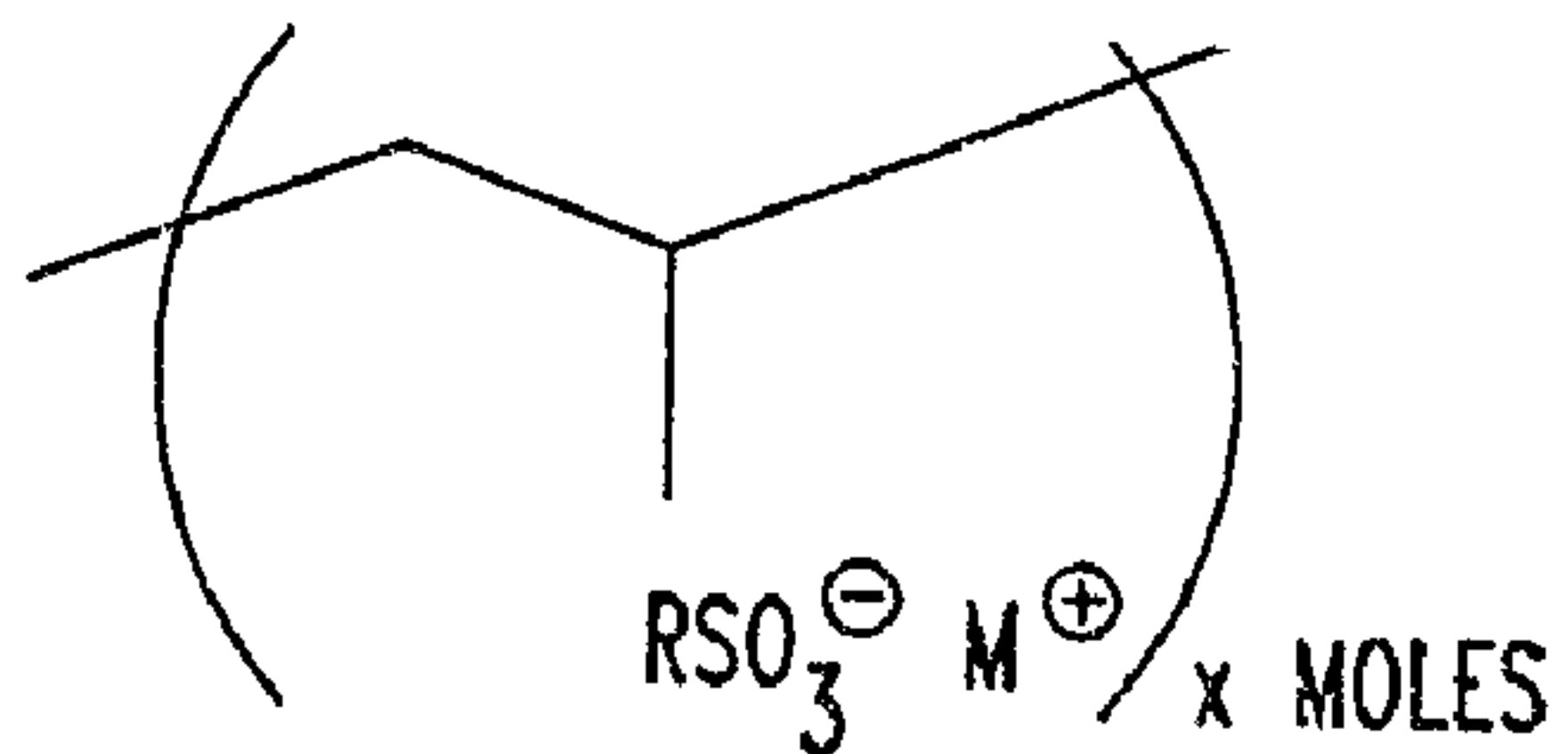
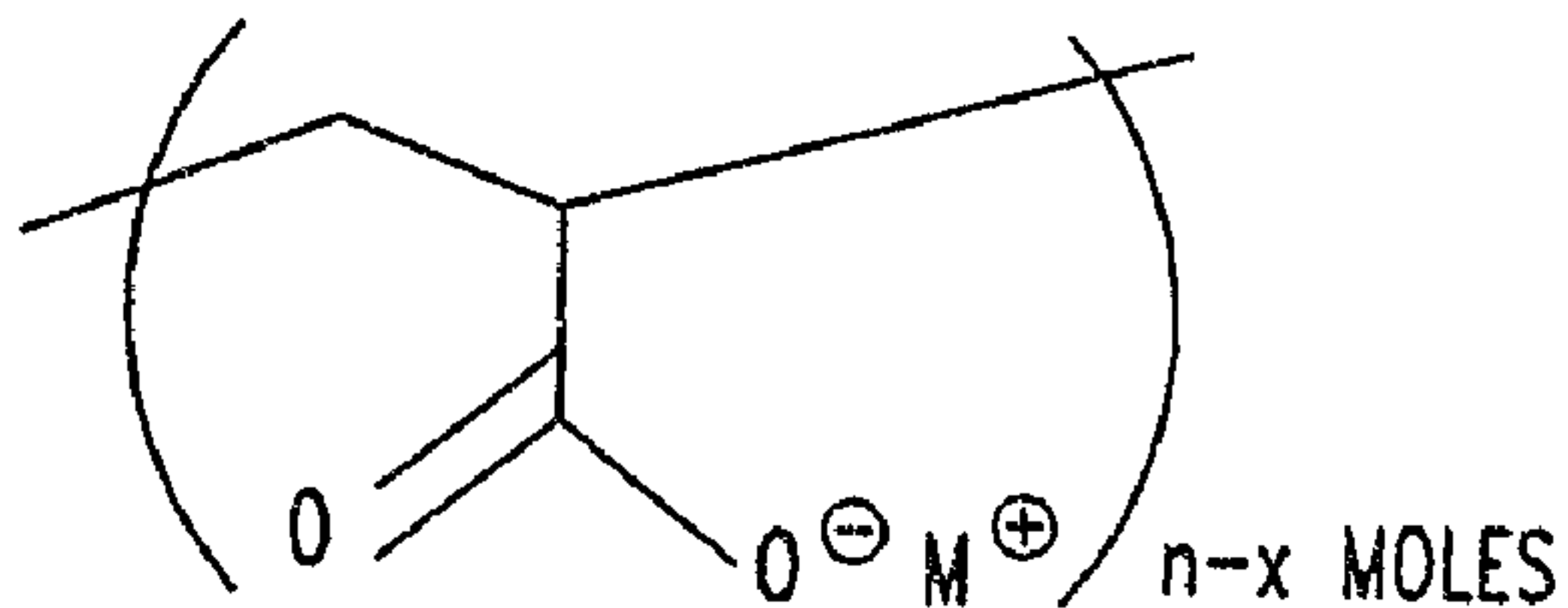
FIG. 6



Kirby, Fades, Gale,
Baker & Potvin



WHERE COUNTER ION $\text{M}^+ = \text{NH}_4^+$,
AMMONIUM CARBOXYLATE HAS LESS IONIC PROPERTY
DUE TO LOWER DISASSOCIATION CONSTANT



SULFONATES