In general, the invention features a polymer having formula (1), where R, through R₆, independently, are hydrogen; an alkyl, e.g., C₆H₄₋₃₋₅₋₁, where a is 1 to 20 or higher; an aryl, e.g., phenyl or substituted phenyl, e.g., substituted with CH₃, CF₃, or OCH₃; an acyl, e.g., COH, COCH₃, or COOCF₃; or a halogen, e.g., F, Cl, Br, or I; R₅ and R₆, independently can be hydrogen; alkyl; aryl; alkoxy carbonyl, e.g., COOCH₃, COOC(CH₃)₂, or COOCH₂CH₃; or silyl, e.g., Si(CH₃)₃, (CH₂)₂Si(CH₃)₃, or Si(CH(CH₃)₂)₃; and n is at least 2. n can be up to 100, 10,000, 1,000,000, or higher.
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POLY(VINYL AMINE) ANALOGS

Statement as to Federally Sponsored Research

This invention was made with Government support under grant number DMR-9350473 and grant number DMR-9634528 awarded by the National Science Foundation. The Government has certain rights in the invention.

Background of the Invention

This invention relates to the formation of vinyl amine derivatives and their polymerization to form new poly(vinyl amine) analogs.

Poly(vinyl amine) and its analogs are members of an important class of cationic polyelectrolytes, which are very desirable materials with applications in the textile, adhesive and coatings, paper, petroleum, water treatment, cosmetic, and pharmaceutical industries.

However, poly(vinyl amine) analogs cannot be obtained through the polymerization of the obvious parent molecule, vinyl amine, because vinyl amine is unstable with respect to its imine tautomer, ethylimine. Poly(vinyl amine) analogs therefore have been obtained by indirect methods, e.g., the Hofmann rearrangement of poly(acrylamide) or the Schmidt reaction of poly(acrylic acid).

Summary of the Invention

The invention is based on the discovery that new poly(vinyl amine) analogs can be prepared by polymerization of precursors obtained by the isomerization of allylamines, allylamides, or allylimides. New copolymers can also be formed using the same precursors in combination with other polymerizable substrates. These new polymers and copolymers are polyelectrolytes, bearing side chains which become positively charged at low pH. Furthermore, the new
methods require fewer steps than methods previously employed to obtain poly(vinyl amines).

In general, the invention features a polymer having the formula (1):

\[
\begin{align*}
\text{R}_1 & \quad \text{R}_2 \\
\text{R}_3 & \quad \text{R}_4 \\
\text{R}_5 & \quad \text{R}_6 \\
\end{align*}
\]

where \( \text{R}_1 \) through \( \text{R}_4 \), independently, are hydrogen; an alkyl, e.g., \( \text{C}_a\text{H}_{2a+1} \), where \( a \) is 1 to 20 or higher; an aryl, e.g., phenyl or substituted phenyl, e.g., substituted with \( \text{CH}_3 \), \( \text{CF}_3 \), or \( \text{OCH}_3 \); an acyl, e.g., \( \text{COH} \), \( \text{COCH}_3 \), or \( \text{COCF}_3 \); or a halogen, e.g., \( \text{F} \), \( \text{Cl} \), \( \text{Br} \), or \( \text{I} \); \( \text{R}_5 \) and \( \text{R}_6 \), independently can be hydrogen; alkyl; aryl; acyl; alkoxy carbonyl, e.g., \( \text{COOCH}_3 \), \( \text{COOC} (\text{CH}_3)_3 \), or \( \text{COOCH}_2\text{CH}_3 \); or silyl, e.g., \( \text{Si} (\text{CH}_3)_3 \), \( (\text{CH}_3)_2\text{SiC} (\text{CH}_3)_3 \) or \( \text{Si} (\text{CH} (\text{CH}_3)_2)_3 \); and \( n \) is at least 2. \( n \) can be up to 10,000, 100,000, or higher.

In some cases, \( \text{R}_1 \), \( \text{R}_2 \), \( \text{R}_3 \), and \( \text{R}_4 \) are all hydrogen to give a polymer having formula (2):

\[
\begin{align*}
\text{CH}_3 & \quad \text{R}_5 \\
\text{R}_6 & \quad \text{R}_6 \\
\end{align*}
\]

\( \text{R}_5 \) also can be hydrogen, and \( \text{R}_6 \) can be an acyl, forming a poly(crotyl amide). Some specific examples include poly(crotyl formamide), poly(crotyl acetamide), poly(crotyl dichloroacetamide), poly(crotyl
trichloroacetamide), and poly(crotyl trifluoroacetamide).

Alternatively, $R_5$ and $R_6$ both can be acyl, forming a poly(crotyl imide). In addition, $R_5$ and $R_6$ can be attached to each other to form a ring structure, as in poly(crotyl N-succinimide) having formula (3).

Another aspect of the invention is a method for preparing a polymer by obtaining and then subjecting to polymerization conditions, a vinylic monomer having formula (4), where $R_1$ to $R_6$ are as defined above.
The monomer can be prepared by isomerization of the allylic species with the formula (5).

\[
\begin{array}{c}
\text{R}_3 \quad \text{R}_2 \quad \text{R}_1 \\
\text{R}_4 \quad \text{H} \\
\text{N} \quad \text{R}_6 \\
\text{R}_5
\end{array}
\]  

(5)

Polymerization methods include, but are not limited to, those described in the detailed description.

In another aspect, the invention features a copolymer having the formula (6):

\[
\begin{array}{c}
\text{H} \\
\text{R}_2 \\
\text{R}_3 \\
\text{R}_4 \\
\text{R}_7 \\
\text{R}_6 \\
\text{R}_8 \\
\text{R}_{10} \\
\sqrt{n}
\end{array}
\]  

(6)

wherein the repeating units (7) and (8) can be linked in any

\[
\begin{array}{c}
\text{R}_2 \\
\text{R}_3 \\
\text{R}_4 \\
\text{R}_1 \\
\text{R}_6 \\
\text{R}_5
\end{array}
\]  

(7)

\[
\begin{array}{c}
\text{R}_7 \\
\text{R}_9 \\
\text{R}_8 \\
\text{R}_{10}
\end{array}
\]  

(8)
order and in any orientation, e.g., the unit (7) can be repeated several times in the copolymer chain before a unit (8) occurs, and vice versa. R₁ to R₆ are defined as above; R₇ and R₉, independently, are hydrogen, alkyl, aryl, acyl, or halogen. R₈ and R₁₀, independently, are hydrogen, alkyl, aryl, acyl, NR₁₁R₁₂, OCOR₁₁, CONR₁₁R₁₂, CO₂⁻, CN, COOR₁₁, or NR₁₁COR₁₂; where R₁₁ and R₁₂, independently, are hydrogen, alkyl, aryl, acyl, or silyl. n is at least 2. n can be up to 10,000, 100,000, 1,000,000, or higher.

In certain examples, the copolymer has the formula (9):

![Chemical Structure](image)

where X can be O or NR₁₃; where R₁₃ can be hydrogen, alkyl, aryl, silyl, or acyl.

In certain other examples, R₇ and R₉ are hydrogen.

In another aspect, the invention features a method for preparing a copolymer from monomers having the formulae (10) and (11), where R₁ to R₁₀ are as defined above, by subjecting these monomers to polymerization conditions.

![Chemical Structure](image)
Monomer (11) can be, for example, maleic anhydride; maleimide; an N-alkyl maleimide, e.g., N-butyl maleimide; an N-aryl maleimide, e.g., N-xylyl maleimide; an N-silyl maleimide, e.g., N-trimethylsilyl maleimide; or an N-acyl maleimide, e.g., N-pivaloyl maleimide.

Alternatively, monomer (11) can be, for example, a vinylic amine, a vinylic ester, a vinylic amide, a vinylic carboxylate, or a vinylic nitrile.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, the preferred methods and materials are described below. All publications, patent applications, patents, and other references mentioned herein are incorporated by reference in their entirety. In case of conflict, the present application, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

An advantage of the new methods is the utilization of easily accessible allylic amine derivatives as monomer precursors. Allylic amine derivatives are inexpensive to prepare and are very stable. The facile isomerization described herein provides the reactive vinyl amine derivatives necessary for polymerization.

The polymers of the invention are unique in that they include not only the amine functionality attached at every other carbon atom along the polymer backbone, conferring polyelectrolytic properties, but also an alkyl or alkyl derivative attached to the intervening carbon atoms of the backbone. In the parent poly(vinyl amine),
this position is simply occupied by a hydrogen atom.
This allows for tremendous diversity in the realm of
poly(vinyl amine) derivatives. For example, a lipophilic
group at this locus can be used to create phase transfer
catalysts or even hydrocarbon soluble polyelectrolytes.
Other features and advantages of the invention
will be apparent from the following detailed description,
and from the claims.

Detailed Description

The isomerization and subsequent polymerization of
allylamines, allylamides, and allylimides yields new
polymers belonging to the family of poly(vinyl amine)
analogs. By combining the intermediate isomerization
products with other polymerizable molecules, new
copolymers are also obtained. Since the side chains on
the polymers bear nitrogen atoms with an unshared
electron pair, the polymers become protonated in acidic
solution to generate polycationic species. The new
methods allow a wide range of poly(vinyl amine) analogs
to be obtained in few steps, as the allylic precursors
are readily available.

Preparation of Monomers

Three classes of substrates can be used to form
stable or transient vinyl amine analogs upon
isomerization: allylamines, allylamides, and
allylimides. These substrates are catalytically
isomerizable to enamines, enamides, and enimides,
respectively, all of which are structurally similar to
either vinyl amine or the protected vinyl amine monomer.

In the following description, primary enamines,
alanyl enamines, and aryl enamines are called unprotected
monomers. Enamides (acyl enamines), enimides (diacyl
enamines), vinlyc carbamates (alkoxycarbonyl enamines), and silyl enamines are protected monomers.

**Unprotected Monomers**

Enamines offer the most direct approach to the preparation of vinyl amine-derived copolymers. The polymerization of these compounds incorporates an amine functionality into the polymer without the need for deprotection of a precursor. Depending on the amine substitution, however, an enamine can be unstable with respect to its imine form. Generally, less substituted enamines, e.g., primary enamines, are less stable than their more substituted relatives. Hence, less substituted monomers are most amenable to copolymerization.

Secondary and tertiary enamines have alkyl or aryl substituents, e.g., ethyl, isobutyl, phenyl or substituted phenyls. These substituents help to stabilize the monomers with respect to the unsubstituted vinyl amines.

A number of routes lead to tertiary enamines, including isomerization. For example, many tertiary allylamines isomerize to tertiary enamines using a catalyst. Examples of isomerization catalysts include those derived from ruthenium, e.g., 10 mol% RuClH(CO)(PPh₃) in refluxing benzene for 1 to 15 hours; cobalt, e.g., 1 mol% CoH(N₂)(PPh₃) in tetrahydrofuran (THF) at 80°C for 15 hours; rhodium, e.g., 1 mol% [Rh(diphosphine)(THF)_n]^⁺ClO₄ in THF at 40°C for 23 hours, the diphosphine ligand can be 2,2′-

bis(diphenylphosphino)-1,1′-binaphthyl (BINAP); or molybdenum, e.g., 1 mol% trans-Mo(N₂)(Ph₂PCH₂CH₂PPH₂)₂ in toluene at 100°C for 1.5 to 5 hours.

Alternatively, the isomerization can be catalyzed by base. Representative examples of basic catalysts
include potassium tert-butoxide or potassium amide on alumina.
Secondary enamines are less stable than tertiary enamines and tend to tautomerize to the corresponding imines, although the isomerization of secondary allylamines with a ruthenium catalyst allows selective, transient formation of secondary enamines. For these compounds, it is necessary to polymerize the intermediate species before tautomerization, e.g., at low temperature, e.g., -100°C to 100°C, and preferably -10°C to 25°C, and under anhydrous conditions, to produce vinyl amine polymers.

Protected Monomers
Silyl enamines, e.g., bis(trimethylsilyl)amino-1-propene (12),

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{N} \quad \text{Si(CH}_3\text{)}_3 \\
\text{N} & \quad \text{Si(CH}_3\text{)}_3 \\
\text{Si} & \quad \text{Si(CH}_3\text{)}_3
\end{align*}
\] (12)

 enamides, e.g., N-(1-isobutenyl)benzamide (13),

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{H}_3\text{C} \\
\text{H}_3\text{C} & \quad \text{H}_3\text{C} \\
\text{N} & \quad \text{Si(CH}_3\text{)}_3 \\
\text{Si} & \quad \text{Si(CH}_3\text{)}_3 \\
\text{Si} & \quad \text{Si(CH}_3\text{)}_3
\end{align*}
\] (13)
vinylic carbamates, e.g., N-(tert-butoxycarbonyl)-1-propenylamine (14),

and enimides, e.g., N-(1-cyclohexenyl)-succinimide (15),

are regarded as "protected" monomers, since their silyl or acyl substituents help to prevent tautomerization to the imines, but can subsequently be removed under hydrolysis conditions, e.g., in aqueous base or acid, to generate the free amine or ammonium salt, respectively. Other specific examples of protected monomers include 2-methyl-1-propenylacetamide, 1-propenyl-tert-butylcarbamate, 1-methyl-
1-propenylphthalimide, N-(1-propenyl)-STABASE (16), where STABASE is N-1,1,4,4-tetramethyldisilylazacyclopentane:

\[ \text{(16)} \]

For certain applications, it is useful to retain the protecting groups on the polymer to mask the reactivity of the free amines, e.g., as Lewis bases. However, the real advantage of using protected enamines is that they allow the preparation of unsubstituted poly(vinyl amine) derivatives, upon deprotection, while avoiding tautomerization.

Examples of polymers which can be obtained through polymerization of a protected monomer, followed by deprotection, include poly(1-(ethylamino)-2-methylpropene), poly(1-amino-3-phenyl-1-butene), and poly(1-cyclohexylamino)-1-pentene).

Enamides, enimides, and enamines differing in the protecting groups attached to nitrogen can be copolymerized. Some protecting groups are easier to hydrolyze, or deprotect, and thus can be selectively deprotected to give partially deprotected polymers or copolymers. An example is the partial deprotection of poly(vinyl trifluoroacetamide-
co-vinyl acetamide) to give poly(vinyl amine-co-vinyl acetamide) (17), where n is as defined above.

\[
\text{Polymerization}
\]

Tertiary enamines, e.g., N,N-dimethyl-N-propenylamine and 2-methyl-N-propenylpiperidine, can be copolymerized with electron-deficient monomers, including maleimide, N-ethyl maleimide, N-butyl maleimide, N-phenyl maleimide, and maleic anhydride. The copolymerization reactions are carried out, for example, using free radical initiators.

Free radical initiation was effected by a diazo compound, azobisisobutyronitrile (AIBN), and a perester, tert-butylperoxybenzoate. Other free radical initiators include water-soluble diazo compounds, such as 2,2′-azobis(amidinopropane) hydrochloride, peroxides, such as tert-butylhydroperoxide and benzoylperoxide, and dithiuram disulfides, such as tetraethylthiuram disulfide.

In general, an acceptable temperature range for the polymerization reactions is -100°C to 100°C, more preferably 0°C to 65°C. Benzene, THF, toluene, water, and isopropyl alcohol have been successfully employed as solvents, although solvent is not essential.

Secondary and tertiary enamides, due to the beneficial electronics imparted by the protective groups, are stable precursor monomers in the production of vinyl amine derivative polymers. Once polymerized, the
precursor polymers can then be hydrolyzed to give poly(vinyl amine) derivatives. The allylamide isomerization products, N-propenylformamide (NPF) and N-propenylacetamide (NPA), were polymerized using either free radical initiators, as described above, or cationic initiators.

The cationic initiators used include a Lewis acid, tin(IV) tetrachloride, and a stabilized cation, triphenylcarbenium pentachlorostannate. Other cationic initiators include protic acids, such as perchloric acid and trifluoromethanesulfonic acid, and Lewis acids, such as boron trifluoride, aluminum trichloride, and titanium tetrachloride. Other initiators include iodine, diaryliodium salts, and ionizing radiation.

The NPF and NPA monomers were copolymerized with electron deficient monomers, such as vinyl formamide, maleimide, N-ethyl maleimide, N-butyl maleimide, N-phenyl maleimide and maleic anhydride, using, for example, free radical initiation, as described above. The N-propenylamide monomers should also copolymerize with vinyl acetate, acrylamide, sodium acrylate, acrylonitrile, methyl methacrylate and n-butyl acrylate, all of which have been previously copolymerized with N-vinylformamide (NVF). N-propenylamides have also been shown to copolymerize with other N-propenylamides and with NVF.

The following are examples of monomer preparation and polymerizations of the invention:

**EXAMPLE 1**

**Preparation of 1-(2-methyl-1-propenyl)-piperidine**

A reaction flask was charged with 5 Å molecular sieves (20g), AlO₃ (4g), diethyl ether (40 mL), piperidine (5.12g, 8.26 mmol), and a stir bar. Isobutyraldehyde (3.60g, 49.9 mmol) was added slowly to the mixture. The flask was then equipped with a condenser and was allowed
to stir for 2 hours. The mixture was filtered and fractionally distilled at 80°C with a pressure of 40 mmHg to give the desired enamine product, having the formula (18).

Proton nuclear magnetic resonance (¹H-NMR) was used to analyze a solution of the product in deuterated chloroform. The ¹H-NMR spectrum collected on a 200 MHz instrument had a multiplet at a chemical shift of 5.3 parts per million (ppm) which integrated to one proton, a triplet at 2.5 ppm which integrated to four protons, two doublets at 1.66 ppm and 1.59 ppm which integrated to three protons each, and a multiplet from 1.4-1.2 ppm which integrated to six protons.

EXAMPLE 2
Poly(2-methyl-1-propenylpiperidine-co-(N-ethylmaleimide))

In a drybox, a reaction vial was charged with N-ethylmaleimide (EtMI) (0.1090 g, 0.087 mmol) and a stir bar. A solution of 2-methyl-1-propenylpiperidine (0.55 M) and AIBN (0.004 M) in benzene was prepared, as described in Example 1. The 2-methyl-1-propenylpiperidine and AIBN solution (1.55 mL, 0.085 and 6.2 x 10⁻³ mmol) was then added to the vial containing EtMI. Upon mixing the solution became light yellow in color. The vial was capped, sealed with TEFLOW™ tape, and quickly brought out of the drybox and placed in the photolysis chamber. During photolysis at 366 nm, the polymer precipitated from solution. The polymer was
isolated by precipitation into diethyl ether and dried in vacuo, and had the formula (19). In all examples, $n$ is as defined above.

![Chemical structure](image)

(19)

Thermolysis of the AIBN initiator was also effective for the copolymerization of the enamides. The procedure used was the same as above except that the reaction mixture was sealed in an ampule under vacuum and placed in an oil bath at 100°C using maleic anhydride and EtMI as comonomers.

**EXAMPLE 3**

**Preparation of N,N-dimethylamino-1-propene**

A reaction tube was charged with N,N-dimethylallylamine (0.5013g, 5.90 mmol) and RuClH(PPh$_3$)$_3$ (0.032g, 0.091 mmol). The reaction tube was heated to 60°C overnight. The isomerized monomer having the formula (20) was isolated from the catalyst by vacuum distillation.

![Chemical structure](image)

(20)
Proton nuclear magnetic resonance (1H-NMR) was used to analyze a solution of the product in deuterated chloroform. The 1H-NMR spectrum collected on a 200 MHz instrument had a doublet at a chemical shift of 5.88 parts per million (ppm) which integrated to one proton, a multiplet at 4.19 ppm which integrated to one proton, a singlet at 2.5 ppm which integrated to six protons, a doublet at 1.60 ppm which integrated to three protons, and a broad peak at 0.8 ppm which integrated to two protons.

EXAMPLE 4

Poly(N,N-dimethylamino-1-propene-co-(N-ethylmaleimide))

In a drybox, a vial was charged with N,N-dimethylamino-1-propene (0.0850 g, 1.00 mmol), EtMI (0.1250 g, 1.00 mmol), and a stir bar. A solution of AIBN (0.500 mL, 0.032 M, 5.11 x 10^-4 mmol) in benzene was then added to the vial containing the monomers. The vial was capped, sealed with TEFLO™ tape, and quickly brought out of the drybox and placed in the photolysis chamber. During photolysis at 366 nm, the polymer precipitated from solution. The polymer was isolated by precipitation into diethyl ether and dried in vacuo, and had the formula (21).
EXAMPLE 5

Preparation of 1-Propenylformamide

In a drybox, a Schlenk flask was charged with N-allylformamide (0.9989 g, 11.8 mmol), RuClH(PPh_3)_3 (0.0495 g, 0.0496 mmol), toluene (5 mL), and a stir bar. The flask was taken from the box, fitted with a condenser, and heated to reflux for several hours under an argon atmosphere. The solvent was then removed under reduced pressure to give a yellow oil. The oil was distilled using a Kugelrohr apparatus under partial vacuum to give an 87% yield of isomerized product with a cis:trans ratio of 0.46:0.54, having the formula (22).

![Formula 22]

Proton nuclear magnetic resonance (¹H-NMR) was used to analyze a solution of the product in deuterated chloroform. The ¹H-NMR spectrum collected on a 200 MHz instrument had a broad peak at a chemical shift of 8.5 parts per million (ppm) which integrated to one proton and four multiplets at 8.0 ppm, 6.7-6.2 ppm, 5.3-4.8 ppm, and 1.6 ppm which integrated to one proton each.

EXAMPLE 6

Poly(1-propenylacetamide)

1-Propenylacetamide was prepared by the method of Stille and Becker (J. Org. Chem. 1980, 45, 2139-2145), by refluxing N-allylacetamide with HRuCl(PPh_3)_3 in benzene under argon for 40 hours. The 1-propenylacetamide was isolated by distillation.

In a drybox, an ampule was charged with 1-propenylacetamide (0.2103 g, 2.15 mmol) and a stir bar. The ampule was removed from the drybox and tert-butyl
peroxybenzoate (0.0073 g, 0.038 mmol) was added under an argon atmosphere using Schlenk techniques. The ampule was then degassed, sealed under vacuum and placed in a 150°C oil bath. After several hours the ampule contents were dissolved in DMF, precipitated into acetone and dried in vacuo.

In a drybox, a reaction flask was charged with 1-propenylacetamide (0.2505 g, 2.56 mmol), benzene (0.5 mL) and a stir bar. The flask was then sealed with a septa and removed from the drybox. A solution of ZnCl₂ (25 μL, 1.0 M, 0.025 mmol) in 1,2-dichloroethane was added to the flask via syringe. After several hours at room temperature the contents became very viscous. The contents were then dissolved in DMF, precipitated into acetone, and dried in vacuo, having the formula (23).

\[
\text{CH}_3
\]
\[
\text{COCH}_3
\]
\[
(23)
\]

An alternative procedure was also used. In a drybox, a reaction vial was charged with 1-propenylacetamide (0.2018 g, 2.06 mmol), triphenylcarbenium pentachlorostannate (0.001 g, 0.002 mmol), benzene (0.75 mL) and a stir bar. The mixture was allowed to stir in the drybox for several days. The vial contents were dried in vacuo.

**EXAMPLE 7**

**Poly(1-propenylacetamide-co-maleimide)**

In a drybox, a reaction vial was charged with maleimide (0.0969 g, 1.00 mmol), 1-propenylacetamide (0.1019 g, 1.04 mmol) and a stir bar. A solution of AIBN
(0.01 M) in benzene was prepared. The AIBN solution (0.50 mL, 5.0 x 10⁻⁴ mmol) was then added to the vial containing the monomers. The vial was capped, sealed with TEFALON™ tape, and quickly brought out of the drybox and placed in the photolysis chamber. During photolysis at 366 nm, the polymer precipitated from solution. The polymer was isolated by precipitation into diethyl ether and dried in vacuo, and had the formula (24).

![Chemical Structure](24)

Additionally, thermolysis of the initiator was also effective for the copolymerization of the enamides. The procedure used was the same as above except that the reaction mixture was sealed in an ampule under vacuum and placed in an oil bath at 65°C.

**EXAMPLE 8**

**Poly(1-propenylacetamide-co-(N-vinylformamide))**

In a drybox, a reaction vial was charged with 1-propenylacetamide (0.0998 g, 1.01 mmol), N-vinylformamide (0.1018 g, 1.43 mmol), triphenylcarbenium pentachlorostannate (0.001 g, 0.002 mmol), and a stir
bar. The vial contents were stirred and solidified overnight, to give polymer (25).

(25)

Uses and Properties of the New Homopolymers and Copolymers

The homopolymers and copolymers of the invention have commercial utility including, but not limited to the known applications of vinyl amide and vinyl amine homopolymers and copolymers. For example, these polymers have applications in the textile, adhesives and coatings, paper, petroleum, water treatment, cosmetic, and pharmaceutical industries. These polymers have broader application than the parent poly(vinyl amine), because the novel alkyl side chains attached at alternate positions on the polymer backbone provide an added diversity element to the new polymers, which allows the properties of the polymer, e.g., solubility, to be specifically tailored for a desired use.

For example, an n-butyl group attached at every other position of the polymer backbone would increase solubility in non-polar solvents, e.g., hydrocarbons. A substituted aryl, e.g., 4-phenol, attached at every other
position of the polymer backbone would increase the solubility in polar organic solvents, e.g., ethyl acetate.

Specific applications of the polymers of this invention can include flocculence enhancement in the paper manufacturing and water treatment, and maintenance of high viscosity for petroleum products, to facilitate pumping. The polymers can also be used to prepare ion-exchange membranes.

Other Embodiments

It is to be understood that while the invention has been described in conjunction with the detailed description thereof, that the foregoing description is intended to illustrate and not limit the scope of the appended claims. Other aspects, advantages, and modifications are within the scope of the following claims.
What is claimed is:

1. A polymer comprising the formula:

   \[ \begin{array}{c}
   R_2 \\
   H \\
   R_3 \\
   R_4 \\
   R_1 \\
   n \\
   R_5 \\
   N \\
   R_6
   \end{array} \]

   wherein \( R_1, R_2, R_3, \) and \( R_4 \) are, independently, selected from the group consisting of hydrogen, alkyl, aryl, acyl, and the halogens; \( R_5 \) and \( R_6 \) are, independently, selected from the group consisting of hydrogen, alkyl, aryl, acyl, alkoxy carbonyl, and silyl; and \( n \geq 2 \).

2. A polymer of claim 1, wherein \( R_1, R_2, R_3, \) and \( R_4 \) are hydrogen.

3. A polymer of claim 1, wherein \( R_5 \) is hydrogen, and \( R_6 \) is an acyl.

4. A polymer of claim 1, wherein \( R_5 \) is selected from the group consisting of formyl, acetyl, dichloroacetyl, trichloroacetyl, and trifluoroacetyl.

5. A polymer of claim 1, wherein \( R_5 \) and \( R_6 \) are both acyl.

6. A polymer of claim 1, wherein \( N, R_5, \) and \( R_6 \) are part of a ring structure.
7. A method for preparing a polymer, said method comprising:

obtaining a monomer having the formula:

```
      R2
     /   \
H-----\---N-----R5
      |    |
     /    /
R3----\---R4
     |     |
      R1  R6
```

wherein R₁, R₂, R₃ and R₄ are, independently, selected from the group consisting of hydrogen, alkyl, aryl, acyl, and the halogens; R₅ and R₆ are, independently, selected from the group consisting of hydrogen, alkyl, aryl, acyl, alkoxy carbonyl, and silyl; and

subjecting said monomer to conditions that allow said monomer to polymerize to form a polymer.

8. A method of claim 7, wherein said monomer is prepared by isomerization of a molecule having the formula:

```
      R2
     /   \   
R3----\---R4
     |    |     
R1----\---R5
     |     |
      R6
```

10. A copolymer comprising the formula:

\[ \text{Diagram: } \]

wherein \( R_1 \), \( R_2 \), \( R_3 \), \( R_4 \), \( R_7 \), and \( R_9 \) are, independently, selected from the group consisting of hydrogen, alkyl, aryl, acyl, and the halogens; \( R_5 \) and \( R_6 \) are, independently, selected from the group consisting of hydrogen, alkyl, aryl, acyl, and silyl; \( R_8 \) and \( R_{10} \) are, independently, selected from the group consisting of \( H \), alkyl, aryl, acyl, \( \text{NR}_{11} \text{R}_{12} \), \( \text{OCOR}_{11} \), \( \text{CONR}_{11} \text{R}_{12} \), \( \text{CO}_2^- \), \( \text{CN} \), \( \text{COOR}_{11} \), and \( \text{NR}_{11} \text{COR}_{12} \); wherein \( R_{11} \) and \( R_{12} \) are, independently, selected from the group consisting of hydrogen, alkyl, aryl, acyl, and silyl; and \( n \geq 2 \).

11. A method for preparing a copolymer, said method comprising:

obtaining a first monomer having the formula:

\[ \text{Diagram: } \]

wherein \( R_1 \), \( R_2 \), \( R_3 \) and \( R_4 \) are, independently, selected from the group consisting of hydrogen, alkyl, aryl, acyl, and the halogens; \( R_5 \) and \( R_6 \) are, independently, selected from the group consisting of hydrogen, alkyl, aryl, acyl, and silyl;
obtaining a second monomer having the formula:

wherein R₇ and R₉ are, independently, selected from the group consisting of hydrogen, alkyl, aryl, acyl, and the halogens; R₈ and R₁₀ are, independently, selected from the group consisting of H, alkyl, aryl, acyl, NR₁₁R₁₂, OCOR₁₁, CONR₁₁R₁₂, CO₂⁻, CN, COOR₁₁, and NR₁₁COR₁₂; wherein R₁₁ and R₁₂ are, independently, selected from the group consisting of hydrogen, alkyl, aryl, acyl, and the halogens; and

subjecting said first and second monomers to conditions that allow said monomers to polymerize to form a copolymer.

12. A method of claim 11, wherein said first monomer is prepared by isomerization of a molecule having the formula:

13. A copolymer prepared by the method of claim 11.

14. A method of claim 11, wherein said second monomer is selected from the group consisting of maleic anhydride, maleimide, N-alkyl maleimide, N-aryl maleimide, N-silyl maleimide, and N-acyl maleimide.
15. A copolymer prepared by the method of claim 14.

16. A method of claim 11, wherein \( R_7 \) and \( R_9 \) are hydrogen; \( R_8 \) is selected from the group consisting of hydrogen, alkyl, aryl, and acyl; and \( R_{10} \) is selected from the group consisting of \( NR_{11}R_{12} \), \( OCOR_{11} \), \( CONR_{11}R_{12} \), \( CO_2^- \), \( CN \), \( COOR_{11} \), and \( NR_{11}COR_{12} \); wherein \( R_{11} \) and \( R_{12} \) are, independently, selected from the group consisting of hydrogen, alkyl, aryl, acyl, and silyl.

17. A copolymer prepared by the method of claim 16.

18. A copolymer of claim 10 comprising the formula:

\[
\begin{align*}
\text{O} & \quad \text{R} \quad \text{R} \\
\text{H} & \quad \text{X} \\
\text{(NR)} & \quad \text{R} \quad \text{N} \quad \text{R} \\
\text{R} & \quad \text{R} \\
\text{R} & \quad \text{n} \\
\end{align*}
\]

wherein \( X \) is selected from the group consisting of \( O \) and \( NR_{13} \); wherein \( R_{13} \) is selected from the group consisting of hydrogen, alkyl, aryl, silyl, or acyl.

19. A copolymer of claim 10, wherein \( R_7 \) and \( R_9 \) are hydrogen.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC(6) : C08F 26/00, 26/06
US Cl.: 526/312, 263
According to International Patent Classification (IPC) or to both national classification and IPC.

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
U.S.: 526/312, 263

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>EP 24,682 A (CONSORTIUM FUR ELEKTROCHEMISCHE INDUSTRIE GMBH) 03 November 1981.</td>
<td>1-19</td>
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</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C.

See patent family annex.

Date of the actual completion of the international search: 14 JANUARY 1998

Date of mailing of the international search report: 01 FEB 1998

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231
Facsimile No. (703) 305-3230

Authorized officer
JEFFREY T. SMITH
Telephone No. (703) 308-2351

Form PCT/ISA/210 (second sheet) (July 1992)