

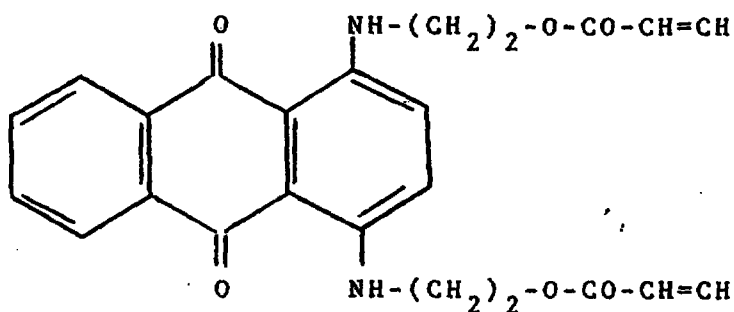
Description

This invention relates to certain anthraquinone compounds which have been found to be valuable in the production of tinted articles, particularly biomedical articles such as contact lenses. Some of these anthraquinone compounds are believed to be novel per se.

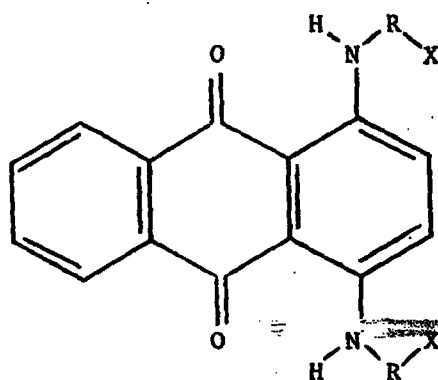
Anthraquinone compounds are well known dyes for different substrates.

In GB-A-1400892 (and DE-A-2323199) it is proposed to prepare a coloured contact lens by copolymerizing a methacrylic ester with, inter alia, various anthraquinone dyes.

Dreyfus et al in Bulletin de la Societe Chimie de France, 1975, (5)-(6), pages 1196-1200 discloses an anthraquinone compound of the following formula as a dyestuff for textiles:



We have now found, in accordance with the present invention that the anthraquinone compounds of general formula I below are valuable dyestuffs when incorporated by copolymerization with other monomers in the manufacture of polymer articles:



(I)

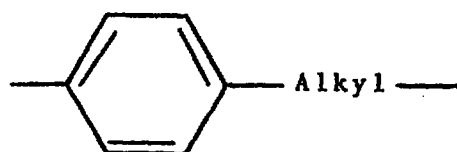
wherein R denotes a divalent radical with 1-12 carbon atoms, and X denotes a polymerizable unsaturated organic radical.

Thus, the present invention broadly provides an article formed by polymerizing a precopolymer mixture comprising an anthraquinone compound of formula I and one or more comonomers.

The present invention is particularly useful for the production of tinted biomechanical devices, such as contact lenses, more especially the production of tinted hydrogel biomedical articles.

In preferred embodiments of the invention X in general formula I is the group $-\text{Y}-\text{CO}-\text{C}(\text{Z})=\text{CH}_2$ wherein Y is $-\text{O}-$ or $-\text{NH}-$ and Z is hydrogen or methyl. Thus, in preferred embodiments X may be, for example, a methacrylate, acrylate, vinyl carbonyl or vinyl carbamate functional moiety.

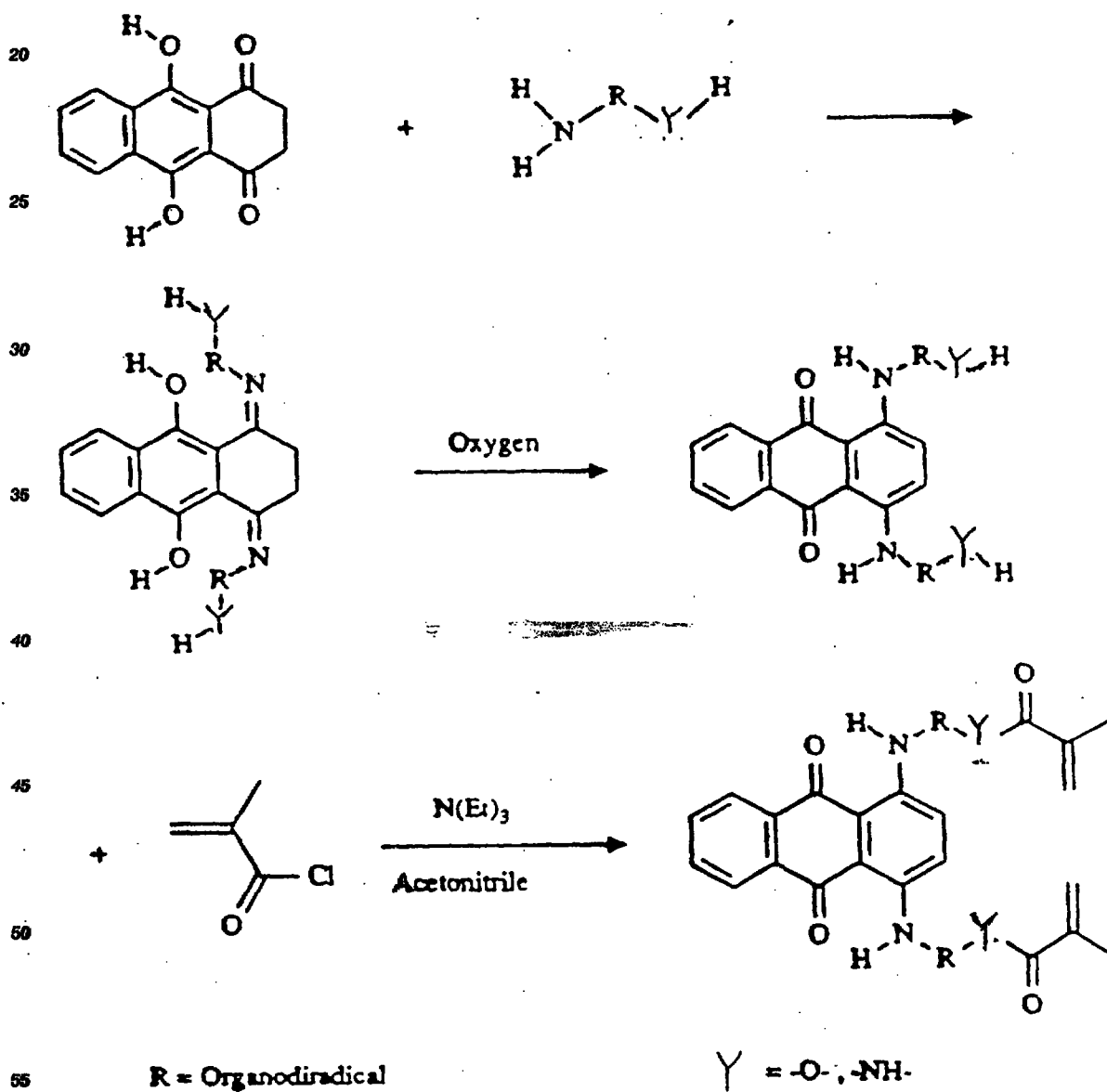
Compounds of formula I wherein R is a phenylenealkylene radical of the formula:



have been found to be especially useful polymerizable dyes, and are believed to be novel compounds.

A general reaction scheme for the preparation of some preferred compounds of general formula I is illustrated below:

General Synthetic Scheme



The comonomers of general formula I have several characteristics which distinguish them over dye comonomers used in biomechanical devices previously. For instance, the dye monomers of formula I are compatible with many monomers used to produce biomechanical materials. This allows the dye to be mixed with the bulk monomer prior to the polymerization of that comonomer.

Furthermore, the functionality of the present dye comonomers allows them to be more completely polymerized with the bulk monomers used to produce state of the art biomechanical materials. This ensures that the dye comonomers become integral parts of the copolymer's matrix and cannot be leached out of that matrix by conditions (e.g., physiological conditions) that are encountered by hydrogel materials, especially biomechanical materials such as contact lenses.

Furthermore, due to the solution compatibility of these dye comonomers with other comonomers, they can be used in various concentration ranges which allows them to be used as tinting (or coloring) agents. This result is a particularly important characteristic in contact lens materials and has heretofore been unavailable in the art.

The comonomer dyes of formula I can be used to produce biomechanical materials in conjunction with known monomers while maintaining all of the advantageous characteristics of polymers produced from the known monomers. This allows for the production of copolymers which are tinted or colored and which still maintain the beneficial physiological characteristics required for biomechanical materials.

The monomers with which the dye monomers of formula I can be copolymerized include both hydrophilic and hydrophobic monomers. Biomechanical materials, of course, include copolymeric mixtures. The dye monomers of formula I can be used as an additional agent in the prepolymer mixtures disclosed in the art. The dye monomer is added in amounts sufficient to impart the desired color intensity. The upper limit of comonomer dye concentration may be restricted by the amount of crosslinking effected by the difunctional dye molecule. Typically the dye concentration will not exceed 5% of the total monomer mixture. More typically the dye concentration will range from about 0.001 to about 2 weight percent of the total monomer mixture. The concentration will of course determine the color intensity of the resulting copolymer.

The polymerizable dye of this invention is particularly useful to color hydrogel materials. Hydrogel materials (i.e., water-containing polymers) are prepared from a wide variety of copolymeric mixtures characterized by the presence of hydrophilic monomers. Examples of hydrophilic monomers are 2-hydroxyethylmethacrylate, N-vinyl pyrrolidone, and methacrylic acid. Copolymeric mixtures used to prepare hydrogels may also include polymers such as polyvinyl alcohol and polyethylene glycol. Hydrogels for contact lenses are generally made by the polymerization of hydrophilic monomers (e.g., 2-hydroxyethylmethacrylate or N-vinyl pyrrolidone) with a crosslinking agent. Useful hydrogels are also obtained by the copolymerization and crosslinking of hydrophilic and hydrophobic monomers to obtain the desired level of water absorption in the gel. Suitable hydrogels are further exemplified by the materials described in U.S. Re. 27,401; U.S. 3,532,679; and U.S. 3,937,680.

The dye monomers of formula I can also be used in conjunction with rigid gas permeable contact lens formulations known in the art as exemplified in U.S. Patent Nos. Re. 31,406, U.S. 4,424,328, U.S. 4,139,548, U.S. 4,433,111, U.S. 4,152,508, U.S. 4,450,264, U.S. 4,153,641, U.S. 4,540,761, U.S. 4,372,203, and U.S. 3,950,315.

The dye monomers of formula I may also be used as comonomers with silicone based systems. Silicones are also well known in the art and are exemplified by the following U.S. Patents: U.S. 4,136,250, U.S. 3,518,324, and U.S. 4,138,382.

The invention is illustrated by the Examples which follow.

EXAMPLE 1a

Synthesis of 1,4-Bis(2-methacrylamidoethylamino)anthraquinone(I)

Into a 250 ml 2 neck round bottom flask equipped with a thermometer was placed 6.0 g of leucoquinizarin and a stir bar, and the flask was flushed with nitrogen. To this was added 75 ml of ethylene diamine through which nitrogen had been bubbled for 15 minutes. While keeping the reactants under nitrogen, the solution was heated to 50°C for one hour during which the solution turned green. The nitrogen blanket was then removed and air was bubbled through the solution for one hour, keeping the temperature at 50°C, causing the solution to turn blue. Water, 250 ml, was added and the intermediate product was isolated by filtration, washed with water and air dried. The intermediate was recrystallized from acetonitrile. The final isolated yield was 37%. A solution of 1.0 g of the intermediate in 250 ml of methanol was cooled to <3°C using an ice bath. To this was added 5.0 ml of triethylamine and 3.5 ml of methacryloyl chloride. After one hour the reaction was complete. The product was precipitated by the addition of 500 ml of water,

isolated by filtration, washed with 1:1 methanol:water and then water, and air dried giving an isolated yield of 80%.

According to the above procedure, the following compounds were also prepared:

- 1,4-bis(2-acrylamidoethylamino)anthraquinone,
 5 1,4-bis(3-methacrylamidopropylamino)anthraquinone (II),
1,4-bis(3-methacrylamido-2,2-dimethylpropylamino) anthraquinone (III),
1,4-bis(2-acrylamidocyclohexylamino)anthraquinone, and
1,4-bis(2-methacrylamidocyclohexylamino)anthraquinone (IV).

10 EXAMPLE 1b

Synthesis of 1,4-Bis(3-methacryloxypropylamino)anthraquinone(V)

The intermediate was prepared as before using 8.0 g of leucoquinizarin and 50 ml of 3-aminopropanol
 15 giving a recrystallized yield of 23%. To a solution of 1.0 g of the intermediate in 200 ml of acetonitrile was
 added 3.0 ml of triethylamine and 1.5 ml of methacryloyl chloride at room temperature. The reaction was
 complete after 1/2 hour. The solution was diluted to 1 liter with water and 1.0 g of NaOH was added. The
 gummy solids were isolated on fluted filter paper, redissolved in 200 ml of acetone and reprecipitated by
 the addition of 200 ml of water. The product was isolated by filtration on a fritted filter, washed with 1:1
 20 acetone:water, water and air dried. The isolated yield was 20%.

EXAMPLE 1c

Synthesis of 1,4-Bis(1-methacryloxy-2-butylamino)anthraquinone (VI)

25 A mixture of 15 g of quinizarin, 75 ml of ($\pm$)-2-amino-1-butanol and 100 ml of water was heated under
 nitrogen at 90°C for 7.5 hours and then diluted to 500 ml to precipitate the product. The intermediate was
 isolated by filtration, washed with water and air dried. Recrystallization from toluene gave a yield of 52%. To
 a solution of 2 g of the intermediate in 100 ml of dry acetonitrile was added 4.0 ml of triethylamine and 3.0
 30 ml of methacryloyl chloride. After 1/2 hour, 300 ml of ethylene glycol was added and 10 minutes later the
 solution was diluted to 1 liter with water. The tacky product was filtered out of the solution, redissolved in
 200 ml of acetone and precipitated by the addition of 500 ml of water. The wet product was redissolved in
 200 ml of acetone a second time and precipitated by the addition of 300 ml of water, isolated by filtration,
 washed with water and air dried. The isolated yield was 52%. The TLC showed the expected two spots for
 35 both the intermediate and the final product.

EXAMPLE 1d

Synthesis of 1,4-Bis(1-methacryloxy-2-pentylamino)anthraquinone (VII)

40 A deoxygenated solution of 3.0 g of leucoquinizarin, 10.0 g of ($\pm$)-2-amino-1-pentanol and 50 ml of
 triethylamine was heated at 60°C under nitrogen overnight. Air was then bubbled through the solution at
 55°C for 3 hours. The resulting oil was diluted with 250 ml of methanol and then with 250 ml of water to
 precipitate the intermediate, which was isolated by filtration, washed with 2:1 water:methanol and the water,
 45 and air dried. The isolated yield was 75%. To a solution of 2.0 g of the intermediate in 50 ml of dry
 acetonitrile was added 4.0 ml of triethylamine and 2.0 ml of methacryloyl chloride. After 30 minutes at room
 temperature, the reaction was completed. The solution was diluted with 50 ml of ethylene glycol followed by
 400 ml of water 15 minutes later. After vigorous stirring for one hour, most of the gummy product was
 sticking to the sides of the flask. The solution was filtered and the solids were dissolved in 500 ml of
 50 methanol. The product was reprecipitated by the addition of 500 ml of water, isolated by filtration, washed
 with 1:1 water:methanol followed by water and air dried. Isolated yield was 34%.

EXAMPLE 1e

55 Synthesis of 1,4-Bis(4-methacryloxy-cyclohexylamino)anthraquinone (VIII)

A deoxygenated solution of 10.0 g of trans-4-aminocyclohexanol hydrochloride, 2.76 g of NaOH, 25 ml
 of water and 45 ml of triethylamine was added to a nitrogen filled flask containing 2.0 g of leucoquinizarin

and the mixture was heated at 55°C for two hours. Air was then bubbled through the solution overnight at 55°C to form the crude intermediate. The slurry was diluted to 250 ml with water and the solids were isolated by filtration. Unoxidized product was removed by placing the solids in 500 ml of boiling 2-propanol for one hour, cooling and filtering. The purified intermediate was washed with methanol and air dried. The isolated yield was 81%. To a slurry of 1.5 g of the intermediate in 100 ml of toluene was added 5.0 ml of pyridine and 1.4 ml of methacryloyl chloride. After boiling for 10 minutes, the product was formed and the solvent was removed on a rotovap. The solids were dissolved in 500 ml of acetone and the product was precipitated by the addition of 500 ml of water. The fine precipitate was isolated on fluted filter paper, redissolved in acetone, precipitated with water and the product was isolated by filtration. After washing with water, the product was air dried. The yield was 60%.

EXAMPLE 1f

Synthesis of 1,4-Bis(2-methacryloxy-cyclohexylamino)anthraquinone (IX)

A deoxygenated solution of 10.9 g of 2-aminocyclohexanol hydrochloride, 2.58 g of NaOH, 50 ml of water and 100 ml of triethylamine was added to a nitrogen filled flask containing 2.0 g of leucoquinizarin and the mixture was heated at 55°C for four hours. Air was then bubbled through the solution overnight with the temperature reaching 80°C. After diluting with water, the solids were filtered out. The solids were slurried and washed with acetone until the filtrate was light blue. The yield of the air dried product was 42%. Over a 1/2 hour period of time, a total of 2.6 ml of methacryloyl chloride, 4.0 ml of triethylamine and 2.0 ml of pyridine was added to a slurry of 1.0 g of the intermediate in 100 ml of dry acetonitrile. Product was formed by boiling the mixture for one hour. Water, 25 ml, was added and the solvents were rotovaped off. The solids were slurried in 1 liter of water containing 0.5 g of NaOH for 1/2 hour and the product was isolated from the highly colored solution by filtration. The product was dissolved in 300 ml of acetone, precipitated by the addition of 600 ml of water and isolated by filtration several times until the filtrate was light blue. The yield of the air dried product was 20%.

EXAMPLE 1g

Synthesis of 1,4-Bis(2-methacryloxy-1-phenylethylamino)-anthraquinone (X)

In an oxygen free solution, 3.0 g of leucoquinizarin and 10.0 g of L-2-phenylglycinol in 150 ml of triethylamine were reacted overnight at 55°C. Air was then bubbled through the solution for 3 hours at 55°C and the mixture was reduced to dryness on a rotovap. The solids were dissolved in acetone and the intermediate was precipitated by the addition water containing NaOH. The product was isolated from the highly colored solution by filtration, washed and air dried. The yield of the intermediate was 45%. Two grams of the intermediate was dissolved in 100 ml of dry acetonitrile to which was added 4.0 ml of triethylamine and 2.5 ml of methacryloyl chloride. After 1/2 hour the reaction was complete. Methanol, 25 ml, was added and the solvents were rotovaped off. The product was dissolved in 250 ml of water and isolated by filtration several times until the filtrate was light blue. The yield of the air dried product was 33%.

EXAMPLE 1h

Synthesis of 1,4-Bis(1-methacryloxy-3-methyl-2-pentylamino) anthraquinone(XI)

A 1.5 g sample of leucoquinizarin was reacted with 5.0 g of L-isoleucinol in 50 ml of triethylamine under nitrogen for 6 hours at 55°C. Air was then bubbled through the solution for 8 hours with the temperature reaching 80°C at one point. The mixture was diluted with 1:1 methanol water and filtered to isolate the intermediate. The intermediate was washed with the same solvent mixture until the filtrate was light blue. The yield of the air dried intermediate was 87%. TLC showed that the intermediate still contained unoxidized and mono-substituted impurities. To a solution of 1.23 g of the impure intermediate in 50 ml of dry acetonitrile was added 3.0 ml of triethylamine and 1.5 ml of methacryloyl chloride. The reaction was complete after 15 minutes at room temperature. Methanol, 50 ml, was added and the solution was evaporated to dryness. The crude product was purified by column chromatography over silica gel using 1:1 toluene:chloroform as the eluent. When the solvent was evaporated, it was found that the product was tacky. Repeated dissolving in methanol and stripping resulted in a dry product. The yield was 63%.

EXAMPLE II**Synthesis of 1,4-Bis(4-(2-methacryloxyethyl)phenylamino-anthraquinone (XII)**

5 A 3.0 g sample of leuquinizarin was heated with 10.0 g of 4-aminophenethyl alcohol (mp 113 °C) under nitrogen at reflux (~150 °C) for 5 hours. TLC showed no further changes occurring. Ethylene glycol, 25 ml, was added and air was bubbled through the hot solution for 3 hours. After cooling, the resulting solid cake was broken up and the solids were dissolved in 1 liter of acetone, the solution filtered and the intermediate was precipitated by the addition of 1 liter of NaOH in water. The intermediate was isolated by filtration, 10 washed with water and air dried. The yield was 38%. To a slurry of 1.6 g of the intermediate in 30 ml of dry acetonitrile was added 3.2 ml of triethylamine and 1.6 ml of methacryloyl chloride at room temperature. After 30 minutes the reaction was complete and 15 ml of ethylene glycol was added. After 15 minutes, the product was precipitated by diluting the solution to 1 liter with water and isolated by filtration. The product was purified by dissolving 800 ml of acetone and precipitated by the addition of 400 ml of water. The 15 product was isolated from the deep rust colored solution by filtration, washed with 1:1 acetone:water and air dried. The isolated yield was 57%.

EXAMPLE 2**Preparation of Tinted Copolymeric Contact Lens Materials**

A monomer mix was prepared from the following formulation:

25	2-hydroxymethacrylate (HEMA)	99.49 wt %
	Ethylene Glycol Dimethacrylate (EGDMA)	0.34 wt %
	Benzoin Methyl Ether Catalyst (NVP)	0.17 wt %
	monomer I	200 ppm

30 Monomer (I) is the dye molecule synthesized in Example 1(a). The monomer mixture was polymerized between silicone treated glass plates using a fluorescent UV source. Similar pHEMA films were cast using 200 ppm of the various monomers synthesized in Example 1.

EXAMPLE 3

35 Discs were cut from the film prepared from monomer I (as described in Example 2). These untinted discs were tinted by a state of the art method using Procion blue (Procian Blue discs). The visible spectra of the film discs of example 2 and the Procion Blue discs were compared. The discs were then subjected to accelerated hydrolysis testing and the resultant visible spectra were again compared. Both types of discs 40 showed about the same loss of color intensity. However, the loss of the color intensity in the Procion disc was from loss of dye from the disc whereas loss of color intensity in the monomer I disc was due to the hydrolysis of the amine functionality rather than actual monomer loss.

EXAMPLE 4

45 pHEMA films were made with 200 ppm of each of the monomers I, II, III, and IV. Incorporation of the bismethacrylamide monomers into the pHEMA was tested with the following results:

50	Monomer	Bridge (R)	% Incorporation
	I	-(CH ₂) ₂ -	92
	II	-(CH ₂) ₃ -	90
	III	-CH ₂ C(CH ₃) ₂ -CH ₂ -	82
55	IV	1,2 - cyclohexylene	82

The hydrolytic stability of the final polymeric material was tested by boiling the samples in buffered saline solution. After 4 weeks the loss of color intensity was as follows:

Monomer	% Loss at 600nm	at 640nm
I	18	26
II	16	28
III	14	26
IV	5	7

The monomer with the largest R radical produced the most stable copolymeric material.

EXAMPLE 5

The dimethacrylate ester monomers were tested for incorporation in to a pHEMA material and for stability. Incorporation was as follows:

Monomer	Bridge (R) Precursor	% Incorporation
V	3-aminopropanol	100
VI	2-aminobutanol	98
VII	2-aminopentanol	98
VIII	4-aminocyclohexanol	98
XI	2-aminocyclohexanol	95
X	2-amino-2-phenylethanol	97
XI	2-amino-3-methylpentanol	97
XII	2-(4-aminophenyl)ethanol	99

The hydrolytic stability of the pHEMA films were tested as described in Example 4. After 4 weeks, the loss of color intensity was as follows:

Monomer	% of Loss at 600nm	at 640nm
V	49	53
VI	14	27
VII	16	28
VIII	25	38
IX (3 weeks)	11	25
X	15	24
XI	14	29
XII	6	6

EXAMPLE 6

Films were cast from a monomer mix as described in Example 2 except that the mix contained 150 ppm of monomer XII. The control was untinted film cast from the same lot of monomer mix.

Film properties were measured with the following results:

Test	Monomer XII Film	Control Film
modulus (g/mm ²)	57	59
tensile	66	71
% elongation	280	290
initial tear	6.8	6.7
propagation tear	4.9	5.0
% H ₂ O	37.3	37.9
O ₂ permeability (cm ³ x cm/sec x cm ² x @35 C)	8.9x10 ⁻¹¹	9.2x10 ⁻¹¹

The results show that the monomer does not affect the physical characteristics of standard contact lens materials.

EXAMPLE 7

A monomer mix was prepared from the following formulation:

Methyl methacrylate	36.4 grams
NVP	88.2 grams
EGDMA	0.033 grams
Allyl methacrylate	0.24 grams
VAZO-64* Catalyst	0.12 grams
Monomer XII	450 ppm

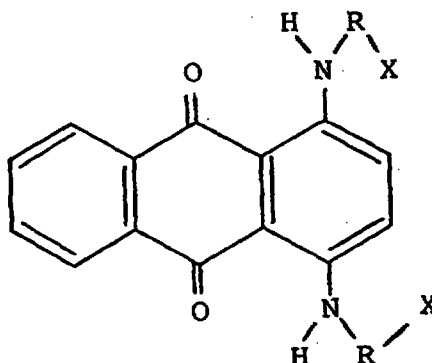
* VAZO is a trade mark

The monomer mix was heat cured into rods from which buttons were cut and discs were lathed. The buttons and discs were blue-green.

Claims

Claims for the following Contracting States : DE, FR, GB, IT, SE

1. A compound having the general chemical formula:



wherein:

R denotes a phenylenealkylene radical with up to 12 carbon atoms; and
X denotes a polymerizable unsaturated organic radical.

2. A compound according to Claim 1, wherein X is $-Y-CO-C(Z)=CH_2$ wherein Y is $-O-$ or $-NH-$ and Z is hydrogen or methyl.
3. A compound according to Claim 2, wherein Y is $-O-$.
4. The compound 1,4-bis(4-(2-methacryloxyethyl)phenylamino)anthraquinone.
5. An article formed by polymerizing a precopolymer mixture comprising one or more comonomers and an anthraquinone compound having the general formula:



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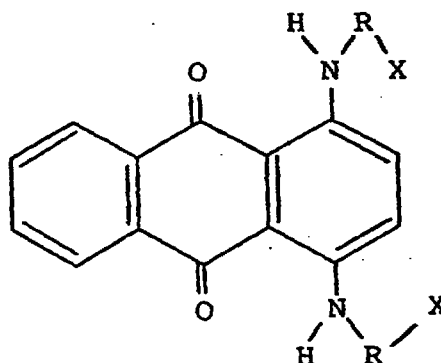
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Claims

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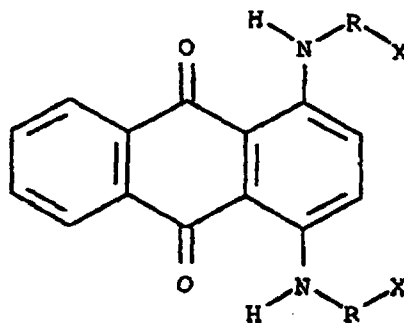
1. A compound having the general chemical formula:



wherein:

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X denotes a polymerizable unsaturated organic radical.

2. A compound according to Claim 1, wherein X is $-Y-CO-C(Z)=CH_2$ wherein Y is $-O-$ or $-NH-$ and Z is hydrogen or methyl.
3. A compound according to Claim 2, wherein Y is $-O-$.
4. The compound 1,4-bis(4-(2-methacryloxyethyl)phenylamino)anthraquinone.
5. An article formed by polymerizing a precopolymer mixture comprising one or more comonomers and an anthraquinone compound having the general formula:



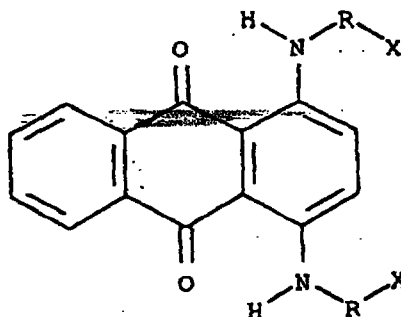
wherein:

R denotes a divalent radical with 1 to 12 carbon atoms; and
X denotes a polymerizable unsaturated organic radical.

6. An article according to Claim 5, wherein said anthraquinone compound is as defined in any one of Claims 1-4.
7. An article according to Claim 5 or Claim 6, wherein the precopolymer mixture comprises a hydrophilic monomer, and the resultant polymer is a hydrogel.
8. An article according to Claim 7, wherein the precopolymer mixture contains 2-hydroxyethyl-methacrylate.
9. An article according to Claim 7, wherein the precopolymer mixture contains N-vinyl pyrrolidone.
10. An article according to any one of Claims 7-9, which is a soft contact lens.

Claims for the following Contracting State : ES

1. A process for preparing a tinted polymeric article, comprising polymerizing one or more comonomers and an anthraquinone compound having the general formula:



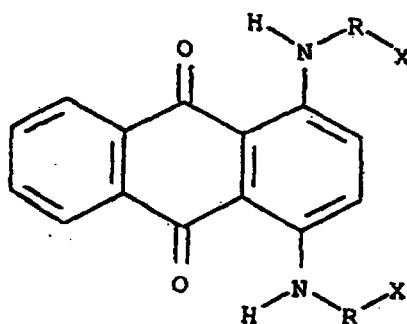
wherein:

R denotes a divalent radical with 1 to 12 carbon atoms; and
X denotes a polymerizable unsaturated organic radical.

2. A process according to Claim 1, wherein R denotes a phenylenealkylene radical with up to 12 carbon atoms.
3. A process according to Claim 1 or Claim 2, wherein X is $-Y-CO-C(Z)=CH_2$ wherein Y is $-O-$ or $-NH-$ and Z is hydrogen or methyl.



4. A process according to Claim 3, wherein Y is -O-.
5. A process according to any preceding claim, wherein the anthraquinone compound is 1,4-bis(4-(2-methacryloxyethyl)phenylamino)anthraquinone.
6. A process according to any preceding claim, wherein the precopolymer mixture comprises a hydrophilic monomer, and the resultant polymer is a hydrogel.
7. A process according to Claim 6, wherein the precopolymer mixture contains 2-hydroxyethyl-methacrylate.
8. A process according to Claim 6, wherein the precopolymer mixture contains N-vinyl pyrrolidone.
9. A process according to any preceding claim, wherein there is formed a soft contact lens.
10. An article formed by polymerizing a precopolymer mixture comprising one or more comonomers and an anthraquinone compound having the general formula:



wherein:

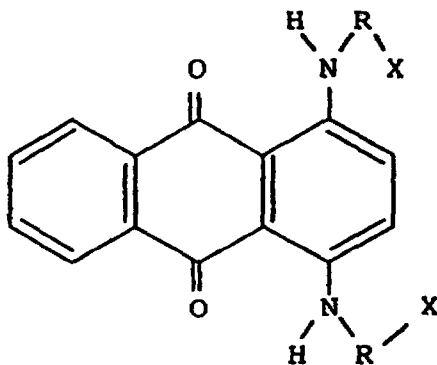
R denotes a divalent radical with 1 to 12 carbon atoms; and
X denotes a polymerizable unsaturated organic radical.

11. An article according to Claim 10, wherein said anthraquinone compound is as defined in any one of Claims 2-5.

Patentansprüche

Patentansprüche für folgende Vertragsstaaten: DE, FR, GB, IT, SE

1. Verbindung der allgemeinen chemischen Formel:

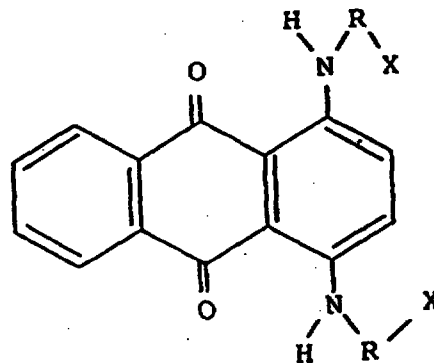


in der



R ein Phenylalkylenradikal mit bis zu 12 Kohlenstoffatomen darstellt; und
X ein ungesättigtes organisches polymerisierbares Radikal darstellt.

2. Verbindung gemäss Anspruch 1, in der X -Y-CO-C(Z)=CH₂ und Y -O- oder -NH- und Z Wasserstoff oder Methyl ist.
3. Verbindung gemäss Anspruch 2, in der Y -O- ist.
4. Die Verbindung 1,4-bis(4-(2-methacryloxyethyl)phenylamino)anthrachinon.
5. Gegenstand geformt mittels Polymerisation einer Präkopolymermischung, die eine oder mehr Komonomere umfasst und eine Anthrachinonverbindung der allgemeinen Formel:



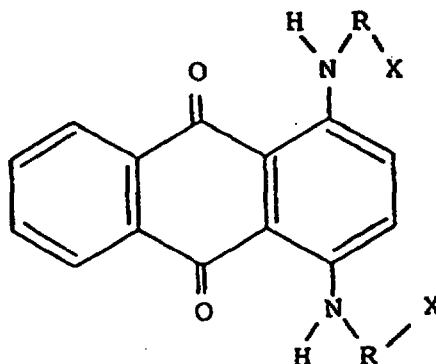
in der

R ein bivalentes Radikal mit 1 bis 12 Kohlenstoffatomen darstellt; und
X ein polymerisierbares ungesättigtes organisches Radikal darstellt.

6. Gegenstand gemäss Anspruch 5, in die besagte Anthrachinonverbindung so wie in jeglichem der Ansprüche 1-4 definiert ist.
7. Gegenstand gemäss Anspruch 5 oder Anspruch 6, in dem die Präkopolymermischung ein hydrophiles Monomer umfasst, und das resultierende Polymer ein Hydrogel ist.
8. Gegenstand gemäss Anspruch 7, in dem die Präkopolymermischung 2-hydroxyethyl-metacrylat enthält.
9. Gegenstand gemäss Anspruch 7, in dem die Präkopolymermischung N-vinyl Pyrrolidon enthält.
10. Gegenstand gemäss eines der Ansprüche 7-9, der eine weiche Kontaktlinse ist.

Patentansprüche für folgenden Vertragsstaat : ES

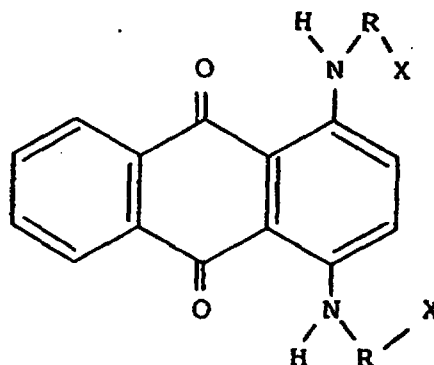
1. Verfahren zur Herstellung eines gefärbten Polymergegenstands umfassend die Polymerisation eines oder mehr Komonomere und eine Anthrachinonverbindung der allgemeinen chemischen Formel:



In der

R ein bivalentes Radikal mit bis zu 12 Kohlenstoffatomen darstellt; und
X ein ungesättigtes organisches polymerisierbares Radikal darstellt.

2. Verfahren gemäss Anspruch 1, R ein Phenylenakylradikal mit bis zu 12 Kohlenstoffatomen darstellt.
3. Verfahren gemäss Anspruch 1 oder Anspruch 2, in der $X - Y - CO - C(Z) = CH_2$ und Y -O- oder -NH- und Z Wasserstoff oder Methyl ist.
4. Verfahren gemäss Anspruch 3, in der Y -O- ist.
5. Verfahren nach einem der vorhergehenden Ansprüche, bei dem die Anthrachinonverbindung 1,4-bis(4-(2-methacryloxyethyl)phenylamino)anthrachinon ist.
6. Verfahren nach einem der vorhergehenden Ansprüche, bei dem die Präkopolymermischung ein hydrophiles Monomer umfasst, und das resultierende Polymer ein Hydrogel ist.
7. Verfahren nach Anspruch 6, bei dem die Präkopolymermischung 2-hydroxyethyl-methacrylat enthält.
8. Verfahren nach Anspruch 6, bei dem die Präkopolymermischung N-vinyl Pyrrolidon enthält.
9. Verfahren nach einem der vorhergehenden Ansprüche, bei dem eine weiche Kontaktlinse geformt wird.
10. Gegenstand geformt mittels Polymerisation einer Präkopolymermischung, die eine oder mehr Komonomere umfasst, und eine Anthrachinonverbindung der allgemeinen Formel:



in der

R ein bivalentes Radikal mit 1 bis 12 Kohlenstoffatomen darstellt; und
X ein polymerisierbares ungesättigtes organisches Radikal darstellt.

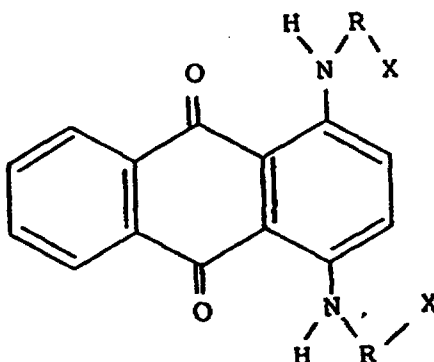


11. Gegenstand gemäss Anspruch 10, in die besagte Anthrachinonverbindung so wie in jeglichem der Ansprüche 2-5 definiert ist.

Revendications

Revendications pour les Etats contractants suivants : DE, FR, GB, IT, SE

1. Un composé ayant la formule chimique générale:



dans laquelle:

R dénote un radical phénylènealkylène avec jusqu'à 12 atomes de carbone; et

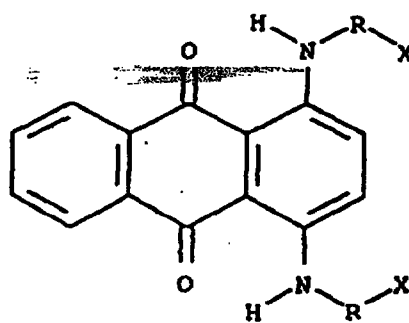
X dénote un radical organique non-saturé polymérisable.

2. Un composé selon la revendication 1, dans lequel X est $-Y-CO-C(Z)=CH_2$, dans lequel Y est $-O-$ ou $-NH-$ et Z est hydrogène ou méthyle.

3. Un composé selon la revendication 2, dans lequel Y est $-O-$.

4. Le composé 1,4-bis(4-(2-méthacryloxyéthyl) phénylamine)anthraquinone.

5. Un article formé par la polymérisation d'un mélange de prépolymères qui comprend un ou plusieurs comonomères et un composé anthraquinone ayant la formule générale:



dans laquelle:

R dénote un radical divalent avec 1 à 12 atomes de carbone; et

X dénote un radical organique non-saturé polymérisable.

6. Un article selon la revendication 5, dans lequel ledit composé anthraquinone est tel qu'il a été défini dans quiconque des revendications 1-4.

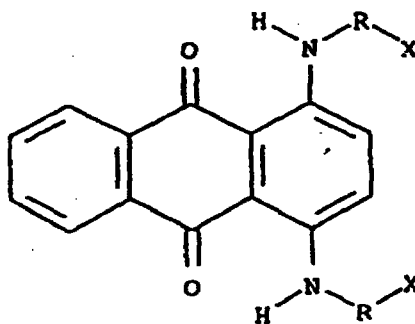
7. Un article selon la revendication 5 ou la revendication 6, dans lequel le mélange de prépolymères comprend un monomère hydrophile et le polymère résultant est un hydrogel.



8. Un article selon la revendication 7, dans lequel le mélange de précopolymères contient 2-hydroxyéthyl-metacrylate.
9. Un article selon la revendication 7, dans lequel le mélange de précopolymères contient N-vynile pyrrolidone.
10. Un article selon quiconque des revendications 7 à 9, qui est une lentille de contact molle.

Revendications pour l'Etat contractant suivant : ES

1. Un procédé pour préparer un article polymérique teint, qui comprend polymériser un ou plusieurs comonomères et un composé anthraquinone ayant la formule générale:

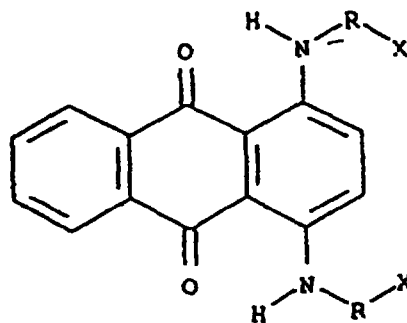


dans laquelle:

R dénote un radical divalent avec 1 à 12 atomes de carbone; et

X dénote un radical organique non-saturé polymérisable.

2. Un procédé selon la revendication 1, dans lequel R dénote un radical phénylènealkylène avec jusqu'à 12 atomes de carbone.
3. Un procédé selon la revendication 1 ou la revendication 2, dans lequel X est $-Y-CO-C(Z)=CH_2$, dans lequel Y est $-O-$ ou $-NH-$ et Z est hydrogen ou méthyl.
4. Un procédé selon la revendication 3, dans lequel Y est $-O-$.
5. Un procédé selon quiconque des revendications précédentes, dans lequel le composé anthraquinone est 1,4-bis(4(2-méthacryloxyéthyl)phénylamine)anthraquinone.
6. Un procédé selon quiconque des revendications précédentes, dans lequel le mélange de précopolymères comprend un monomère hydrophile, et le polymère résultant est un hydrogel.
7. Un procédé selon la revendication 8, dans lequel le mélange de précopolymères contient 2-hydroxyéthyl-metacrylate.
8. Un procédé selon la revendication 6, dans lequel le mélange de précopolymères contient N-vynile pyrrolidone.
9. Un procédé selon quiconque des revendications précédentes, dans lequel une lentille de contact molle est formée.
10. Un article formé par polymérisation d'un mélange de précopolymères qui comprend un ou plusieurs comonomères et un composé anthraquinone ayant la formule générale:



dans laquelle:

R dénote un radical divalent avec 1 à 12 atomes de carbone; et
X dénote un radical organique non-saturé polymérisable.

11. Un article selon la revendication 10, dans lequel ledit composé anthraquinone est tel que défini dans quiconque des revendications 2-5.