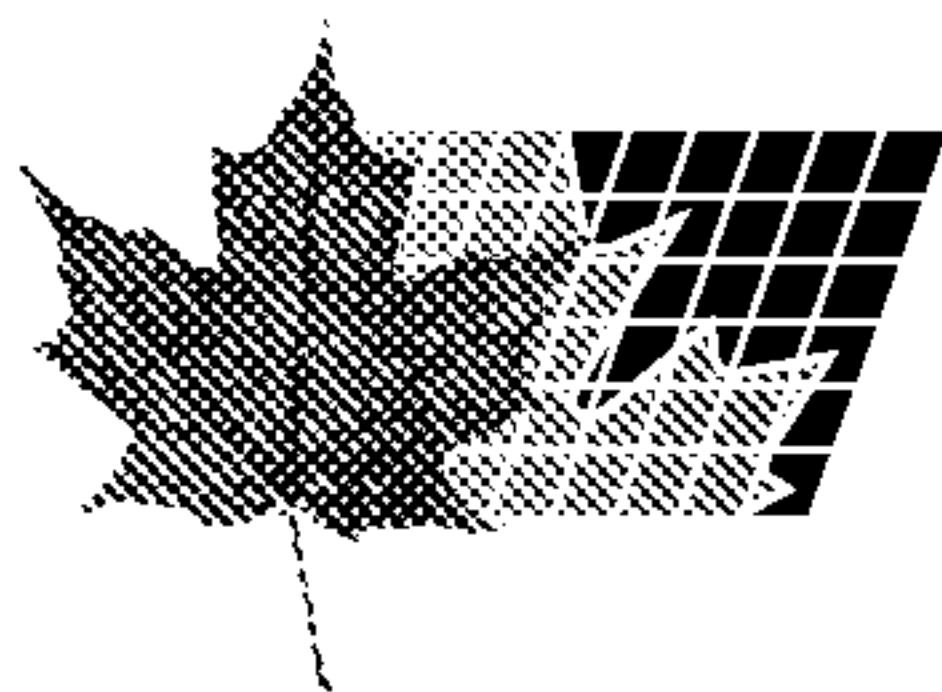




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(54) **POLYMERES SILICONES CHELATEURS**
(54) **CHELATING SILICONE POLYMERS**

Chelating Silicones

Background of the Invention

A wide variety of applications require control of the interfacial properties. Generally, for good performance it is necessary to stabilize interfaces. Some simple examples include the use of coupling agents to modify silica surfaces so that silica may be used to reinforce organic polymers, with which it is otherwise incompatible, and the use of surfactants to stabilize oils in water, such as in hair conditioner applications.

Silicones are among the most surface active materials known. They diffuse rapidly to interfaces and readily spread. Spreading of the silicone is facilitated by the incorporation of polar groups on the silicone backbone. Some of the most effective spreading compounds, particularly at solid/liquid/air surfaces, are the so-called superwetters (made by manufacturers including Witco and Dow Corning)¹ of the general structure $(\text{Me}_3\text{SiO})_2\text{SiMe}(\text{CH}_2)_3(\text{OCH}_2\text{CH}_2)_n\text{OZ}$, $\text{Z} = \text{H}, \text{Me}, \text{OAc}$, etc. The stabilization of liquid-liquid interfaces, rather than simply the efficiency of wetting biphasic interfaces, is generally accomplished by the use of silicones bearing non-ionic hydrophilic groups. Common examples include derivatives of so-called silicone polyols; silicones containing polyether sidechains. These are useful in particular at stabilizing water/silicone interfaces as taught by US5707613.² Ionic silicone copolymers can also be used to stabilize interfaces. US5124466 teaches that ammonium-modified silicone surfactants are useful in the stabilization of silicones emulsions in water.³

The surface active of silicones, whether cationic, zwitterionic or non-ionic, cannot be readily changed, although pH modifications may affect the behaviour of some types of ammonium compounds. There are advantages in being able to change the surface activity of a surface active material so as to change the properties of systems; for instance, to flocculate emulsions on demand. pH sensitive materials of this are well known. Carboxylic acids and polymers derived from them (e.g., carbopol) change their ability to swell water and to stabilize interfaces upon pH changes that convert neutral carboxylic acids to carboxylates or vice-versa. Silicones containing carboxylic acids are known, and change surface properties as a function of pH as taught by US5447997.⁴

The properties of ionic surfactants may not only be changed by pH, but by the nature of the counterions. For example, carboxylates with monovalent counterions such as sodium swell well with water. By contrast, multivalent counterions in the same system, however, lead to ionic crosslinking and a reduction of swelling. At an interface, the surface activity of such materials will be affected similarly by the nature of the counterion.

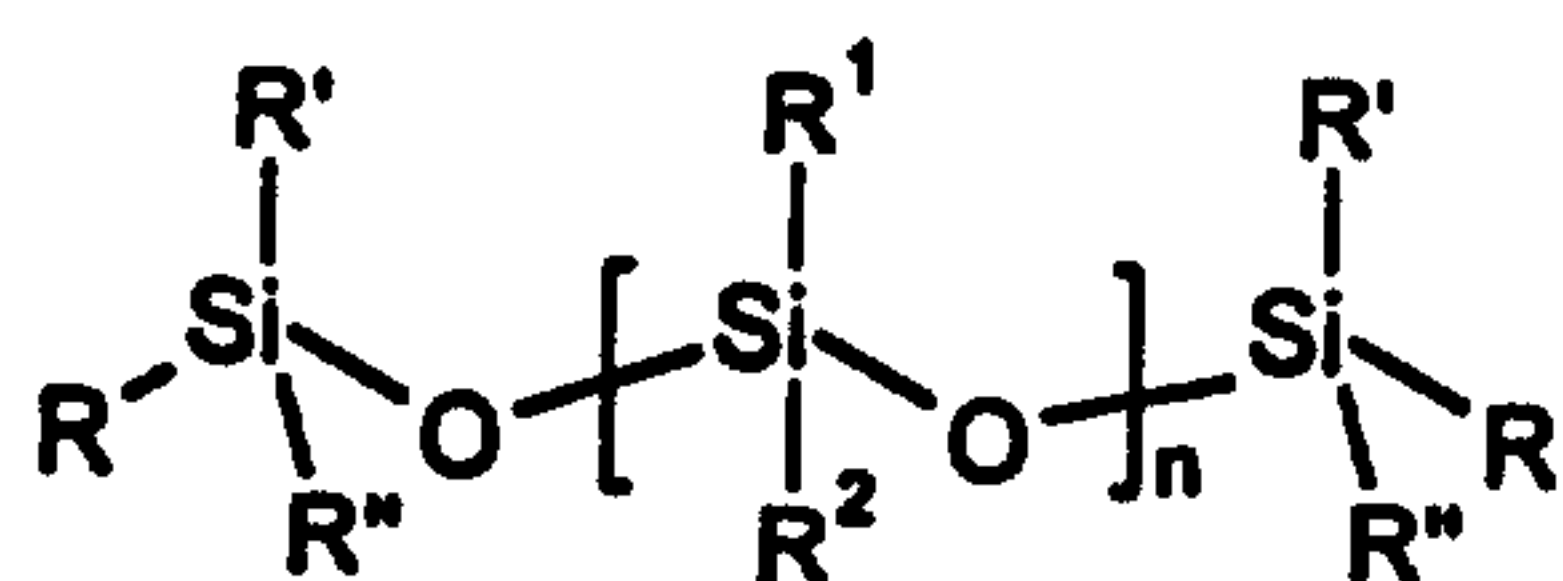
Multidentate ligands bind metals very tightly. The classic example is EDTA (ethylenediaminetetraacetic acid). This material, normally in its calcium, disodium salt form, is frequently found in food products. Any heavier metals coming into contact with the EDTA will complex to three of four of the carboxylic acid groups, displacing the sodium/calcium ions. The binding efficiencies of many metals and different oxidation states, to EDTA and related derivatives are well known. Many patents exist in which chelators have been added to a formulation.⁵ Multidentate ligands have also been bound to polymers. For instance, chelating groups similar to those mentioned above are used as supports in affinity chromatography. We describe in this invention surface active materials, based on silicone, which are able to sequester metal ions using complementary binding.

Summary of the Invention

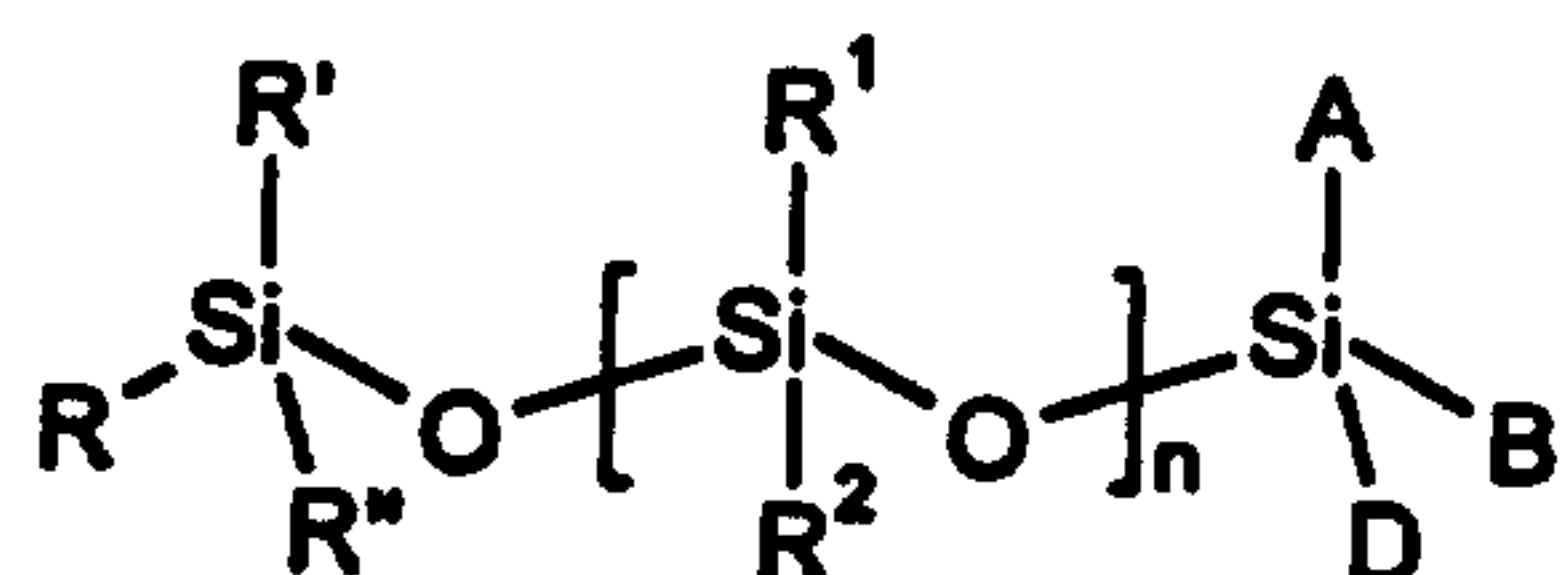
As described above, described within is a composition of a polymeric species containing two components; a hydrophilic component that is responsive to, and which can bind with, a variety of metals, and, a hydrophobic component. The hydrophobic component can be an organometallic polymer with surface active properties. The preferred embodiment of the hydrophobic component is a silicone polymer. The hydrophobic nature of the silicone is provided by organic radicals bound to silicon, such as methyl. The hydrophilic component is comprised of multiple binding sites for metals, clustered in segments on the silicone such that more than one ligand (binding site) can cooperatively bind a metal centre. Such hydrophilic binding sites can include carboxylic acids and derivatives, amines, phosphines, alcohols, and unsaturated systems (π bonds) that are rendered hydrophilic by incorporation of other polar groups located nearby.

Description of the Invention

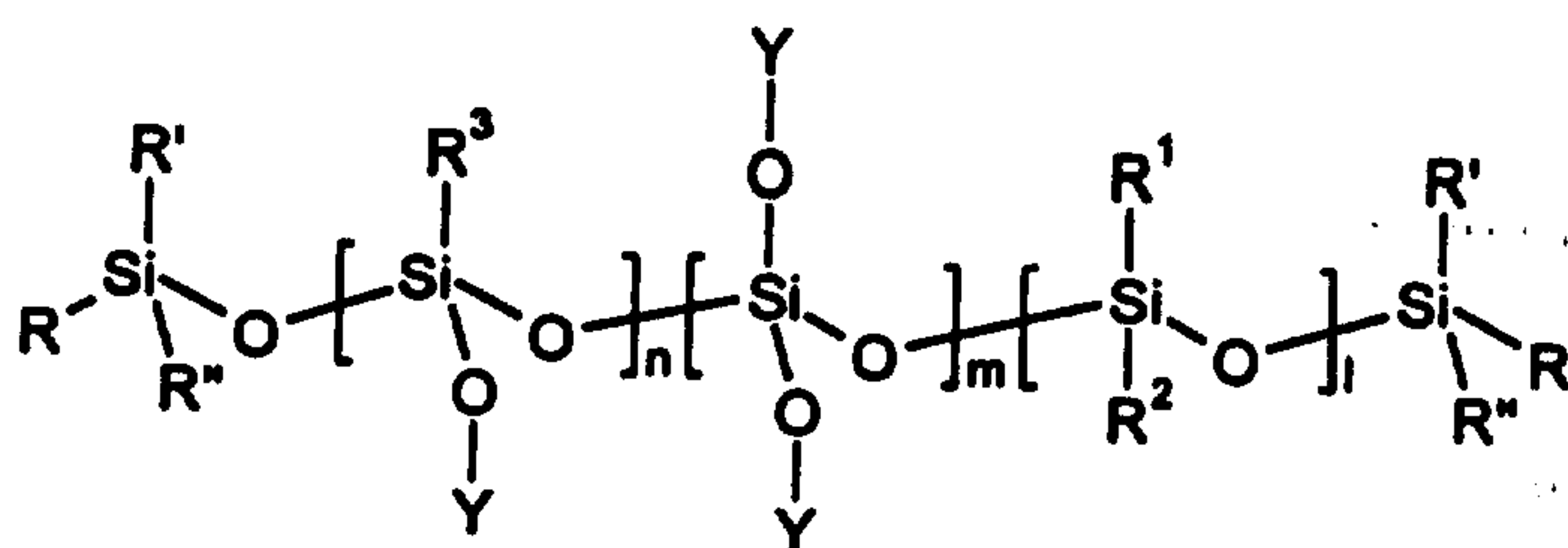
In accordance with the present invention, a silicone polymer is modified by hydrophilic groups. The silicone may have a linear structure of the general formula,



where R, R', R'', R¹, R² = H, alkoxy, alkyl, allyl, aryl, vinyl, propargyl, groups that can be covalently bound to the hydrophilic component and substituted versions of the preceding groups. The molecule may be symmetric, or may have different substituents at each terminus, such as the general formula,



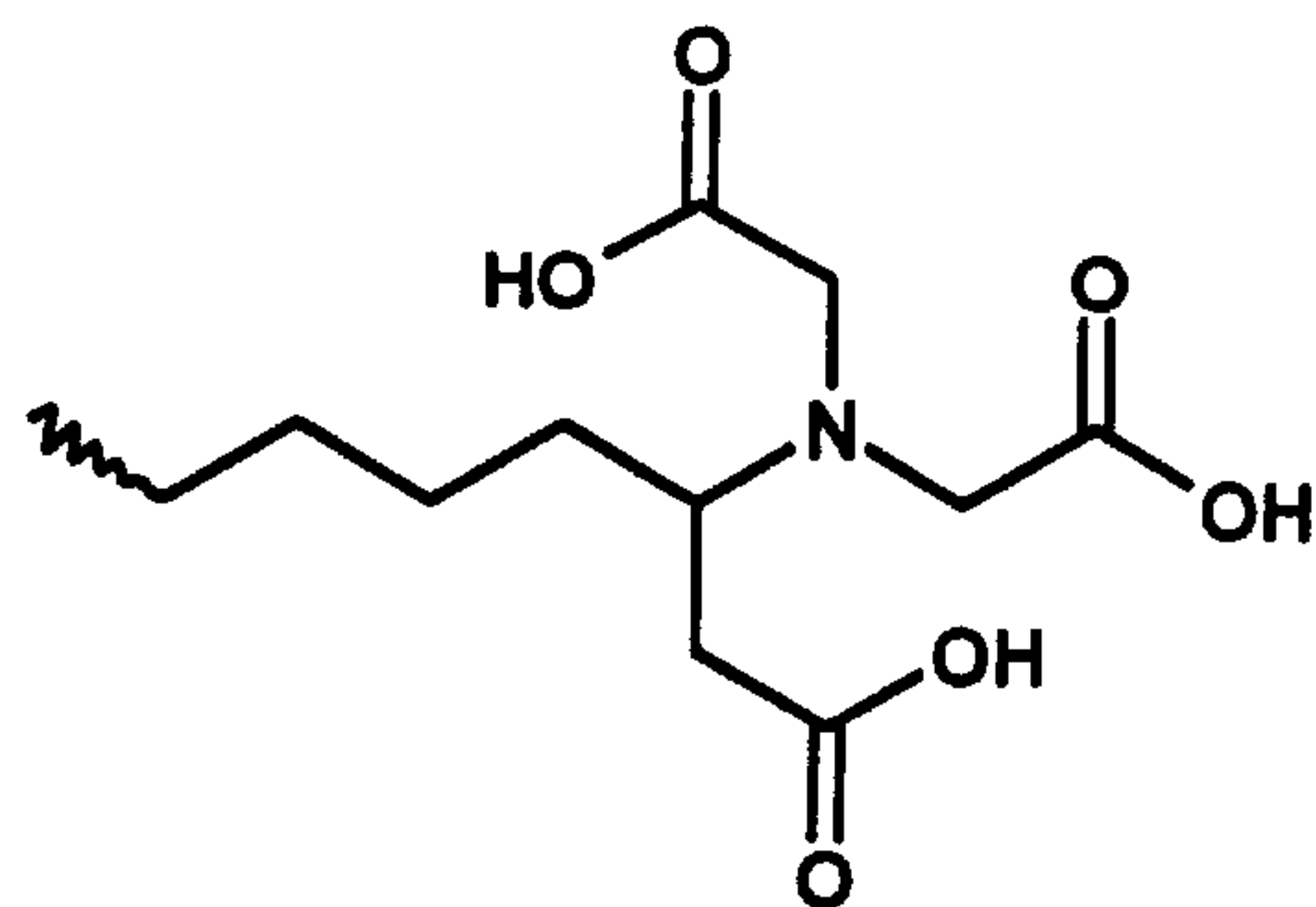
Alternatively, the silicone may be a branched silicone polymer incorporating terminal, difunctional, trifunctional and tetrafunctional silanes, of general type



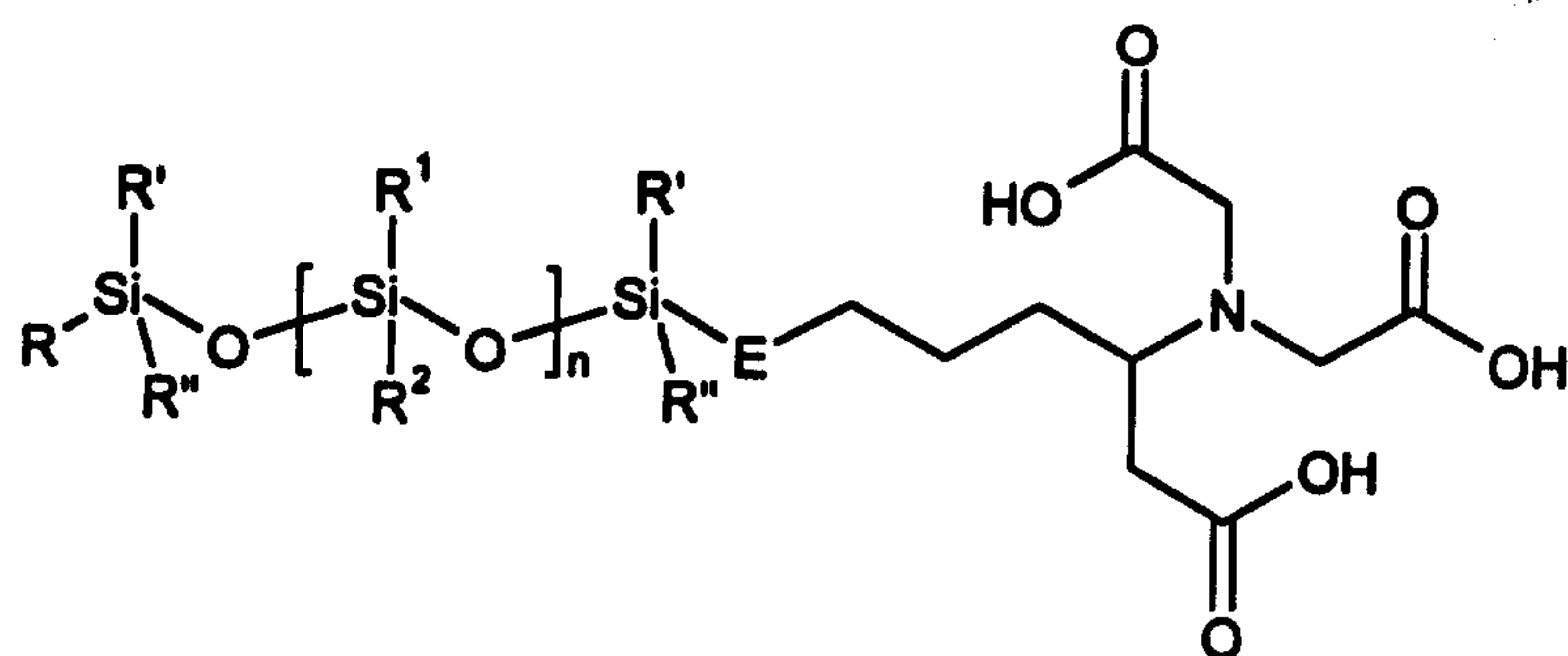
where R, R', R'', R¹, R², R³ = H, alkoxy, alkyl, allyl, aryl, vinyl, propargyl, groups that can be covalently bound to the hydrophilic component and substituted versions of the preceding groups and Y = SiX_z where z = 0-3 and X = R, R', R'', R¹, R², and/or R³. The molecule may be symmetric, or may not any planes or axes of symmetry.

The hydrophilic component will comprise clusters of at least two groups that may act as ligands for metals. Such ligands may include, but are not limited to groups that possess exchangeable hydrogens (OH, NH, and less-exchangeable hydrogens SH, PH), neutral groups that are known to be good ligands for metals RR'R''N, RR'R''P, carbonyl groups, thiocarbonyl groups, alkenes, alkynes and other π -systems and ionic groups including carboxylates. The preferred embodiment

of the invention utilizes clusters of carboxylic acids that may both change character as a result of pH changes and by binding metals with different coordination numbers; such metals may be charged or neutral. A general formula for the hydrophilic component, without limitation is,

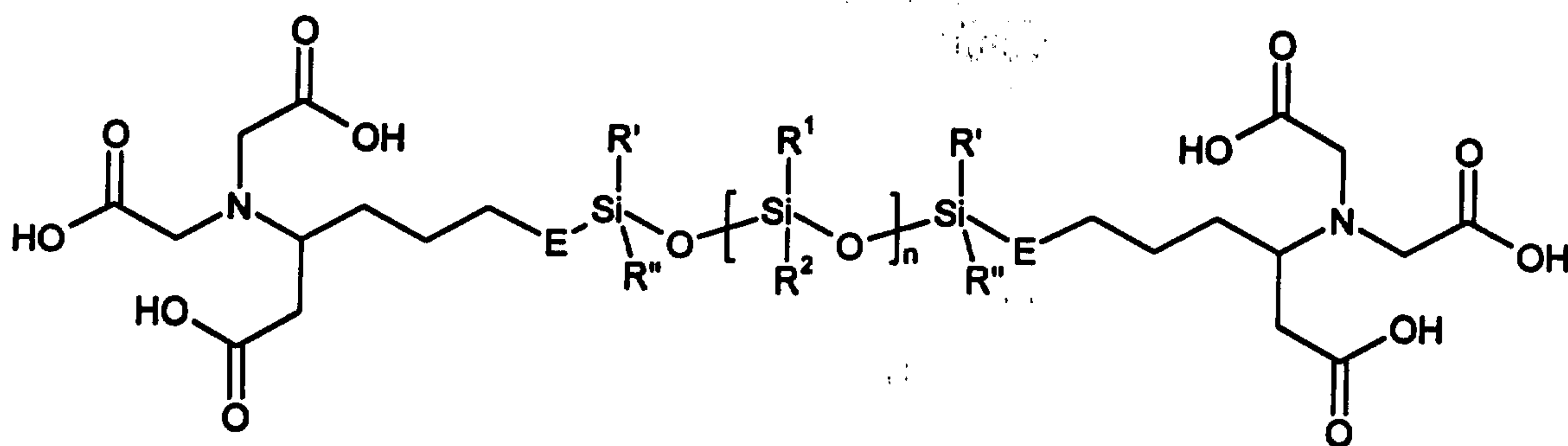


The invention comprises a combination of hydrophilic and hydrophobic components. Several general ways of combining the two distinct components are disclosed. The hydrophilic clusters may appear at the terminus of a silicone, as in the general formula,



, where E is a linker.

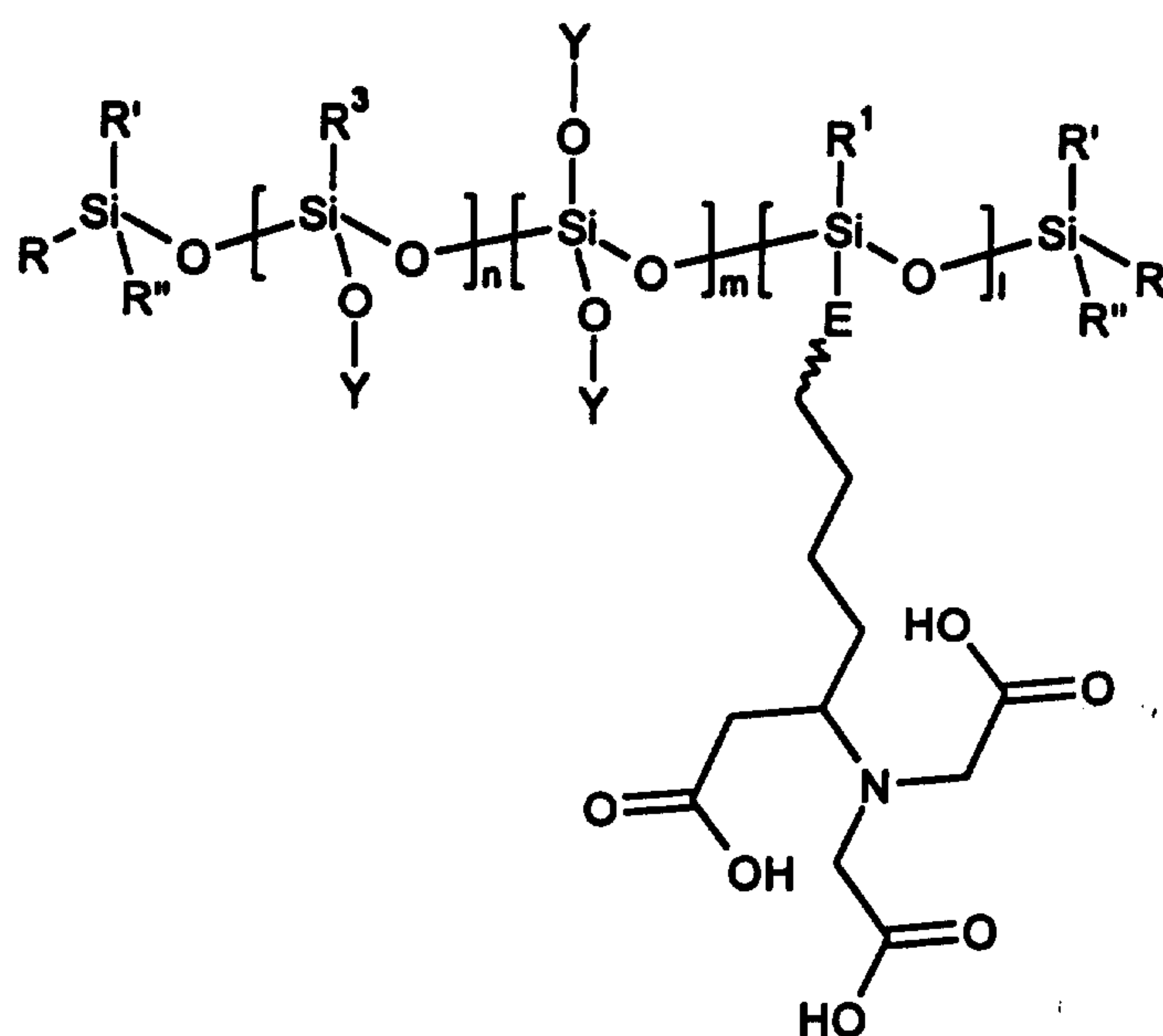
Alternatively, the hydrophilic clusters may appear at both termini of a linear silicone, as in the general formula,



E is a linker.

, where

Alternatively, the hydrophilic clusters may appear at various sites along the backbone of a silicone chain, as in the general formula,

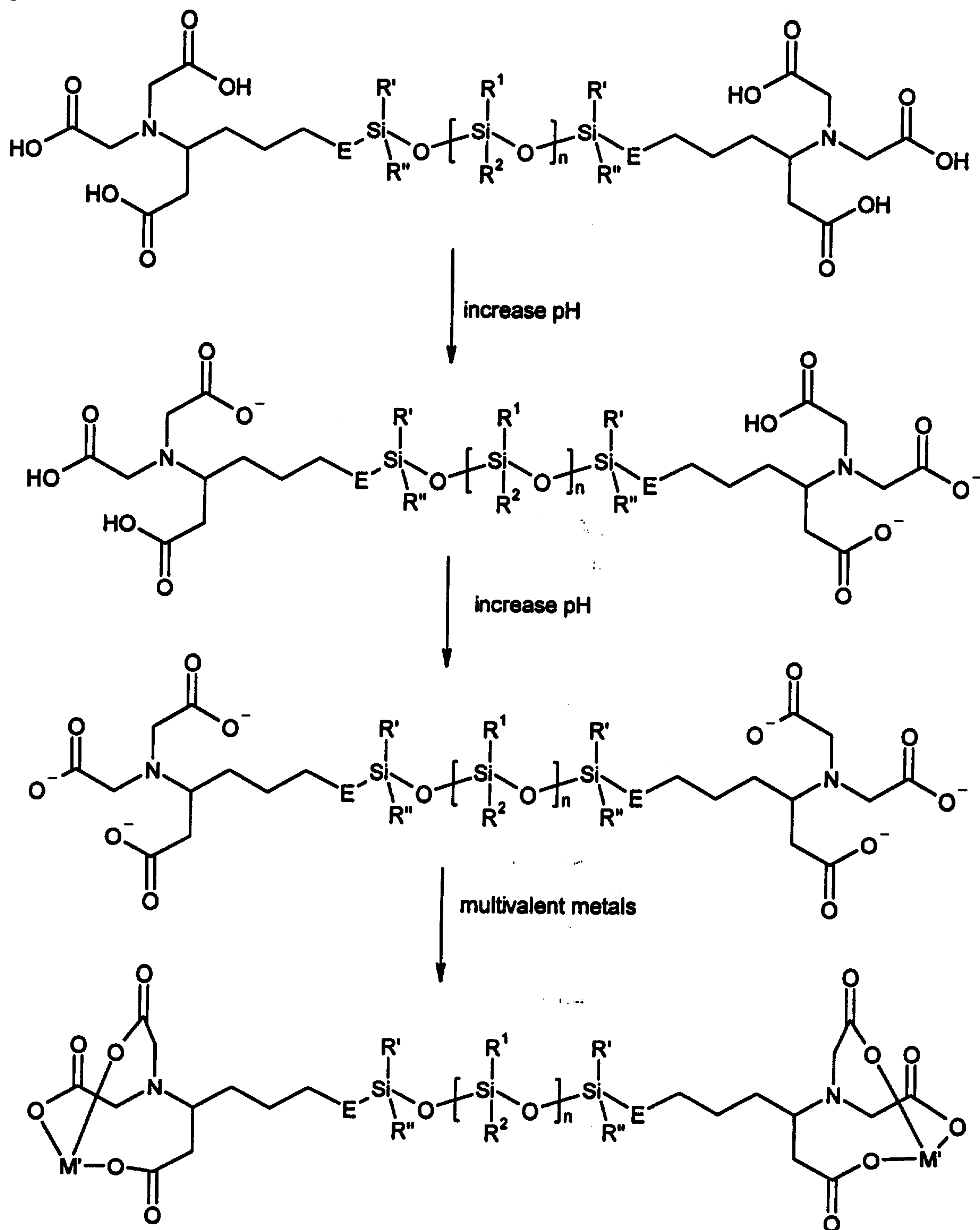


, where E is a linker.

The linkers in the preceding general formula may consist, but is not limited to, organic functional groups such as esters, ethers, amines, amides, alkanes and derivatives thereof. One specific example is shown in example 1.

The behaviour of the hydrophilic/hydrophobic compounds may be changed by pH and by the addition of metals with greater than one binding site. Thus, a neutral compound can be converted to an ionic species whose behaviour in turn can be modified by the addition of metals, as in the

general scheme,



Examples

Example 1:

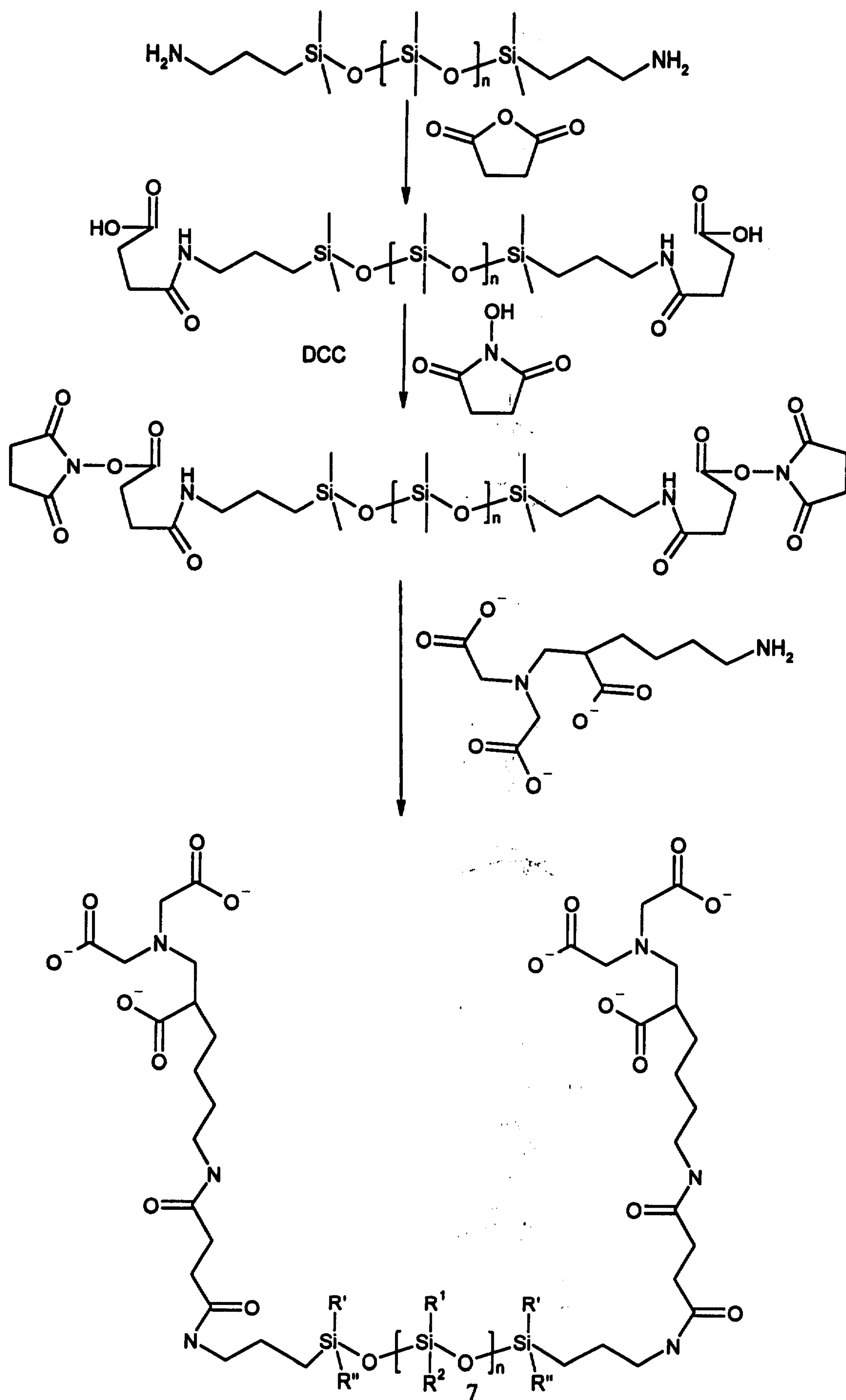
A series of surface active polymers were prepared using silicones of different molecular weight. Thus, amino-terminated linear silicones of molecular weights ranging from about 500 - 5000 (8 parts) were reacted with succinic anhydride (16 parts) in methylene chloride (3000 parts) to give

carboxylic acid-terminated silicones after aqueous extraction first with water and then with 1N HCl and drying with sodium sulfate.

Activation of the carboxyl groups on the silicones (2.5 parts) was performed by reaction with *N*-hydroxysuccinimide (5 parts) in the presence of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (5 parts) in 1,2-dimethoxyethane (220 parts). After removal of the solvents *in vacuo*, it was dissolved in methylene chloride (900 parts), washed with water, 1N HCl and then dried over sodium sulfate.

The succinimidyl-terminated polydimethylsiloxane (65 parts) dissolved in 1,2-dimethoxyethane (150 parts) was vigorously stirred with N^{α},N^{α} -bis(carboxymethyl)-*L*-lysine sodium salt (1.5 parts) dissolved in water (270 parts) overnight. The two layers were separated and the solvents were removed *in vacuo* from the bottom aqueous layer. The solid obtained was purified by dialysis against deionized water. Lyophilization led to the desired product as a white solid.

These compounds readily complexed metals including iron, copper and cobalt. The most diagnostic characteristic of the complexed materials were the mass spectral molecular fragments showing components of the tricarboxylic acid, silicone and the metal.



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- ¹ (a) Ananthapadmanabhan, K. P.; Goddard, E. D.; Chandar P. *Coll. Surf* 1990, 44, 281. (b) Zhu, S.; Miller, W. G.; Scriven, L. E.; Davis, H. T. *Coll. Surf A*. 1994, 90, 79. (c) He, M.; Hill, R. M.; Lin, Z.; Scriven, L. E.; Davis, H. T. *J. Phys. Chem.* 1993, 97, 8820. (d) Gentle, T. E.; Snow, S. A. *Langmuir* 1995, 11, 2905.
 - ² Hill, R.M., US5707613, *Spontaneously formed clear silicone microemulsions*, to Dow Corning Corporation, 1998.
 - ³ Azechi, S.; Meguriya, N.; Tanaka, M. US5124466, *Cationic silicone surfactant and method of its manufacture*, to Shin-Etsu Chemical Company Limited 1992.
 - ⁴ Raleigh, W. J.; Campagna, J. A.; Lucarelli, M. A. US5447997, *Silicone polyether carboxylic acids*, to General Electric Company, 1995.
 - ⁵ Bolich, Jr., R. E.; Norton, M. J.; Russell, G. D. US5106609, *Vehicle systems for use in cosmetic compositions*, to Procter & Gamble Company, 1992.

That which is claimed is:

1. A polymer comprised of hydrophobic and hydrophilic groups.
2. The composition according to claim 1 in which the hydrophobic component of the molecule is an organometallic polymer.
3. The composition according to claim 2 in which the organometallic polymer is a silicone.
4. The composition according to claim 3 in which the silicone is a linear silicone $RR'R''SiO(R^1R^2SiO)_nSiRR'R''$ where $n = 2-4000$, $R, R', R'', R^1, R^2 = H$, alkoxy, alkyl, allyl, aryl, vinyl, propargyl, groups that can be covalently bound to the hydrophilic component and substituted versions of the preceding groups.
5. The composition according to claim 3 in which the silicone is a branched silicone $(RR'R''SiO)_k(R^1R^2SiO)_l(SiO_{4/2})_m(R^3SiO_{3/2})_n$, where $k, l, m, n = 0 \rightarrow 4000$, $R, R', R'', R^1, R^2, R^3 = H$, alkoxy, alkyl, allyl, aryl, vinyl, propargyl, groups that can be covalently bound to the hydrophilic component and substituted versions of the preceding groups.
6. The composition according to claim 1 in which the hydrophilic group contains exchangeable hydrogen groups.
7. The composition according to claim 6 in which the hydrophilic groups may be comprised solely or in combination of OH, COOH and less easily exchanged hydrogens including NH, SH, PH.
8. The composition according to claim 1 in which the hydrophilic group contains polar groups known to act as ligands to metals including carbonyl group, phosphines, amines, alkenes, alkynes and conjugated alkenes and alkynes, arenes.
9. The composition according to claim 6 where the hydrophilic group contains carboxylic acids.
10. The composition according to claim 6 where the hydrophilic group contains clusters of carboxylic acids.
11. The composition according to claim 6 where the hydrophilic group contains clusters of carboxylic acids that are oriented so as to bind mono-, di-, tri- and tetravalent metals.
12. The composition according to claim 11 where the metals that may be bound in a mono, bi, tri- or tetradentate fashion.
13. The composition according to claim 12 where the metals that can be bound are neutral or are formally charged.
14. The composition according to claim 13 where the charged metals possess charge varying from $+1 \rightarrow +4$.
15. The composition according to claim 1 where the hydrophobic group constitutes a core and the hydrophilic group constitutes one terminal site.
16. The composition according to claim 1 where the hydrophobic group constitutes a core and the hydrophilic groups constitute two terminal sites.
17. The composition according to claim 1 where the hydrophobic group constitutes a core and the hydrophilic groups are attached at multiple points along the hydrophobic segment.