

FUNCTIONAL GROUP TERMINATED POLYMERS
CONTAINING SULFONATE GROUP VIA
POLYMERIZATION OF SULFONATED MONOMERS

1 The present invention relates to water-
dispersible polymers, and more particularly to water-
dispersible polyesters, polyamides and polyethers as
5 well as copolymers thereof.

Polyester resins, as well as polyamide and
polyether resins, find use in a variety of
applications, including coatings, paints, adhesives,
10 and the like. Such resins are typically soluble in
organic solvents, and exhibit little if any solubility
in aqueous solvents or in systems in which water and a
second water-soluble solvent are employed. Organic
solvent-based resin solutions have thus typically been
15 the vehicle of choice for use in forming coatings and
the like of the resins. However, many organic
solvents commonly used in conjunction with such resins
present environmental problems associated with their
toxicity. There has been a growing concern based on
20 the effects of such organic solvents on the
environment, as well as on the long-term health of
individuals who come into contact with such solvents.
There has, therefore, been a growing interest in the
use of aqueous resin compositions as a means of
25 eliminating toxicity problems associated with organic
solvents, and as a means of complying with
governmental edicts with respect to the use of such
solvents.

30 Examples of aqueous polyester and other
resin dispersions are known in the art. The

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dispersion of the resin into the aqueous medium has
1 customarily been achieved through the use of
dispersing or emulsifying agents such as nonionic or
ionic surfactants. However, the use of surfactant-
stabilized aqueous resin dispersions is far from
5 desirable, since a proportion of free surfactant can
be carried through to the final product, which can
result in a diminution of the desired properties of
the final product.

The prior art has thus attempted to
10 incorporate moieties directly into the polymer
molecule which affords greater water dispersibility to
the polymer. Typically, these attempts involve
copolymerization of a water-soluble or water-
dispersible comonomer together with the other monomers
15 which react together to form the desired polymer
molecule. Typical of this approach is U.S. Patent No.
3,563,942, which discloses copolymerization of an
aromatic sulfonate moiety in the synthesis of the
desired polyester polymer.

20 Similar approaches are disclosed in U.S.
Patent No. 4,525,524, U.S. Patent No. 4,910,292, and
U.S. Patent No. 4,973,656, which disclose other
techniques for copolymerizing a sulfonate-type monomer
directly into the polymer when it is formed from its
25 monomeric constituents. These techniques require very
high reaction temperatures, whereas the process of the
present invention can be carried out at much milder,
less energy-intensive conditions themselves.

The prior art approach to the objective of
30 incorporating a water-dispersible moiety into the

polymer molecule has other drawbacks in addition to
1 the severe reaction conditions. Notable among these
is the fact that under such severe reaction
conditions, the polymer easily decomposes and/or is
converted to a yellowish or dark product. This
5 decomposition is difficult to control or eliminate.
Also, aromatic sulfonates can cause 1, 4-butanediol,
which is ordinarily a preferred reactant, to be
converted to tetrahydrofuran; and can cause diethylene
glycol, another preferred reactant, to be converted to
10 dioxane. These conversions occur because of the
strong acidity of the aromatic sulfonate. Both such
conversions are undesirable as they lead to losses of
yield and to unsatisfactory properties of the product.
It is also difficult to identify satisfactory water-
15 dispersible, e.g. sulfonate-based, comonomers which
can successfully copolymerize with the other
comonomers to form the desired copolymeric product.
The reaction conditions that become necessary are
constrained by the additional comonomer present, such
20 that harsher reaction conditions are often required
that are in turn more difficult to control.

The present invention is thus directed to
an improved technique for forming water-dispersible
polymeric resins, particularly resins formed by
25 condensation polymerization such as polyesters,
polyamides and polyethers, which technique affords
improved ease of operation, more satisfactory yields,
improved properties (such as desirably light color of
polyesters and polyethers produced by this invention),
30 and offers a greater variety in the selection of

reactants and in the range of properties of the
1 products that can be obtained.

The present invention is further directed to
an improved process for obtaining such water-
dispersible polymers which can be used as final
5 products or can be used as intermediates for the
subsequent formulation of other polymeric derivatives
such as polyurethanes.

One aspect of the present invention is a
process for producing a water-dispersible polymer
10 comprising: (a) sulfonating an ethylenically
unsaturated monomeric precursor which has no aromatic
ring and which is substituted with at least two groups
selected from the group consisting of -OH, -COOH and -
NH₂, to form a sulfonated monomeric precursor; and (b)
15 reacting said sulfonated monomeric precursor with a
difunctional second monomer capable of undergoing
condensation polymerization with said sulfonated
monomeric precursor, under conditions whereunder said
precursor and said second monomer undergo condensation
20 polymerization.

Preferably, said sulfonation is carried out
with a sulfonating agent selected from the group
consisting of bisulfites, metabisulfites, and mixtures
thereof, under conditions such that said sulfonating
25 agent sulfonates said monomeric precursor by reaction
at said ethylenic unsaturation.

Optionally, the monomeric precursor is
simultaneously sulfonated and end-capped with a
difunctional precursor to form a sulfonated,
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difunctional "dimer" which is capable of undergoing
1 condensation polymerization in step (b).

The polymeric product can be all of one type
of polymer, or can comprise two or more (preferably up
to four) blocks each of which is a polyester, a
5 polyamide, or a polyether, wherein the blocks are
either bonded directly to each other or are each
bonded through a -C(O)NH-, -C(O)O- or -O- linkage to
an intervening alkyl moiety containing 2 to 20 carbon
atoms which is saturated or contains ethylenic
10 unsaturation provided that adjacent blocks bonded
directly to each other are types of polymer different
from each other.

The present invention is useful in making
water-dispersible polymers, particularly water-
15 dispersible condensation polymers. The products of
the process of this invention can be used per se to
form coatings, films and the like. The products of
the process of this invention can also be used as
intermediates in the formation of other polymeric
20 species, for instance by reacting appropriate di-
isocyanate compounds or other di-substituted cross
linking agents with the carboxylic acid, amino, or
hydroxyl substituent groups present on the polymers
produced by the present invention.

25 The condensation polymerization reactions
with which the present invention may be used include
any reactions among reactants in which appropriate
functionalities on the reactants react to form a
covalent linkage, the reaction typically (but not
30 always) resulting in the formation of a byproduct

1 molecule, typically water, as a result of the
reaction.

5 The functionalities present on the reactants
usually include one or both of -COOH (or anhydride)
and/or -COH, and one or both of -OH and -NH₂. The
reactants that enter into such condensation reactions
are usually substituted with two, or more, of such
functionalities. More often, reactants are
substituted with the same functionalities (e.g.,
diacids, diols, diamines), but they can be substituted
10 with two or more different functionalities (e.g.,
amino acids, hydroxyacids).

Preferred examples of condensation
polymerization reactions include reactions which form
polyesters, polyethers and polyamides. As is well
15 known, polyesters form by the reaction of, for
instance, diols with dicarboxylic acids or anhydrides
thereof. Polyamides form by the reaction of, for
instance, diamines with dicarboxylic acids or
anhydrides thereof. Polyethers within the scope of
20 the present invention can be formed by the
polymerization of, for instance, ethylene oxide or
propylene oxide under ring-opening conditions.
Condensation polymerization reactions also include
such reactions of glycol or alkoxy-terminated
25 polyethylene glycol with a diacid or anhydride to form
a polyester of the polyethylene glycol.

The polymers within the scope of the present
invention also include those composed of blocks
wherein blocks adjoining each other are different
30 types of condensation polymers. Examples include

polyester/polyamide, polyester/polyether, and
1 polyamide/polyether. Other examples include triblock
polymers, wherein the inner block is different from
each of the outer blocks which can be the same as each
other or different from each other. Examples include
5 polyether/polyester/polyether, and so forth.

Also included are molecules wherein one or
two polymeric chains meeting any of the descriptions
herein is pendant from an alkyl moiety containing 2 to
20 carbon atoms through a $-C(O)NH-$, $-C(O)O-$, or $-C-O-$
10 C- linkage. An example of this type of compound is
that formed by esterifying both carboxylic
functionalities of maleic acid or maleic anhydride
with polyethylene glycol or polypropylene glycol at a
molar ratio of glycol:maleic acid or anhydride of at
15 least 2:1.

One essential aspect of the process of the
present invention is that at least one of the
difunctional monomeric reactants contains ethylenic
unsaturation, that is, a carbon-carbon double bond,
20 either in its main chain or pendant from its main
chain.

Thus, for instance, the desired ethylenic
unsaturation is present as an ethylenically
unsaturated diacid, an ethylenically unsaturated
25 anhydride (such as maleic anhydride), an ethylenically
unsaturated diol, an ethylenically unsaturated
diamine, or mixtures of any two or more of such
compounds. Also, ethylenically unsaturated compounds
which contain nonidentical functional groups can be
30 used.

The ethylenically unsaturated diacid
1 component can comprise in whole or in part one or more
ethylenically unsaturated polycarboxylic acids,
especially dicarboxylic acids or their anhydrides,
including but not limited to fumaric acid, maleic
5 acid, mesaconic acid, citraconic acid, muconic acid
(e.g. trans-trans muconic acid) and itaconic acid, and
any anhydrides thereof, such as maleic anhydride. In
general, the preferred ethylenically unsaturated
dicarboxylic acids and anhydrides will contain 4 to 8
10 carbon atoms but may contain anywhere from 4 to 36
carbon atoms.

Diacids wherein the ethylenic unsaturation
is pendant from the principal chain of the diacid are
also contemplated within the scope of the present
15 invention. Examples include any of the dicarboxylic
acids disclosed herein, and their anhydrides, having a
pendant chain containing 2 to 8 carbon atoms at least
two of which are connected by a carbon-carbon double
bond, such as vinyl, propenyl, butenyl, and the like.
20 One example is 2-vinyl-butane-1, 4-dioic acid.

Preferred ethylenically unsaturated diol
compounds contain 4 to 10 carbon atoms. Examples of
such compounds include allyl diglycol, as well as any
ethylenically unsaturated analogs of the exemplary
25 glycols set forth herein.

Included within the scope of ethylenically
unsaturated diols useful in the process of the present
invention are those wherein the ethylenic unsaturation
is present in, or in a substituent pendant from, the
30 chain connecting the two diol groups. Preferred

examples include the mono-acrylates and mono-

- 1 methacrylates of triols such as glycerol, wherein two
hydroxyl groups remain available to cooperate in the
formation of the polyester molecule. Other examples
of satisfactory ethylenically unsaturated diols
5 include 1,4-butenediol, 1,4-butyne-1,3-diol, glycerine
allyl ether and glyceryl monostearate.

Ethylenically unsaturated diamines can also
be used. Preferably they contain 2 to 12 carbon atoms
and can be straight or branched-chain. Preferred
10 diamines include straight and branched chain diamino-
substituted alkenes, esters and amides such as diamino
analogs of any di-hydroxyl (e.g. glycol) derivatives
disclosed herein.

In the first step of the process of the
15 present invention, the ethylenically unsaturated
monomeric precursor (e.g. diacid, anhydride, diol, or
diamine) is sulfonated. Sulfonation is carried out by
reacting the compound under appropriate sulfonating
conditions with a sulfonating agent which comprises
20 one or more bisulfites and/or one or more
metabisulfites. Preferred sulfonating agents are the
ammonium and alkali metal sulfites and alkali metal
metabisulfites. Thus, the more preferred sulfonating
agents are sodium bisulfite and sodium metabisulfite.
25 Other preferred sulfonating agents include lithium
bisulfite, lithium metabisulfite, potassium bisulfite,
potassium metabisulfite, ammonium bisulfite and
ammonium metabisulfite.

Sulfonation of the monomeric precursor
30 should be carried out using a stoichiometric excess of

the sulfonating agent. The sulfonation is preferably
1 carried out in a suitable solvent such as water.
Satisfactory sulfonation conditions include
maintaining a temperature of about 10°C to about 120°C
for a time on the order of 2-15 hours. The
5 sulfonation also can be catalyzed by fine air bubbles
purged through the reaction medium, or by any
peroxides such as hydrogen peroxide, benzoyl peroxide,
or t-butyl hydrogen peroxide.

Optionally, one may include in the reaction
10 mixture of ethylenically unsaturated difunctional
monomeric precursor and sulfonating agent, a second
difunctional precursor reactant which enters into a
condensation reaction with the ethylenically
unsaturated monomeric precursor and endcaps it. If
15 such another reactant is present, the reaction product
is a sulfonated difunctional dimer which contains an
amide, ether or ester linkage, depending on the
chemical identity of the reactants and thus the nature
of the endcapping reaction. Compounds suitable for
20 use as the second difunctional precursor include
compounds substituted with at least two groups
selected from the group consisting of -OH, -NH₂ and
-COOH at least one of which can enter into a
condensation reaction with the monomeric precursor.
25 Examples include diacids, diols and diamines
containing 2 to 8 carbon atoms, such as 1,6-hexanediol
and 1,6-diaminohexane.

Whether or not the indicated optional
reactant was also present, the product of the first
30 step of the process of the present invention is a

sulfonated product, at least di-substituted with
1 groups selected from the group consisting of
-OH, -COOH and -NH₂. This product is termed a
monomeric precursor in that it has either no, or at
most one, -C(O)NH- or -C(O)O-linkage. This product
5 must be capable of undergoing condensation
polymerization with a suitable difunctional second
monomer in the second step of the present invention.

The second step of the present invention can
be carried out with any of a considerable number of
10 reactants. The choice depends on the nature of the
functional groups present, and in part on the
properties desired of the eventual product.

One reactant preferably employed in the
desired condensation polymerization reaction is a
15 diacid component, by which is meant one or more
dicarboxylic acids, one or more anhydrides of
dicarboxylic acids, or mixtures thereof.

The dicarboxylic acids that can be used in
the present invention include aliphatic dicarboxylic
20 acids, alicyclic dicarboxylic acids, aromatic
dicarboxylic acids, ethylenically unsaturated alkenyl
dicarboxylic acids, or mixtures of two or more of
these acids. Preferred are alkyl dicarboxylic diacids
which generally will contain 4 to 36 carbon atoms, and
25 aromatic dicarboxylic diacids which generally contain
9 to 20 carbon atoms. Examples of useful dicarboxylic
acids include oxalic, malonic, dimethylmalonic,
succinic, glutaric, adipic, trimethyladipic, pimelic,
2,2-dimethylglutaric, azelaic, sebacic, suberic, 1,3-
30 cyclopentanedicarboxylic, 1,2-cyclohexanedicarboxylic,

1,3-cyclohexanedicarboxylic, 1,4-cyclohexanedicarboxylic, phthalic, terephthalic, isophthalic, tetrahydrophthalic, hexahydrophthalic, 2,5-norbornanedicarboxylic, 1,4-naphthalic, diphenic, 4,4'-oxydibenzoic, diglycolic, thiodipropionic, 4,4'-sulfonyldibenzoic, and 2,5-naphthalenedicarboxylic acids. Anhydrides of any of the foregoing are also contemplated.

Preferred difunctional dicarboxylic acids include isophthalic acid, terephthalic acid, phthalic acid, adipic acid, tetrachlorophthalic acid, pivalic acid, dodecanedioic acid, sebacic acid, azelaic acid, 1,4-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, maleic acid, fumaric acid, succinic acid, 2,6-naphthalenedicarboxylic acid, glutaric acid, and any of the anhydrides thereof.

Diol compounds that can be used in the present invention include glycols, of which ethylene glycol is the preferred diol.

In cases where glycols in addition to, or instead of, ethylene glycol are utilized, it is preferable for them to contain from 3 to 10 carbon atoms. In cases where glycol ethers are utilized in conjunction with ethylene glycol in the diol component, it is preferable for them to contain from 4 to 10 carbon atoms. Some representative examples of glycols that can be used in conjunction with or instead of ethylene glycol include 1,3-propylene glycol, 1,2-propylene glycol, 2,2-diethyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, 2-ethyl-2-isobutyl-1,3-

propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-
1 pentanediol, 1,6-hexanediol, 2,2,4-trimethyl-1,6-
hexanediol, 2,4-dimethyl-2-ethylhexane-1,3-diol, 1,2-
cyclohexanediol, 1,3-cyclohexanedimethanol, 1,4-
cyclohexanedimethanol, p-xylenediol, and 2,2,4,4-
5 tetramethyl-1,3-cyclobutanediol.

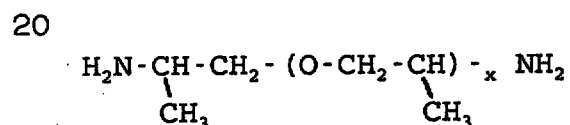
As the diol component, polyether glycols can
also be used, such as polypropylene glycol having a
molecular weight of 200 to 6,000 (examples of which
include ("Rezol ED-1000" and "Rezol ED-2000", sold by
10 Witco Corporation); polyethylene glycol having a
molecular weight of 200 to 6,000 (examples of which
include ("Rezol PEG-400" and "Rezol PEG-1000", sold by
Witco Corporation); and block and random copolymers of
propylene glycol and ethylene glycol, having a
15 molecular weight of 200 to 6,000 (examples of which
include "Rezol EPD-112", "Rezol EPD-225", "Rezol EPD-
56", and "Rezol EPD-28" sold by Witco Corporation).

If branching is desirable, then it will be
advantageous to use a branching agent in the
20 condensation polymerization reaction. Such branching
agents may contain three or more functional groups,
and they preferably contain three or four functional
groups. The reactive groups may be carboxyl or
aliphatic hydroxyl. The branching agent may contain
25 both types of groups. Examples of acidic branching
agents include trimesic acid, trimellitic acid,
pyromellitic acid, butanetetracarboxylic acid,
naphthalene tricarboxylic acids and cyclohexane-1,3,5-
tricarboxylic acid. Examples of hydroxyl branching
30 agents (polyols) include glycerin, trimethylpropane,

pentaerythritol, dipentaerythritol, 1,2,6-hexanetriol
1. and 1,3,5-trimethylolbenzene. Examples of hydroxy
acid branching agents are 2,2-dihydroxymethyl
propionic acid, 10,11-dihydroxy-undecanoic acid, and
5- (2-hydroxyethoxy)isophthalic acid. Generally from 0
5 to 3 percent of a polyol containing from 3 to 12
carbon atoms will be used as the branching agent
(based upon the total diol component).

Instead of, or in addition to, the diol and
polyol components, there can be present a diamine
10 component. One type of suitable diamine is di-amino-
substituted alkyl, preferably containing 3 to 8 carbon
atoms, examples of which include compounds analogous
to the aforementioned glycols and diols, wherein the
hydroxyl substituents are replaced by amino groups.

15 Another type of suitable diamine is diamine-
substituted polyoxyalkylene compounds, preferably
poly(ethoxy) and/or poly(propoxy) compounds endcapped
with amino groups. Examples of this type of reactant
include compounds generalizable by the formula



known as Jeffamine D230, D400, D2000, and D4000
25 (previously sold by Texaco Chemical Co., now Huntsman
Chemical) corresponding to said formula wherein x is
2-3, 5-6, about 33, and about 68, respectively.

As indicated, condensation polymers useful
in this invention also include bifunctional compounds
30 such as hydroxyacids and amino acids, which are

polymerized head-to-tail in known manner. Such

- 1 reactants would have to include some ethylenically unsaturated compounds. Examples of such reactants include 6-hydroxy (or 6-amino) hexanedioic acid, and the like.

- 5 The acid component (which, as defined above, comprises one or more acids and/or anhydrides) and the one or more reactants destined to react with the acid or anhydride component are selected so that the reactants that enter into the condensation

- 10 polymerization include a sufficient amount of sulfonation so that the sulfonated reaction product of the present invention provides a satisfactory degree of water dispersibility in the polymer.

- Thus, the amount of sulfonated reactant can
15 comprise 1 mol.% to 50 mol.% of the reaction mixture in the second step of the process. Generally, the sulfonated reactant(s) comprise about 1 mol.% to about 10 mol.% of the reaction mixture. The reactants are otherwise selected to be approximately equimolar in
20 relationship to each other with the proviso that the component which carries the substituent group identical to the desired terminal group or groups of the polymer should be provided in stoichiometric excess.

- 25 Thus, for instance, if it is desired that the polymer product contains carboxylic terminal groups, then an excess of the acid component should be provided. If it is desired that the polymer should be endcapped with hydroxyl terminal groups, then an
30 excess of the diol component should be supplied. On

the other hand, if it is desired that the polymer
1 should be endcapped with amino terminal groups, then
an excess of the diamine component should be supplied.
It should be recognized that for these purposes the
terms "diacid component," "diol component," and
5 "diamine component" are intended to include all
components of the reaction mixture whether or not
ethylenically unsaturated. It will also be recognized
that to ensure that the polymer is capped with the
desired terminal groups, it may be necessary to
10 provide in the reaction mixture more than simply a
slight stoichiometric excess of the indicated
component; the degree of excess is tempered, however,
by the effect of that excess on the distribution of
polymeric chain lengths formed by the condensation
15 polymerization.

The condensation polymer can also be one
which contains only one terminal carboxylic acid,
hydroxyl or amino group. For instance, a C_1 - C_6 alkoxy
(e.g. methoxy)-capped polyethylene glycol is reacted
20 with ethylene glycol, acetic anhydride and maleic
anhydride to form a polyester which is capped with a
hydroxyl group and a methyl group, and which contains
ethylenic unsaturation. In addition, one can prepare
a polymer that is mono-capped with a desired
25 functional group by preparing a condensation polymer
which is disubstituted with functional terminal
groups, and then capping one end of the molecule. For
instance, a diamine-capped or di-hydroxyl-capped
polymer can be reacted with a lower (C_1 - C_6) alkanolic
30 carboxylic acid to cap one end of the polymer with an

1 ester or amide. Likewise, a dicarboxylic acid-capped
polymer can be reacted with a (C₁-C₆) alcohol or (C₁-C₆)
alkyl amine, to cap one of the two carboxylic acid
moieties with an ester or amide.

5 The reaction mixture is then subjected to
condensation polymerization conditions effective to
cause the reactants to react with each other to form
the desired condensation polymers. In general,
effective condensation polymerization conditions are
readily familiar to (and ascertainable by) the
10 practitioner. It is preferred not to carry out the
reaction in a solution. However, if a solvent is
desired, it should be high boiling (i.e. a boiling
point above about 140°C.) Examples of suitable
solvents include DMF (dimethylformamide), DMA (N,N-
15 dimethylacetamide), xylene and DMSO.

Preferably, the reactant mixture for
carrying out the condensation polymerization includes
a small but effective amount such as up to about 0.02
wt.% of a catalyst for the polymerization. Useful
20 catalytic compounds include protonic acids, tin
compounds, titanium compounds and antimony compounds.

Typical condensation polymerization
conditions are provided by exposing the reactants to
temperatures on the order of about 150°C to about
25 250°C. During the progress of the reaction, it is
preferred to draw off water of condensation. To
effectively carry out the desired condensation
polymerization it is preferred to use nitrogen to
purge the reaction mixture in order to carry out the
30 water.

1 The chain length or molecular weight of the
polymers that are useful and produced in the process
of the present invention can fall within a rather wide
range; typically, useful polymers will have a
molecular weight in the range of about 200 to about
5 50,000. Thus, amounts and identities of the reactants
can readily be tailored to achieve any desired
molecular weight and distribution.

 At the end of the condensation
polymerization, the product can be recovered and
10 separated from the reaction mixture.

 The process of the present invention affords
several significant advantages compared to other
processes for producing water-dispersible sulfonated
polymers. In particular, each of the foregoing steps
15 can be carried out under relatively mild conditions
and are not particularly constrained by the choice of
reactants. In particular, a much greater freedom in
choice of reactants is provided, as the reactants in
the condensation polymerization step can be
20 polymerized under relatively straightforward
condensation polymerization conditions and the
sulfonation step can be carried out under fairly
conventional sulfonation conditions. This freedom in
the choice of reactants is an advantage in that it
25 affords greater range in the tailoring of the
properties of the final, water-dispersible product.

 In addition, the ability to select the
identity of the terminal groups on the polymers
affords the operator greater freedom in incorporating
30 the process of the present invention into processes

that use the water-dispersible product as an
1 intermediate in the synthesis of, for example,
polyurethanes by reaction of the appropriately end-
capped polymer with other reactive species such as
diisocyanates or additional quantities of dicarboxylic
5 acids, as the case may be.

The invention will be described further in
the following examples. These examples are intended
for illustrative purposes, and are not intended to
limit the scope of applicants' invention.

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EXAMPLE 1

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A. Preparation of adduct (50%) [2-(sodiosulfo)-1,4-butanedioic acid]

5 RAW MATERIAL

Maleic Anhydride	111.4	grams
Water	270.5	grams
Sodium Bisulfite	118.2	grams

10 PROCEDURE

A four neck glass flask, equipped with a nitrogen inlet, a stirrer, a water condenser, and a thermometer, was charged with maleic anhydride. A clear water solution of sodium bisulfite was added under constant agitation and the temperature was maintained at 75-80°C for four hours. The conversion of sulfonation was 100%, and the solid content was 50%.

20 B. Preparation of sodium sulfonate-containing polyester.

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RAW MATERIAL

1	1,6-Hexanediol	997 grams
	Neopentyl Glycol (90%)	853 grams
	Product of step A.	
	(as 50 wt.% aqueous solution)	1,017 grams
5	Adipic Acid	1,821 grams
	Total Load	4,688 grams
	Organotin Catalyst	0.30 grams
	Water to distill	1,156 grams
	Theoretical Yield	3,532 grams

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PROCEDURE

15 A four neck glass flask, equipped with a nitrogen inlet, a stirrer, a column, and a thermometer, was charged with catalyst, 1,6-hexanediol, neopentyl glycol, a 50 wt.% solution of the product of step A, and adipic acid. The temperature was increased to 150°C +/-5°, while the column was kept hot using steam. The nitrogen and agitation were increased, as the reaction proceeded, to facilitate the water removal, but not rapid enough to blow out the glycol.

20 Hydroxyl value and acid number were checked as needed and the loss of glycol during the reaction was adjusted to reach the theoretical hydroxyl value. Reaction was considered complete when the hydroxyl number and the acid number reached the expected values. The final sodium sulfonate-containing polyester had a hydroxyl number of 108, and an acid number of 3.0. The polymer, a sulfonate polyester,

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dispersed in water very easily, and demonstrated good
1 stability.

C. Preparation of sodium sulfonate-
containing branched polyester.

5 RAW MATERIAL

	Diethylene Glycol	771 grams
	Glycerine	18.1 grams
	Product of step A. (as 50 wt.% aqueous solution)	732 grams
10	Adipic Acid	752 grams
	Total Load	2,273 grams
	Organotin Catalyst	0.14 grams
	Water to distill	611 grams
	Theoretical Yield	1,662 grams

15 PROCEDURE

A four neck glass flask, equipped with a
nitrogen inlet, a stirrer, a column, and a
thermometer, was charged with catalyst, diethylene
glycol, glycerine, a 50 wt.% solution of the product
of step A., and adipic acid. The temperature was
20 increased to 150°C +/-5°, while the column was kept
hot using steam. The nitrogen and agitation were
increased, as the reaction proceeded, to facilitate
the water removal, but not rapid enough to blow out
the glycol.

25 Hydroxyl value and acid number were checked
as needed and the loss of glycol during the reaction
was adjusted to reach the theoretical hydroxyl value.
Reaction was considered complete when the hydroxyl
30 number and the acid number reached the expected

values. The final sodium sulfonate-containing polyester had a hydroxyl number of 53.6, and an acid number of 1.85. The polymer, a sulfonate polyester, dispersed in water very easily, and the dispersed polyester demonstrated good stability.

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D. Preparation of sodium sulfonate-containing amine-terminated polyether/polyamide.

RAW MATERIAL

Jeffamine D-1000	499 grams
10 Product of step A. (as 50 wt.% aqueous solution)	101 grams
Total Load	600 grams
Organotin Catalyst	0.04 grams
Water to distill	59 grams
15 Theoretical Yield	541 grams

PROCEDURE

A four neck glass flask, equipped with a nitrogen inlet, a stirrer, a column, and a thermometer, was charged with catalyst, Jeffamine D-1000, and the product of step A. The temperature was increased to 150°C +/-5°, while the column was kept hot using steam. The nitrogen and agitation were increased, as the reaction proceeded, to facilitate the water removal. Reaction was considered complete when the amine number and the acid number reached the expected values. The final sodium sulfonate-containing polyamide had a amine number of 62.5, and an acid number of 5.2.

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EXAMPLE 2

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A. Preparation of Adduct [half ester from one mole of maleic anhydride and one mole of 1, 6-hexanediol].

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RAW MATERIAL

1,6-Hexanediol	546.3 grams
Maleic Anhydride	453.7 grams
Total Load	1,000.0 grams
Theoretical Yield	1,000.0 grams
10 Sodium Bisulfite	661.0 grams
Water	2,061.0 grams

PROCEDURE

15 A four neck glass flask, equipped with a nitrogen inlet, a stirrer, a water condenser, and a thermometer, was charged with 1,6-hexanediol, and maleic anhydride (the molar ratio of 1,6-hexanediol to maleic anhydride is 1/1), and heated to approximately 80°C. After two hours, a clear water solution of sodium bisulfite was added under constant agitation and the temperature was maintained at 75-80°C for 20 eight hours. The conversion of sulfonation was 100%, and the solid content was 50%.

25 B. Preparation of sodium sulfonate-containing polyester.

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RAW MATERIAL

1	1,6-Hexanediol	421 grams
	Product of step A. (as 50 wt.% aqueous solution)	303 grams
	Adipic Acid	390 grams
5	Total Load	1,114 grams
	Organotin Catalyst	0.07 grams
	Water to distill	248 grams
	Theoretical Yield	866 grams

PROCEDURE:

10 A four neck glass flask, equipped with a nitrogen inlet, a stirrer, a column, and a thermometer, was charged with catalyst, 1,6-hexanediol, a 50 wt.% aqueous solution of the product of step A., and adipic acid. The temperature was
15 increased to 190°C +/-5°, while the column was kept hot using steam. The nitrogen and agitation were increased, as the reaction proceeded, to facilitate the water removal, but not rapid enough to blow out the glycol.

20 Hydroxyl value and acid number were checked as needed and the loss of glycol during the reaction was adjusted to reach the theoretical hydroxyl value. Reaction was considered complete when the hydroxyl number and the acid number reached the expected
25 values. The final sodium sulfonate-containing polyester had a hydroxyl number of 108.3, and an acid number of 0.7. The polymer, a sulfonate polyester, dispersed in water very easily, and the dispersed polyester demonstrated good stability.

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EXAMPLE 3

1 A. Preparation of Adduct [bis(hydroxyhexyl)
maleate, one mole of maleic anhydride and two moles of
1,6-hexanediol].

RAW MATERIAL

5	1,6-Hexanediol	3,228 grams
	Maleic Anhydride	1,341 grams
	Total Load	4,569 grams
	Organotin Catalyst	0.38 grams
	Water to distill	246 grams
10	Theoretical Yield	4,323 grams
	Sodium Bisulfite	1,417 grams
	Water	4,234 grams

PROCEDURE

15 A four neck glass flask, equipped with a
nitrogen inlet, a stirrer, a column, and a
thermometer, was charged with catalyst, 1,6-
hexanediol, and maleic anhydride (the molar ratio of
1,6-hexanediol to maleic anhydride is 2/1), and heated
20 to approximately 80°C. The temperature was increased
to 225°C +/-5°, while the column was kept hot using
steam. The nitrogen and agitation were increased, as
the reaction proceeded, to facilitate the water
removal, but not rapid enough to blow out the glycol.

25 Hydroxyl value and acid number were checked
as needed and the loss of glycol during the reaction
was adjusted to reach the theoretical hydroxyl value.
Reaction was considered complete when the hydroxyl
number and the acid number reached the expected

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1 values. The final polyester had a hydroxyl number of
353.6 and an acid number of 0.3.

The reaction mixture was cooled to 85°C.
The column was replaced with a water condenser and
nitrogen was shut off. A clear water solution of
5 sodium bisulfite was added under constant agitation
and the temperature was maintained at 75-80°C for
eight hours. The conversion of sulfonation was 100%,
and the solid content was 60%.

B. Preparation of sodium sulfonate-
10 containing polyester.

RAW MATERIAL

1,6-Hexanediol	457 grams
Product of step A. of Ex.3 (as 60 wt.% aqueous solution)	141 grams
15 Adipic Acid	532 grams
Total Load	1,130 grams
Organotin Catalyst	0.08 grams
Water to distill	188 grams
Theoretical Yield	942 grams

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PROCEDURE

A four neck glass flask, equipped with a
nitrogen inlet, a stirrer, a column, and a
thermometer, was charged with catalyst, 1,6-
25 hexanediol, a 60 wt.% aqueous solution of the product
of step A., and adipic acid. The temperature was
increased to 190°C +/-5° while the column was kept hot
using steam. The nitrogen and agitation were
increased, as the reaction proceeded, to facilitate

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1 the water removal, but not rapid enough to blow out
the glycol.

Hydroxyl value and acid number were checked
as needed and the loss of glycol during the reaction
was adjusted to reach the theoretical hydroxyl value.
5 Reaction was considered complete when the hydroxyl
number and the acid number reached the expected
values. The final sodium sulfonate-containing
polyester had a hydroxyl number of 43.1, and acid
number of 0.8.

10 C. Preparation of sodium sulfonate-
containing polyester via transesterification method.

RAW MATERIAL

Fomrez 66-56*	832 grams
15 Product of step A. of Ex.3 (as 60 wt.% aqueous solution)	296 grams
Total Load	1,128 grams
Water to distill	128 grams
Theoretical Yield	1,000 grams
20 *Poly(hexamethylene adipate) glycol, molecular weight 2,000, from Witco Corporation	

PROCEDURE

A four neck glass flask, equipped with a
nitrogen inlet, a stirrer, a column, and a
25 thermometer, was charged with Fomrez 66-56, and a 60
wt.% aqueous solution of the product of step A. The
temperature was increased to 190°C +/-5°, while the
column was kept hot using steam. The nitrogen and
agitation were increased, as the reaction proceeded,

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1 to facilitate the water removal, but not rapid enough
to blow out the glycol.

5 Hydroxyl value and acid number were checked
as needed. The final sodium sulfonate-containing
polyester had a hydroxyl number of 73.4. The polymer,
a sulfonate polyester, dispersed in water very easily,
and the dispersed polyester demonstrated good
stability.

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EXAMPLE 4

1 A. Preparation of adduct [2-(sodiosulfo)-
1,4-butanediol] (50%).

RAW MATERIAL

2-Butene-1,4-diol	350 grams
5 Water	765 grams
Sodium Bisulfite	414 grams
t-Butyl hydroperoxide	42 grams

PROCEDURE

10 A four neck glass flask, equipped with a
nitrogen inlet, a stirrer, a water condenser, and a
thermometer, was charged with 2-butene-1,4-diol. A
clear water solution of sodium bisulfite was added
under constant agitation, then t-butyl hydroperoxide
was added. The temperature was maintained at 75-80°C
15 for 24 hours. The conversion of sulfonation was 70%,
and the solid content was 50%.

 B. Preparation of sodium sulfonate-
containing polyester.

20 RAW MATERIAL

1,4-Butanediol	773 grams
Product of step A. of Ex. 4 (as 50 wt.% aqueous solution)	299 grams
Adipic Acid	1,089 grams
25 Total Load	2,161 grams
Organotin Catalyst	0.14 grams
Water to distill	445 grams
Theoretical Yield	1,716 grams

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PROCEDURE

1 A four neck glass flask, equipped with a
nitrogen inlet, a stirrer, a column, and a
thermometer, was charged with catalyst, 1,4-
butanediol, the 50 wt.% aqueous solution of the
5 product of step A., and adipic acid. The temperature
was increased to 150°C +/-5°, while the column was
kept hot using steam. The nitrogen and agitation were
increased, as the reaction proceeded, to facilitate
the water removal, but not rapid enough to blow out
10 the glycol.

 Hydroxyl value and acid number were checked
as needed and the loss of glycol during the reaction
was adjusted to reach the theoretical hydroxyl value.
Reaction was considered complete when the hydroxyl
15 number and the acid number reached the expected
values. The final sodium sulfonate-containing
polyester had a hydroxyl number of 96.8, an acid
number of 3.9.

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EXAMPLE 5

A. Preparation of adduct [half ester from one mole of maleic anhydride and one mole of diethylene glycol].

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RAW MATERIAL

Diethylene Glycol	1559 grams
Maleic Anhydride	1441 grams
Total Load	3,000 grams
Theoretical Yield	3,000 grams
10 Sodium Bisulfite	1,499 grams
Water	4,499 grams

PROCEDURE

A four neck glass flask, equipped with a nitrogen inlet, a stirrer, a water condenser, and a
15 thermometer, was charged with diethylene glycol and maleic anhydride (the molar ratio of diethylene glycol to maleic anhydride was 1/1), and heated to approximately 80°C. After two hours, a clear water solution of sodium bisulfite was added under constant
20 agitation and the temperature was maintained at 75-80°C for eight hours. The conversion of sulfonation was 100%, and the solid content was 50%.

B. Preparation of dicarboxylic acid-terminated sodium sulfonate-containing polyester.

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RAW MATERIAL

1	Diethylene Glycol	530 grams
	Product of step A. of Ex.5 (as 50 wt.% aqueous solution)	359 grams
	Total Load	1,832 grams
5	Organotin Catalyst	0.12 grams
	Water to distill.	370 grams
	Theoretical Yield	1,462 grams

10 PROCEDURE

A four neck glass flask, equipped with a nitrogen inlet, a stirrer, a column, and a thermometer, was charged with catalyst, diethylene glycol, a 50 wt.% aqueous solution of the product of step A., and adipic acid. The temperature was increased to 180°C +/-5°, while the column was kept hot using steam. The nitrogen and agitation were increased, as the reaction proceeded, to facilitate the water removal, but not rapid enough to blow out the glycol.

Hydroxyl value and acid number were checked as needed. Reaction was considered complete when the hydroxyl number and the acid number reached the expected values. The final dicarboxylic acid-terminated sodium sulfonate-containing polyester had a hydroxyl number of 13.6, and an acid number of 108.7. The polymer, a dicarboxylic acid-terminated sulfonate polyester, was dispersed in water very easily, and the dispersed polyester demonstrated good stability.

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EXAMPLE 6

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A. Preparation of Adduct [half ester from one mole of maleic anhydride and one mole of 1,4-butanediol].

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RAW MATERIAL

1,4-Butanediol	670 grams
Maleic Anhydride	730 grams
Total Load	1,400 grams
Theoretical Yield	1,400 grams
Sodium Bisulfite	758 grams
Water	2,158 grams

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PROCEDURE

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A four neck glass flask, equipped with a nitrogen inlet, a stirrer, a water condenser, and a thermometer, was charged with 1,4-butanediol, and maleic anhydride (the molar ratio of 1,4-butanediol to maleic anhydride was 1/1), and heated to approximately 80°C. After two hours, a clear water solution of sodium bisulfite was added under constant agitation and the temperature was maintained at 75-80°C for eight hours. The conversion of sulfonation was 100%, the solid content was 50%, and the pH of the aqueous solution was 3.0.

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B. Preparation of sodium sulfonate-containing polyester.

RAW MATERIAL

1,4-Butanediol	1,829 grams
Product of step A. of Ex.6 (as 50 wt.% aqueous solution)	1,625 grams
Adipic Acid	2,313 grams

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	Total Load	5,768 grams
1	Organotin Catalyst	0.36 grams
	Water to distill	1,433 grams
	Theoretical Yield	4,300 grams

5 PROCEDURE

A four neck glass flask, equipped with a nitrogen inlet, a stirrer, a column, and a thermometer, was charged with catalyst, 1,4-butanediol, a 50 wt.% aqueous solution of the product of step A. (pH 3.0), and adipic acid. The temperature was increased to 190°C +/-5°, while the column was kept hot using steam. The nitrogen and agitation were increased, as the reaction proceeded, to facilitate the water removal, but not rapid enough to blow out the glycol.

Hydroxyl value and acid number were checked as needed and the loss of glycol during the reaction was adjusted to reach the theoretical hydroxyl value. Reaction was considered complete when the hydroxyl number and the acid number reached the expected values. The final sodium sulfonate-containing polyester had a hydroxyl number of 52.2, an acid number of 2.1. The polymer, a sulfonate polyester, dispersed in water very easily, and the dispersed polyester demonstrated good stability. However, the loss of the 1,4-butanediol was significant and tetrahydrofuran formation from 1,4-butanediol during the reaction was observed.

C. Preparation of sodium sulfonate-containing polyester.

RAW MATERIAL

1	1,4-Butanediol	394 grams
	Product of step A. of Ex. 6 (as 50 wt.% aqueous solution)	213 grams
	Adipic Acid	562 grams
5	Total Load	1,169 grams
	Organotin Catalyst	0.08 grams
	Water to distill	252 grams
	Theoretical Yield	907 grams

10

PROCEDURE

A four neck glass flask, equipped with a nitrogen inlet, a stirrer, a column, and a thermometer, was charged with catalyst, 1,4-
15 butanediol, a 50 wt.% aqueous solution of the product of step A. (pH adjusted to 4.0 by adding sodium hydroxide), and adipic acid. The temperature was increased to 190°C +/-5°; while the column was kept hot using steam. The nitrogen and agitation were
20 increased, as the reaction proceeded, to facilitate the water removal, but not rapid enough to blow out the glycol.

Hydroxyl value and acid number were checked as needed and the loss of glycol during the reaction
25 was adjusted to reach the theoretical hydroxyl value. Reaction was considered complete when the hydroxyl number and the acid number reached the expected values. The final sodium sulfonate-containing polyester had a hydroxyl number of 57.26, an acid
30 number of 2.0. The polymer, a sulfonate polyester,

dispersed in water very easily, and the dispersed polyester demonstrated good stability. No tetrahydrofuran formation from 1,4-butanediol during the reaction was observed.



WHAT IS CLAIMED IS:

1. A process for producing a water-dispersible polymer, comprising:

(a) sulfonating an ethylenically unsaturated monomeric precursor which has no aromatic ring and which is substituted with at least two groups selected from the group consisting of -OH, -COOH, and -NH₂, with a sulfonating agent to form a sulfonated monomeric precursor which is substituted with at least two groups selected from the group consisting of -OH, -COOH, and -NH₂; and

(b) reacting said sulfonated monomeric precursor with a difunctional second monomer capable of undergoing condensation polymerization with said sulfonated monomeric precursor, under conditions whereunder said precursor and said second monomer undergo condensation polymerization.

2. A process according to Claim 1 wherein said sulfonating agent is selected from the group consisting of bisulfites, metabisulfites, and mixtures thereof.

3. A process according to Claim 1 or 2 wherein said ethylenically unsaturated monomeric precursor is a diacid.

4. A process according to Claim 3 wherein said diacid contains 4 to 36 carbon atoms.

5. A process according to claim 3 wherein said diacid is selected from the group consisting of maleic acid, fumaric acid, mesaconic acid, citraconic acid, muconic acid, itaconic acid, and 2-vinyl-butane-1,4-dioic acid.



6. A process according to Claim 1 or 2 wherein said ethylenically unsaturated monomeric precursor is an anhydride.

7. A process according to Claim 6 wherein said anhydride contains 4 to 36 carbon atoms.

8. A process according to Claim 6 wherein said anhydride is selected from the group consisting of anhydrides of maleic acid, fumaric acid, mesaconic acid, citraconic acid, muconic acid, itaconic acid, and 2-vinyl-butane-1,4-dioic acid.

9. A process according to Claim 1 or 2 wherein said ethylenically unsaturated monomeric precursor is a diamine.

10. A process according to Claim 9 wherein said diamine contains 2 to 12 carbon atoms.

11. A process according to Claim 9 wherein said diamine is a diamino-alkene containing 2 to 12 carbon atoms.

12. A process according to Claim 1 or 2 wherein said ethylenically unsaturated monomeric precursor is a diol.

13. A process according to Claim 12 wherein said diol contains 4 to 10 carbon atoms.

14. A process according to Claim 12 wherein said diol is selected from the group consisting of 1,4-butenediol, 1,4-butyne-1,3-diol, glycerine allyl ether, glyceryl monostearate, and mono-acrylates and mono-methacrylates of glycol.

15. A process for producing a water-dispersible polymer, comprising



(a) reacting an ethylenically unsaturated anhydride or diacid which has no aromatic ring, a diol or diamine, and a sulfonating agent, to form a reaction product which is a sulfonated mono- or bis-ester or amide, which is substituted with at least two groups selected from -COOH , -OH and -NH_2 ; and

(b) reacting said reaction product with a difunctional second monomer capable of undergoing condensation polymerization with said sulfonated monomeric precursor, under conditions whereunder said precursor and said second monomer undergo condensation polymerization.

16. A water-dispersible polymer prepared by the process of any one of claims 1-15.