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Inventor: ALOK SINGH

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PATENT APPLICATION/TECHNICAL DIGEST PUBLICATION RELEASE REQUEST

FROM: Associate Counsel (Patents) (1008.2)

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Via: (1) Alok Singh (Code 6930)
(2) Division Superintendent (Code 6900)
(3) Head, Classification Management & Control (Code 1221)

SUBJ: Patent Application/Technical Digest entitled: **"METHOD FOR MAKING CROSSLINKED POLYESTER"** request for release for publication.

REF: (a) NRL Instruction 5510.40C
(b) Chapter 6, ONRINST 5870.1C


ENCL: (1) Copy of patent Application/Technical Digest

1. In accordance with the provision of references (a) and (b), it is hereby requested that the subject Patent Application/Technical Digest be released for publication.

2. It is intended to offer this Patent Application/Technical Digest to the National Technical Information Service, for publication.

3. This request is in connection with Navy Case No. 79,820.

3/8/61
(date)



JOHN J. KARASEK
Associate Counsel (Patents)

FIRST ENDORSEMENT

Date: 3/14/61

FROM: Alok Singh (Code 6930)
TO: Division Superintendent (Code 6900)

1. It is the opinion of the Inventor(s) that the subject Patent Application/Technical Digest (is) (is not) classified and there is no objection to public release.



Inventor's Signature

Inventor's Signature

SECOND ENDORSEMENT

Date:

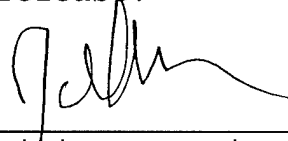
FROM: Division Superintendent (Code 6900)

TO: Classification Management & Control (Code 1221)

1. Release of Patent Application/Technical Digest (is) (is not) approved.

2. To the best knowledge of this Division, the subject matter of this Patent Application/Technical Digest (has) (has not) been classified.

3. This recommendation takes into account military security, sponsor requirements and other administration considerations and there in no objection to public release.



Division Superintendent

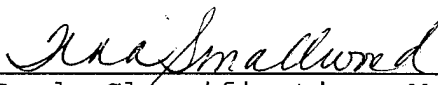
THIRD ENDORSEMENT

Date:

FROM: Head, Classification & Control (Code 1221)

TO: Associate Counsel (Patents) (1008.2)

1. This Patent Application/Technical Digest is authorized for public release.



Head, Classification, Management & Control

Inventors Name: A. Singh

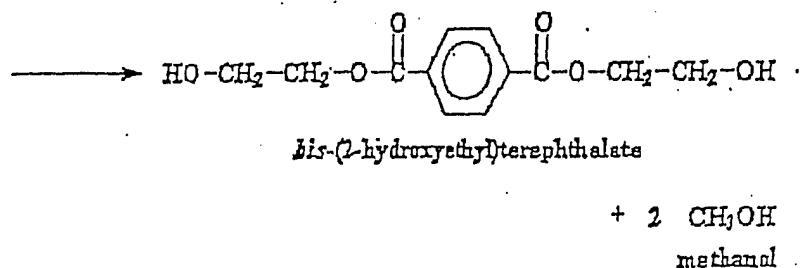
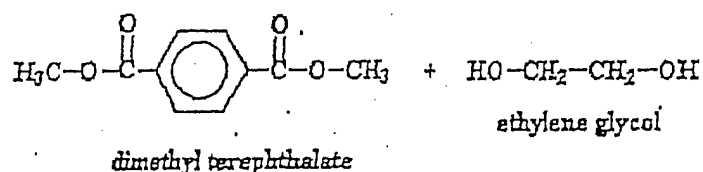
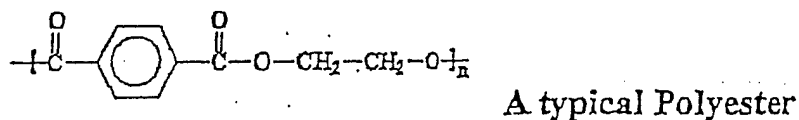
CROSSLINKED POLYESTERS

Field of the Invention

The present invention relates to a method for using a single monomer, having a chiral backbone, to make crosslinked polyesters having a variety of properties.

Background of the Invention

Conventional polyesters are linear polycondensation products of diacids and diols. The reaction process is triggered by special catalysts at temperatures above 300°C. The following scheme depicts the conventional method for making polyesters:



Prior attempts to make polyesters from single monomers required harsh reaction conditions, and the resulting polyesters were not crosslinked.

Moldenhauer et al., in U.S. Patent No. 2,378,571, discloses polycondensation products of pure or mixed hydrazine

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dicarboxylic acids. All of the examples in this patent require the addition of a second dicarboxylic acid, and reactions occur at temperatures of at least 190°C.

Harada et al., in U.S. Patent No. 4,696,981, discloses a method for synthesizing biopolymers that includes a step for making polyamino acids with microwaves. Homo-polyamino acids are made by polycondensing one kind of monoammonium, diammonium, monoamide, diamide, or monoamideammonium salts of malic acid and/or maleic acid and/or fumaric acid, with application of microwaves. The resulting imides are converted to the corresponding peptides or homo-polyamino acids upon partial hydrolysis.

Perrault, in U.S. Patent No. 5,800,685, discloses conductive hydrogels made from cationic acrylates, such as acrylic esters of quaternary chlorides and/or sulfates, and/or acrylic acids of quaternary chlorides.

Wulff et al., in U.S. Patent No. 4,111,863, discloses polymers made from polyfunctional monomers which include polymerizable or polycondensable monomers. These polymers are formed with optically active compounds to form polymers which are analogous to enzymes.

Summary of the Invention

It is an object of the present invention to overcome the foregoing deficiencies of the prior art.

It is another object of the present invention to provide efficient and environmentally benign methods for making crosslinked polyesters.

It is another object of the present invention to

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provide crosslinked polyesters derived from a single, inexpensive monomer precursor.

It is a further object of the present invention to provide crosslinked polyesters into which desired properties can be incorporated, including thermal, photochromic, mechanical, conducting, or metal chelating properties.

The present invention implements the principles of molecular self-assembly, in which participating molecules align and self organize to facilitate intermolecular reactions. In the present invention, these monomers have a chiral backbone and at least two carboxylic acid groups and at least two hydroxyl groups. Previous reports described the stabilizing of self-assembled structures in which the self-assembly process brought the monomer molecules in close vicinity to facilitate intermolecular cross linking (*cf.* Figure 2). Figure 3 compares the surface pressure-area isotherm of the precursor material and that of ideal octadecyloxy tartarate.

The self-assembly, which is chemically similar to precursor material except that it does not have a hydroxyl group at the chain terminus, manifests in the isotherm of Figure 3, graph a, in the pressure isotherm area. The bulk self-assembly scenario is represented in Figure 3, graph b, when a broad transition in the pressure-area isotherm representing a larger molecular area is occupied by precursor material during self assembly. The larger area is indicative of the fact that some of the hydroxyl-group terminated chains bend over to associate with the amide groups of the precursor molecules.

Bilayer stabilization by cross linking the self-

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organized molecules is described in more detail in Singh, A. and Schnurr, J.M. *Phospholipid Handbook*, Marcel Dekker, New York, 1993, 233-291.

According to the present invention, polyesters form via intermolecular polycondensation between acid and alcohol moieties in aqueous medium. This leads to the formation of ester linkages. Although this ester formation proceeds via a combination of inter- and intra-molecular processes, considering the molecular organization, intramolecular condensation should prevail over intermolecular condensation.

The preferred monomers are tartaric acid or derivatives of tartaric acid, which compounds have two carboxylic acid groups protected with dialkylamine and two hydroxyl groups available at the terminus of the alkoxy chain. Using the proper strategy, these monomers can be used to propagate a chain reaction that leads to intermolecular polycondensation and, therefore, to the formation of a polymer.

Ideally, the polymer synthesis proceeds as follows: In the precursor material, the carboxyl groups are protected with an amine such as dimethylamine and the hydroxyl groups present at the terminus segment of tartaric acid are O-alkylated. The resulting diamide is then hydrolyzed to deprotect the amido groups. Quaternary ammonium intermediates formed during hydrolysis foster the formation of an ester bond via reaction of the terminal hydroxyl groups. Because the precursor molecule is bifunctional, the esterification process propagates with precursor molecules to yield a highly crosslinked polymer.

By choosing the appropriate halo-alkanols which O-

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alkylate the hydroxyl groups, one can tailor the polymers to have properties desired, such as mechanical strength, photochromism, etc.

The polymers so formed are insoluble in most solvents, although they exhibit some swelling in methanol. These polymers can be used in making fibers, structural materials, substrates for electronic devices, etc. Because the polyesters of the present invention are crosslinked, they are novel in nature and therefore their technical utility has not yet been fully explored.

The polymers of the present invention are thermosetting in nature. After formation, they were found to be insoluble in most of the common organic solvents tried, including chloroform, methanol, methylene chloride, acetone, DMF, DMSO, and MEK.

The polymers swelled in methanol and became sticky to glass surfaces. The polymers did not melt. Rather, they softened around 300°C, and decomposed above this temperature.

The polymers of the present invention can be used for moisture resistant surface coatings, coatings that can easily be printed, sticky films, temperature and solvent resistant coatings, and thermochromic films. By adjusting the reactants, one can tailor the physical characteristics of the polymer to the desired parameters.

Brief Description of the Drawings

Figure 1A illustrates introducing known groups into the polymer to alter the properties thereof.

Figure 1B illustrates some groups that can be introduced into the polymers.

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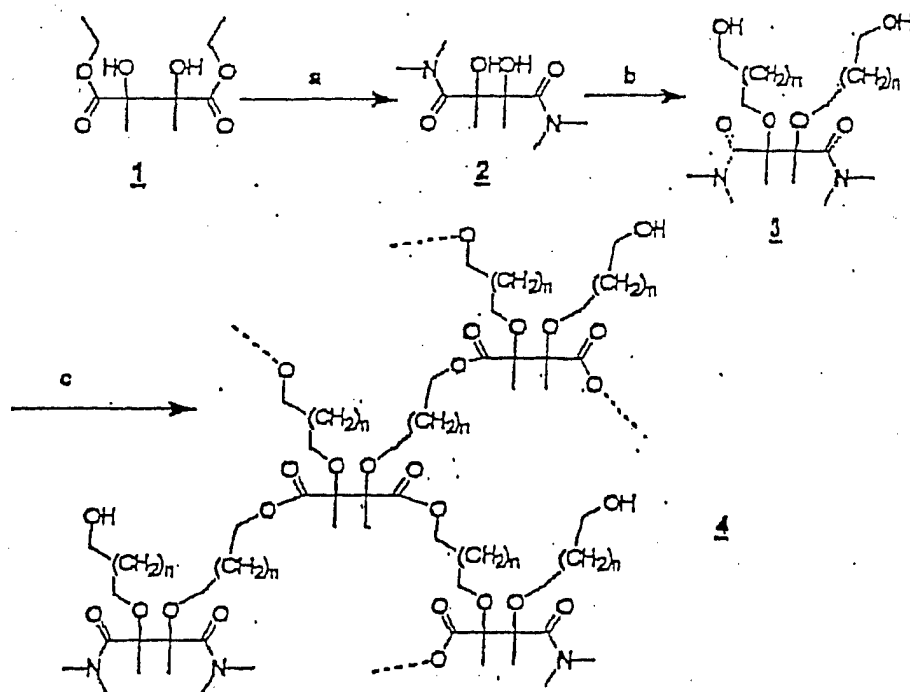
Figure 2A illustrates polymerization mediated by the ideal self-assembly of molecules.

Figure 2B illustrates polymerization mediated by self-assembly of hydroxy terminated precursors.

Figure 3 compares surface pressure-area isotherms on water at 25°C for precursor material of the present invention (graph a) and that of ideal octadecyloxy tartarate (graph b).

Detailed Description of the Invention

Scheme 1 shows the synthesis of tartaric acid based polymers:



a- dimethylamine/methanol, r.t., 24 hr, b- NaH/DMF, Br-(CH₂)_n-OH; c- 3M HCl
n=8,11

Scheme 1. Synthesis of tartaric acid based polyesters

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As shown in step a, above, the carboxyl groups of tartaric acid are protected with dimethylamine. The hydroxyl groups are O-alkylated with an ω -haloalkanol having from about 2 to about 20 carbon atoms. The resulting 2, 3-bis-(ω -hydroxyalkoxy)-N,N,N',N'-tetramethylbutane-1,4-diamide in step b is hydrolyzed to deprotect the amide groups. Formation of quaternary ammonium intermediate during hydrolysis incites the reaction of the terminal hydroxyl group to form an ester bond, as shown in step c.

Diamines are used to protect the carboxyl groups. Although dimethyl amine is inexpensive and can readily be used in the present invention, other amines, such as di-ethyl and propyl amines, can also be used. Water is the best solvent for these reactions, although mixtures of water with ether or THF have successfully been used. The most useful solvents are protic solvents.

The polymerization reaction of the present invention is both temperature and time dependent. Conducting the reaction at higher temperatures reduces the reaction time. At room temperature virtually no polymerization was observed, while at about 80°C polymerization was observed within about 30 minutes.

Bifunctional precursor molecules (see compound 3 in scheme 1), where n ranges from about 2 to about 20, facilitates the ester bond formation leading to the polymerization necessary to produce compound 4 in scheme 1. The polycondensation polymerization proceeds efficiently at a temperature at which the turbid water suspension of the precursor amphiphile (scheme 1, compound 3) turns clear. At temperatures lower than those at

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which the turbid water suspension of the precursor amphiphile turns clear, only the oligomers were produced. Generally, preferred temperatures range from about 40°C to about 90°C.

Materials and Methods

All of the chemicals and solvent used in the synthesis and work up were of technical grade. Anhydrous DMF was used in the reaction. NMR and IR spectra were recorded on a Bruker DRX-400 400 MHz FT-NMR Spectrometer. Nicolet Impact 400D-FT-IR spectrophotometer resp. DSC thermograms were obtained by using Perkin Elmer DSC-7 differential scanning calorimeter.

L(+)-N,N,N',N'-tetramethyl tartaramide was prepared starting from 1, cf. Seebach et al., *Org. Synth.* 1983, 24 24.

Synthesis of 2, 3-bis(w-hydroxy)-N,N,N',N','-tetramethylbutane-1,3-diamide (Compound 3, n=11)

A 10 mL DMF solution of 0.88g (4.3 mmol) tartaramide was added to 0.34 g NaH (14 mmol) suspension in 10 mL DMF. The mixture was stirred for one hour at room temperature and 30 minutes at 70°C. The fluffy reaction mixture was cooled to room temperature and 2.5 grams (10 mmol) 11-bromoundecanol in 10 mL DMF was slowly added. The reaction mixture was stirred overnight at 70°C. A new spot at Rf 0.1 on TLC (silica, 9/1 methylene chloride/methanol) indicated the presence of the product. After workup, the product was purified on a short silica column using 90% methylene chloride in methanol, with a yield of 1.5, or 63%. PMR (CDCl₃) δ ppm 1.2-1.4 (m, 28H), 1.5-1.5 (m, 8H), 2.2 (broad s, 2H), 2.89 (s, 6H), 3.14 (s, 6H), 3.4-3.5 (m, 4H, HC-O-CH₂), 3.58 (t, J=6Hz, 4H, -CH₂-OH), 4.69 (s, 2H). CMR δ, ppm: 26.0, 26.2, 29.6, 29.7, 30.2, 33.0, 36.0, 37.4, 63.0, 70.1, 77.5,

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170.0. IR spectrum showed a strong band at 3450, 2930 and 1650 (amide) Cm^{-1} . Analysis: Calculated for C, 66.14%, H, 10.10. Found: C, 65.42%, H, 11.59%.

Synthesis of Compound 3 (n=8)

Following the procedure above, 0.84 g (4.1 mm) of tartaramide was sequentially reacted with 0.25 g (10.4 mmol) NaH and 2.72 g (13 mmol) 8-bromo-1-octanol in 10 mL DMF. Workup and purification on a short silica column provided 1.35 gram product in 71% yield. PMR (CDCl_3) δ ppm 1.2-1.4 (m, 16H), 1.5-1.5 (m, 8H), 1.9 (broad s, 2H), 2.92 (s, 6H), 3.18 (s, 6H), 3.4-3.5 (m, 4H, HC-O-CH₂), 3.58 (t, J=6Hz, 4H, -CH₂-OH), 4.69 (s, 2H). CMR δ , ppm: 25.8, 26.2, 29.6, 29.4, 30.2, 33.0, 36.0, 37.5, 63.1, 70.0, 77.4, 170.0. IR spectrum showed a strong band at 3450, 2930 and 1650 (amide) Cm^{-1} . Analysis: Calculated for C, 62.58%, H, 10.50. Found: C, 62.12%, H, 11.14%.

Polymer Preparation and Characterization

Monomer 3 was polymerized both in the solvent (THF and dichloromethane) and as a solid dispersed in water. In a typical reaction, 1.4 of 3, where n=11, was dissolved in 5mL THF and added to 15 mL 3N HCL. The reaction was then heated to 60°C for twelve hours to produce the desired cross-linked polymer. At the end of the reaction, the polymer was observed floating on the top of the aqueous layer. This polymer was separated and dried under vacuum to yield 0.8 g product. The properties of the dried polymeric material were determined using DSC, NMR, IR, and elemental analysis. The polymer exhibited a glass transition temperature of 55°C.

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**Example 1: Preparation of Polymer from HO-C₁₁-TAM2
(Compound 3, n=11)**

Two hundred fifty mg of ω -hydroxyalkyloxy (C=11) tetramethyldiamide was dissolved in 5 mL diethylether by warming up the solution. The ether solution was spread in the flat bottom of a beaker, and then most of the solvent was removed under a stream of nitrogen. Final traces were removed by warming the thin film. To this, concentrated hydrochloric acid was added in an amount just enough to cover the film. The beaker was closed tightly with parafilm and left for about five minutes in an oven set at 70°C. The solution was removed from the oven and shaken well to mix the contents. Dispersion resulted. The dispersed material was transferred to another wide, flat-bottomed vial, which was tightly capped and left in the oven at 70°C for one hour. This capped vial showed a polymer floating on the top of the water layer as a continuous film. It was left at 70°C for two additional hours. The vial was removed, and water was removed carefully by puncturing the film at one small point. At the same time and temperature, a thin, transparent film was produced which stuck to the walls of the glass beaker. The film was scratched out of the bottom of the beaker as a translucent polymeric material.

**Example 2: Preparation of Polymer from HO-C₈-TAM2
(Compound 3, n=8)**

The same protocol was followed using 1.3 grams of 3 (n=8). A semi-transparent, gel-like polymer was produced.

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Example 3: Preparation of Polymer from HO-C₁₁-
TAm2 (Compound 3, n=11)

Polymer formation was conducted in water dispersion in a manner as described above. NMR analysis of the oligomeric samples revealed the formation of ester bond at the expense of Me₂N. IR analysis showed the disappearance of the band at 1650cm⁻¹, which is due to an amide bond. Elemental analysis revealed the presence of nitrogen atom in the polymer, indicating that remnant amide bonds were still present in the polymer.

The unique feature of the present invention is the acid catalyzed propagation of intermolecular chain reaction via formation of an ester bond, and control of the properties of the polymer by choosing the appropriate ω -haloalkanol. The system becomes particularly interesting when ester formation proceeds efficiently in an aqueous medium without involving additional catalysts. The monomer precursor also plays an important role, because of its ability to provide both reactants in a single molecule.

Because the monomer plays a crucial role in the reaction scheme, special care was taken to adopt a reproducible means of synthesizing a pure product. The synthesis of monomer 3 was performed following a straightforward route by reacting ω -hydroxy alkyl bromide to the sodium hydride reaction product with 2. It was discovered that there was no need to protect the hydroxyl end of the alkyl bromide, and decent yield could be obtained if the stoichiometry of sodium hydride and 2 was maintained equimolar. A faster procedure, described by extant literature, whereby thallos ethoxide reagent is used in creating

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the ether linkage between the alkyl bromide and the hydroxyl group, was foregone because of the toxicity of said thallos oxide reagent. (Seebach, *Helv. Chim. Acta* 1977, 60, 301). Nor was it practical to use alkyl tosylates in sodium hydride mediate alkylation of 2,3-hydroxyl groups, as this route required the additional step of making monotosylates from an alkanediol precursor. (Anantanarayan, A.; Charmichael, V.A.; Dutton, P.J.; Flyes, T.N.; Pitre, M.J; *Synth. Commun.* 1986, 16, 1771; Fouquey, C.; Lehn, J-M.; Levelut, A.-M. *Adv. Mater.* 1990, 2, 254.

In classical reaction schemes, amide functionality is used for protecting acid groups, thereby enabling reactions to proceed in a basic medium. The acid groups may then be deprotected by acid catalyzed hydrolysis (Behr, J.-P.; Girodeau. J.-M.; Hayward, R.C.; Lehn, J.-M.; Sauvage, J.-P.; *Helv. Chim. Acta* 1980, 63, 2096; Vaughn, H.L.; Robbins, M.D.; *J. Org. Chem.* 1975, 40, 1187; Gassman, P.G.; Hodgson, P.K.G.; Balchunis, R.J., *J. Amer. Chem. Soc.* 1976, 1275).

Compounds with structural features similar to 3 (except for terminal hydroxyl groups) have been successfully hydrolyzed to expose the carboxylic acid.

Polymers prepared according to the above procedure were found to be insoluble in most organic solvents indicating that the material is highly crosslinked.

In studying the properties of 4 (n=11), IR spectra on thin polymer film showed the disappearance of the characteristic amide peak at 1650 cm⁻¹, and the appearance of new, broad peaks at 1732 cm⁻¹. The polymer manifested an affinity to absorb organic solvents in the following order:

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methanol<methylenechloride<chloroform. The polymer exhibited a slight amount of flexibility. DSC analysis indicated a glass transition at 55°C. This polymer did not melt upon heating, and decomposed above 300°C.

The polymer was assessed by examining the remaining nitrogen contents in its composition. Precursor monomer 3 (n=11) contains 5.14% nitrogen. The polymer derived therefrom contained 1.09% nitrogen, 66.13% carbon, and 10.62% hydrogen. The 80% decrease in nitrogen content indicates that dimethyl amide groups are involved in the polymerization, and that the process did not proceed to completion.

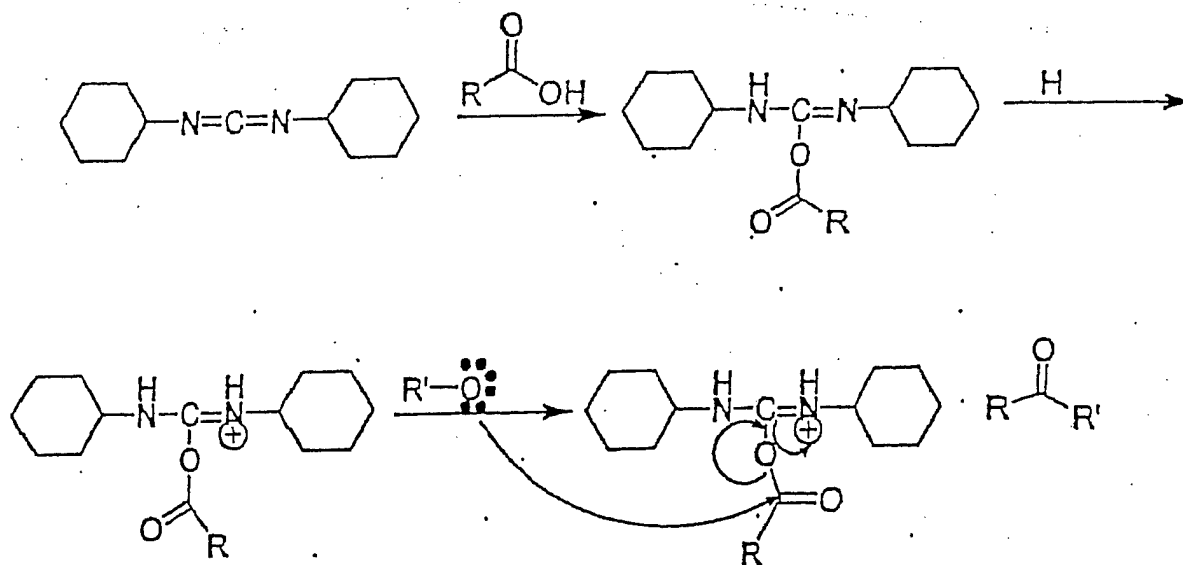
The polymerization process is temperature dependent. A monomer did not react to form an insoluble, crosslinked polymer if stirred only at room temperature, or heated to 60°C after stirring at room temperature. Nor did acid catalysis, at room temperature, result in any visible hydrolysis or polymer product. However, proton NMR spectra showed the presence of a new triplet at 3.4 ppm due to $-\text{CH}_2-\text{OC}(\text{O})-$ bond formation. After the sample was heated at 60°C for twelve hours, most of the starting material disappeared, but still a crosslinked polymer did not form. This material was soluble in chloroform. An NMR spectrum of this product showed the presence of trace amounts of N-methyl proton and the appearance of several islands of chemical shifts centered around 3.4 ppm. The ratio of peak intensity between protons due to $-\text{CH}_2-\text{OH}$: $-\text{CH}_2-\text{OCH}-$: $-\text{CH}_2-\text{OC}(\text{O})-$: NMe_2 was found to be 11:20:32:1; in the monomer this ratio is 1:1:0:1.5.

The polymer formed from monomer 3 during an acid catalyzed deprotection step is unexpected. Interestingly, amide

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deprotection methods using sodium peroxide or potassium *t*-butoxide failed to hydrolyze monomer 3. This indicates that the acid catalyzed hydrolysis step proceeds according to an unconventional mechanism, as opposed to the traditionally-recognized mechanisms.

It is believed that the polymerization mechanism of the present invention situation is similar to that of esterification involving carbodiimide reagents, as shown in scheme 2.

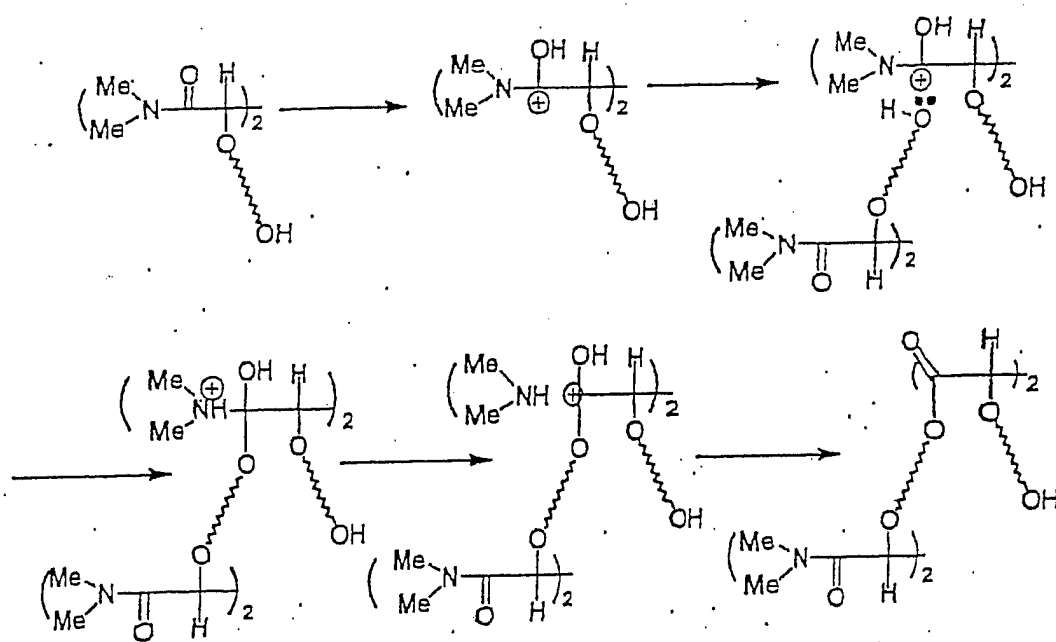


Scheme 2: Carbodiimide catalyzed esterification

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The structural features of molecule 3 are similar to that of an anionic amphiphile. It is safe to assume that in aqueous media, the amide amphiphiles self-organize in a manner that permits the terminal hydroxyl group to remain in close proximity to the amide groups, as similarly occurs in the interdigitation of amphiphiles. Indeed, it has been observed that at room temperature, molecule 3, like other amphiphiles, forms a turbid dispersion which turns clear when heated to about 50°C or more.

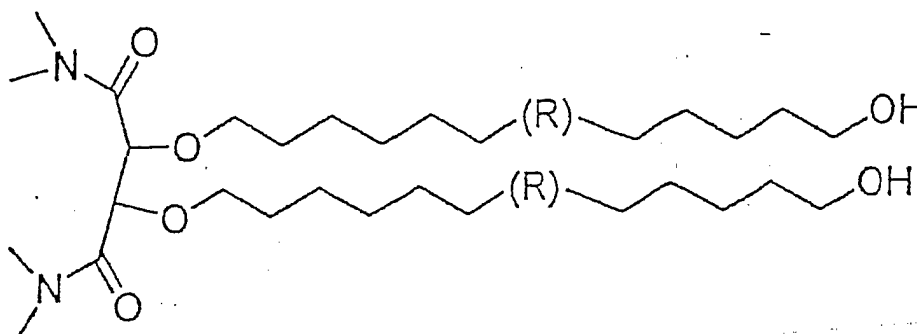
Most likely, the acid catalyzed polymerization of molecule 3 proceeds according to scheme 3.



Scheme 3 Rationalization of acid catalyzed polymerization of 3

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The ω -haloalkanols employed in the present invention can be chosen to introduce moieties that provide predetermined properties to the resulting polymer. For example, using a known chromophore such as azobenzene provides mesogenic units that produce a polymer with photochromic properties. An aromatic ring provides additional mechanical strength:



In this formula, R is a chromophore, a chelator, or biphenyl. The alkyl chain length before and after R can range, inclusively, from about 5 to about 20 carbon atoms.

Figure 1 illustrates some of the groups that can be introduced into the polymer to improve photochromic properties or mechanical strength, as well as a cyclic tetramine that can act as a metal-ligand chelator embedded in the polymer. These metal-ligand chelators have potential for use as catalysts for pesticides such as paraoxon, methyl parathion, and similar chemical agents.

Other chelating moieties which can be incorporated in the ω -haloalcohols to produce chelating polymers are well known

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to those skilled in the art. Among these moieties are porphyrins, macrocyclic ligands including cyclic polyethers, and macrocyclic amine and thioether compounds. The chelating moieties may be derived from conventional chelating molecules such as polyphosphates, aminocarboxylic acids, 1,3-diketones, hydroxycarboxylic acids, polyamines, aminoalcohols, aromatic heterocyclic bases, phenols, aminophenols, oximes, Schiff bases, tetrapyrroles, sulfur compounds, synthetic macrocyclid compounds, and phosphonic acids.

Chromophoric moieties which may be incorporated in the ω -haloalcohols to produce chromophoric polymers include moieties which can reversibly change color or darken upon absorption of ultraviolet or visible light. As is well known to those skilled in the art, photochromism may be based upon geometric isomerism, such as from azobenzene or stilbenes; cycloaddition reactions such as dibenzo(a,j)perylene-8,16-dione; tautomersim, such as with N-salicylidene-2-chloroaniline; dissociation such as results with triphenylmethyl chloride; triplet formation such as 1,2;5,6-dibenzacridine; redox reactions such as tetra-bis[3,5-di(trifluoromethyl)phenyl]borate anion; and electrocyclic reactions, such as the indolino spiropyrans and indolino spiroxazines.

The foregoing description of the specific embodiments so fully reveals the general nature of the invention that others can, by applying current knowledge, readily modify and/or adapt for various applications such specific embodiments without undue experimentation and without departing from the generic concept. Therefore, such adaptations and modifications should and are

Docket No.: 79,820

PATENT APPLICATION

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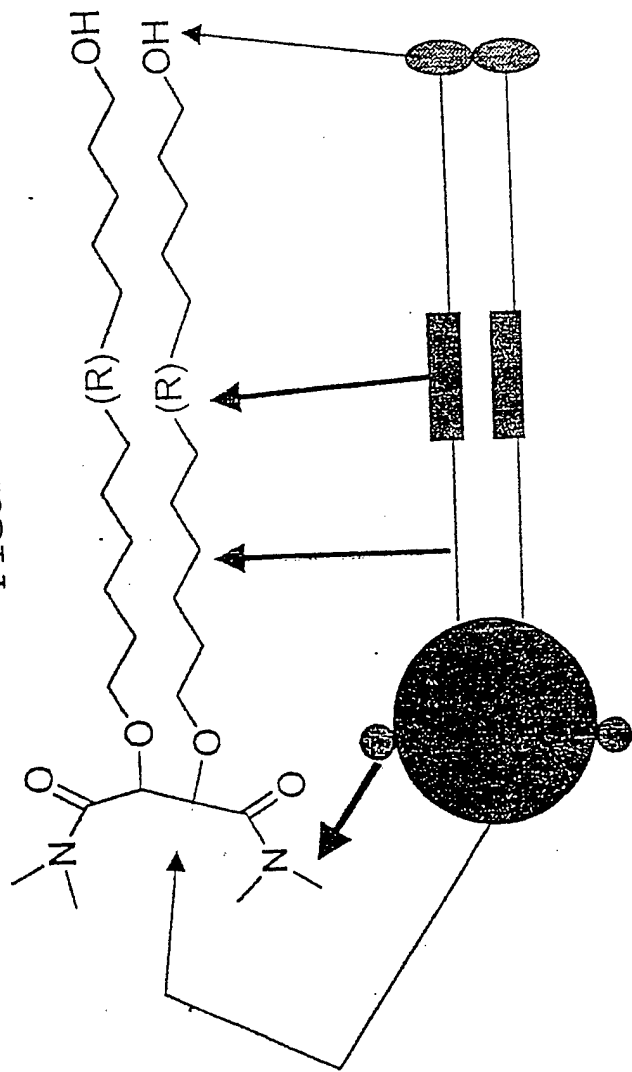
intended to be comprehended within the meaning and range of equivalents of the disclosed embodiments. It is to be understood that the phraseology or terminology employed herein is for the purpose of description and not of limitation. The means and materials for carrying out various disclosed functions make take a variety of alternative forms without departing from the invention. Thus, the expressions "means to..." and "means for..." as may be found in the specification above and/or in the claims below, followed by a functional statement, are intended to define and cover whatever structural, physical, chemical, or electrical element or structures which may now or in the future exist for carrying out the recited function, whether or not precisely equivalent to the embodiment or embodiments disclosed in the specification above; and it is intended that such expressions be given their broadest interpretation.

Inventors Name: A. Singh

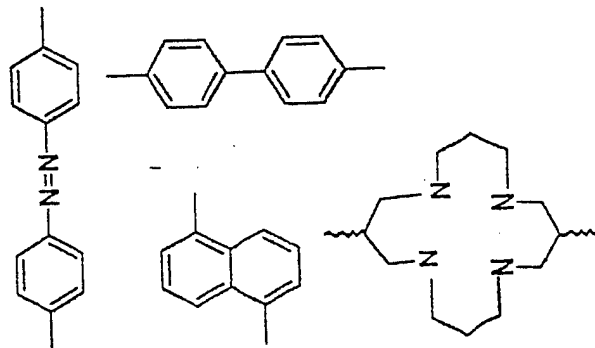
ABSTRACT OF THE DISCLOSURE

According to the present invention, polyesters are formed in aqueous media by the formation of ester linkages via the intermolecular polycondensation between the acid and alcohol moieties of a single monomer. The preferred monomers are derivatives of tartaric acid, which has two carboxylic acid groups and two hydroxyl groups. Using the proper strategy, these groups can be used to propagate a chain reaction that leads to the formation of a desired polymer. The carboxyl groups are protected with an amine, such as dimethylamine, and the hydroxyl groups are O-alkylated with a haloalkanol. The resulting diamide is then hydrolyzed to deprotect the amido groups. Formation of quaternary ammonium intermediates during hydrolysis fosters the reaction of terminal hydroxyl groups to form an ester bond. Because the precursor monomer is bifunctional, possessing both hydroxyl and carboxyl groups, the esterification process propagates to give a highly crosslinked polymer. The haloalkanol which o-alkylates the monomers is chosen to impart the desired properties to the polymer.

FIGURE 1A



R=



Photochromic and /or mechanical strength

Metal ion chelating

FIGURE 1B

Polymerization mediated by Self-assembly of Molecules

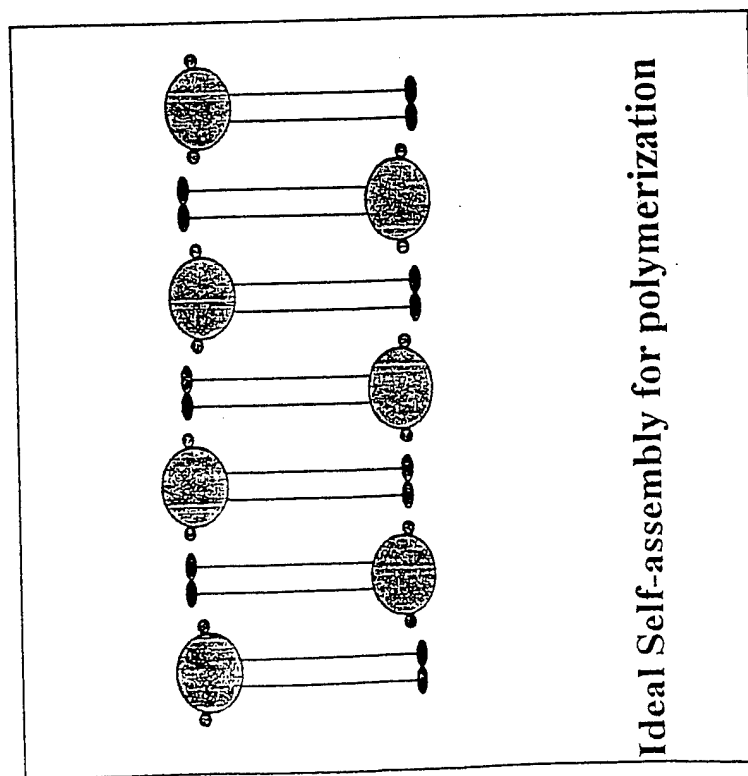
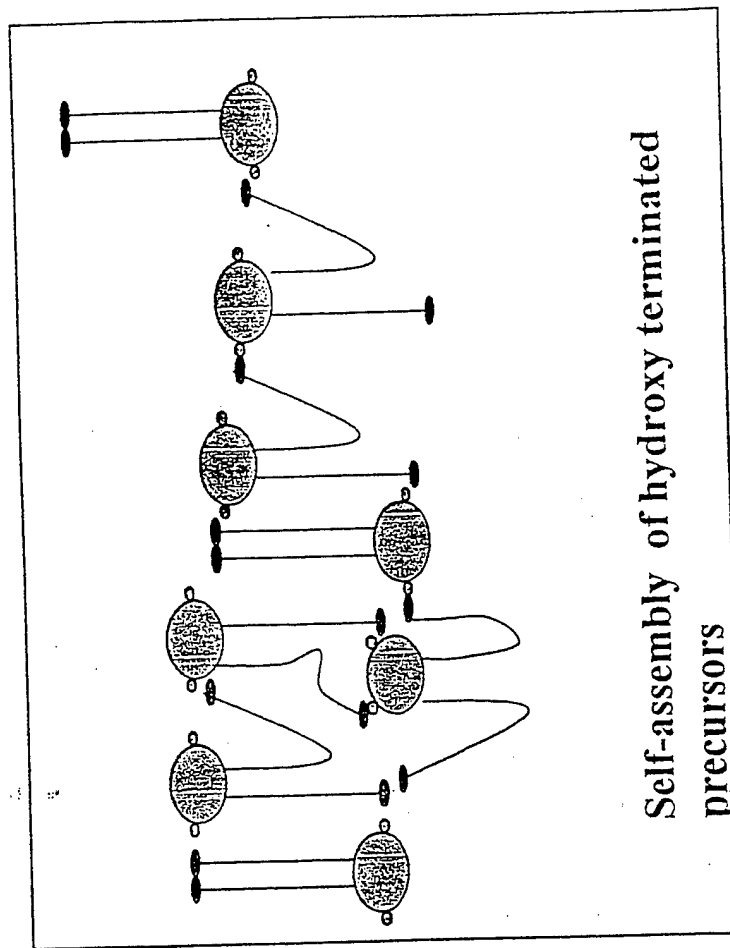


FIGURE 1B

FIGURE 2A

Surface Pressure-Area Isotherms on Water at 25 °C

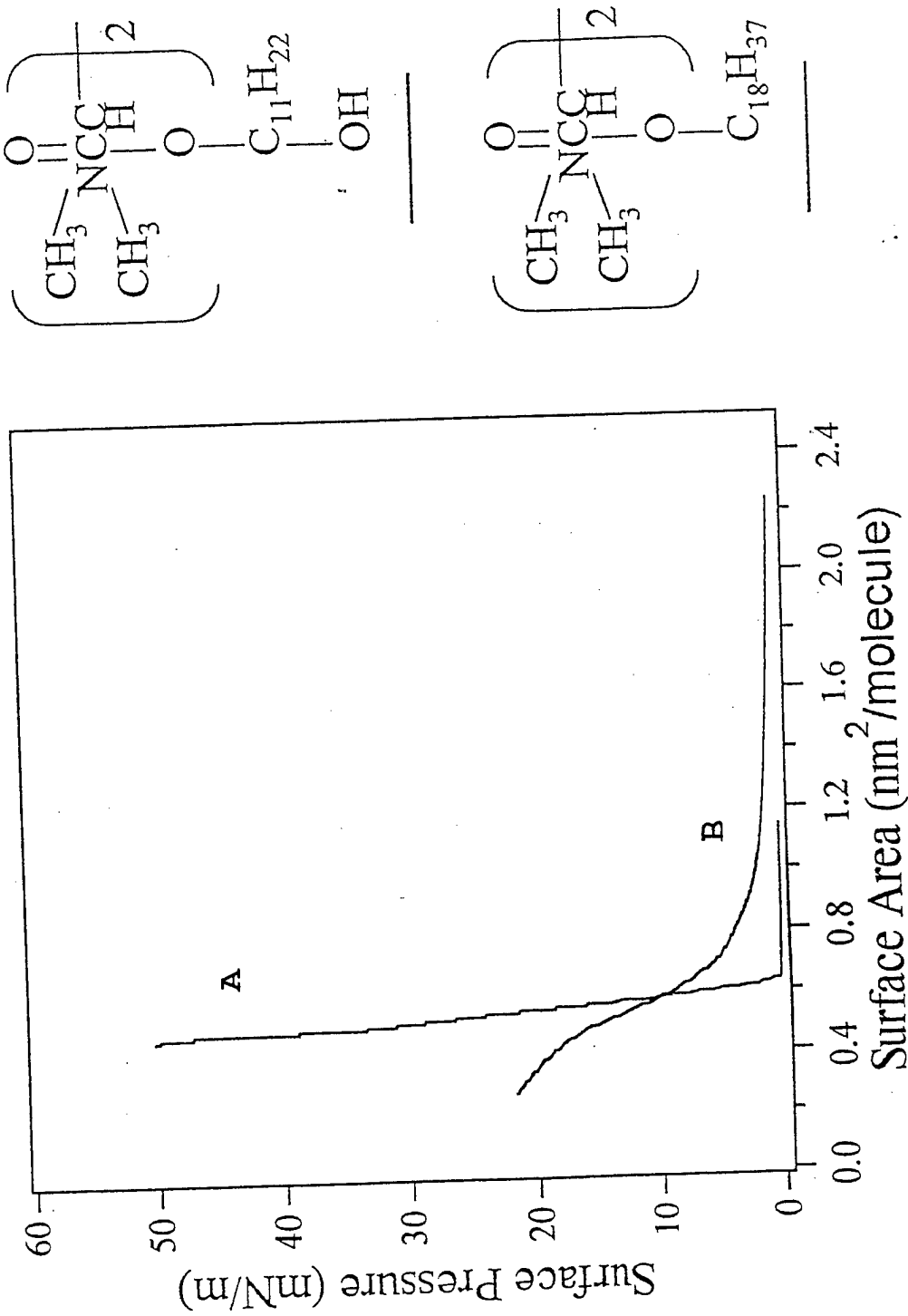


FIGURE 1