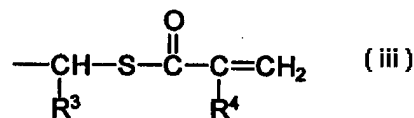
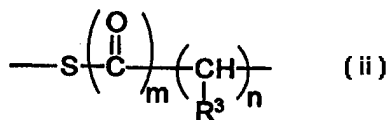
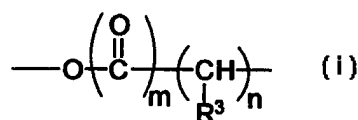
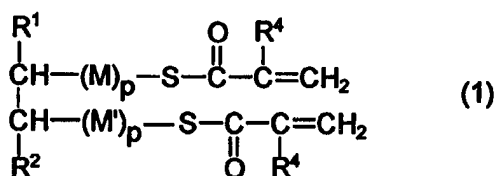




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(21) International Application Number: PCT/AU97/00816 (22) International Filing Date: 3 December 1997 (03.12.97) (30) Priority Data: PO 3958 3 December 1996 (03.12.96) AU (71) Applicant (for all designated States except US): SOLA INTERNATIONAL HOLDINGS LTD. [AU/AU]; Sherriffs Road, Lonsdale, S.A. 5160 (AU). (72) Inventors; and (75) Inventors/Applicants (for US only): TOH, Huan, Kiak [MY/AU]; 24 Medway Street, Fullarton, S.A. 5063 (AU). CHEN, Fang [AU/AU]; 20 Nalimba Street, Hallett Cove, S.A. 5158 (AU). KOK, Chong, Meng [AU/AU]; 17 Georgiana Street, Flagstaff Hill, S.A. 5159 (AU). (74) Agent: PHILLIPS ORMONDE & FITZPATRICK; 367 Collins Street, Melbourne, VIC 3000 (AU).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>

(54) Title: ACRYLIC THIO MONOMERS



(57) Abstract

A cross-linkable polymeric casting composition including an effective amount of an acrylic or methacrylic di- or polythiol monomer of the formula (1) wherein p is an integer of 0 or 1, M and M' are each spacer groups selected from one or more of the following formulae (i), (ii) wherein m is an integer of 0 or 1 and n is an integer of 0 to 3, R¹, R², R³ and R⁴, which may be the same or different, are selected from hydrogen, alkyl or substituted alkyl of 1 to 10 carbon atoms, alkoxy or substituted alkoxy of 1 to 10 carbon atoms, or R¹ or R² is (iii) and optionally a polymerisable comonomer.

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ACRYLIC THIO MONOMERS

The present invention relates to the manufacture of plastic optical articles such as video discs and ophthalmic lenses.

The most widely used plastic ophthalmic lens material is polymerised diethylene glycol bis (allyl carbonate). This polymer has proved a satisfactory material for the manufacture of ophthalmic lenses because of a combination of features, including excellent transmission, resistance to discolouration, high strength and high impact resistance. The material has a reasonable abrasion resistance and can be coated to improve that resistance.

In Australian Patent Application 81216/87, the entire disclosure of which is incorporated herein by reference, applicant describes a cross-linkable casting composition including at least polyoxyalkylene glycol diacrylate or dimethacrylate and at least one poly functional unsaturated cross-linking agent. Whilst the lenses produced from the prior art compositions provide advances in the art, difficulties may be encountered in certain applications. For example, difficulties may be encountered in some patients in fitting lenses made from such compositions. Eye discomfort, including eye fatigue problems, may be encountered. Moreover, such lenses have been found to be cosmetically unattractive.

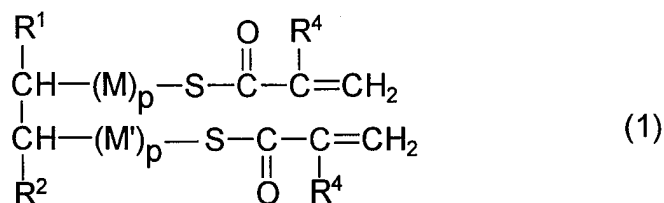
Further, in Australian Patent Application 75160/91, the entire disclosure of which is incorporated herein by reference, applicant describes a polyoxyalkylene glycol diacrylate or dimethacrylate; a monomer including a recurring unit derived from at least one radical-polymerisable bisphenol monomer capable of forming a homopolymer having a high refractive index of more than 1.55; and a urethane monomer having 2 to 6 terminal groups selected from a group comprising acrylic and methacrylic groups.

However, there remains a need in the prior art for optical articles of high refractive indices, high rigidity, very low densities and excellent colour, that still retain excellent mechanical properties.

Accordingly, it is an object of the present invention to overcome, or at least alleviate, one or more of the difficulties related to the prior art.

Accordingly, the present invention provides a cross-linkable polymeric casting composition including an effective amount of

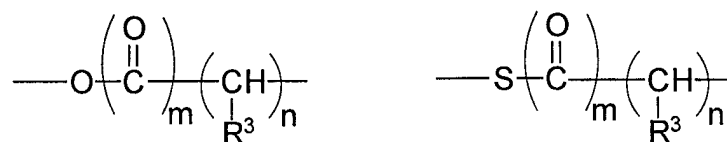
an acrylic or methacrylic di- or polythiol monomer of the formula



wherein

p is an integer of 0 or 1

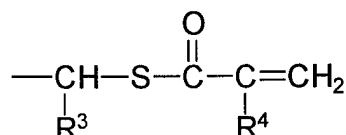
5 M and M' are each spacer groups selected from one or more of the following



wherein

m is an integer of 0 or 1 and n is an integer of 0 to 3,

10 R¹, R², R³ and R⁴, which may be the same or different, are selected from hydrogen, alkyl or substituted alkyl of 1 to 10 carbon atoms, alkoxy or substituted alkoxy of 1 to 10 carbon atoms, or R¹ or R² is



; and optionally

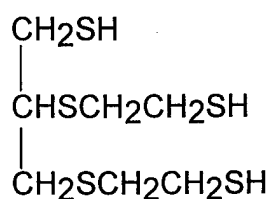
15 a polymerisable comonomer.

The casting composition may be heat and/or UV-curable, preferably UV curable.

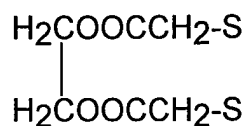
A tri- or tetra- acrylic or methacrylic polythiol monomer is preferred.

20 The acrylic di- or poly-thiol monomer may be derived from a thiol selected from one or more of the following:

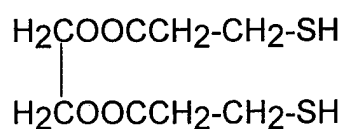
- (a) 4-mercaptomethyl-3,6-dithia-1,8-octanedithiol [MDO]



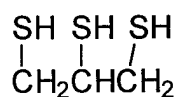
- (b) Glycol Dimercaptoacetate



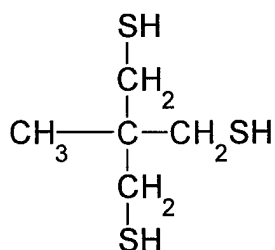
- 5 (c) Glycol Dimercaptopropionate Ethylene bis(3-Mercaptopropionate)



- (d) 1,2,3-trimercaptopropane

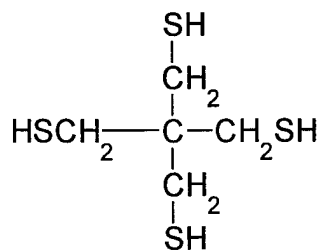


- (e) 2-mercaptomethyl-2-methyl-1,3-propanedithiol

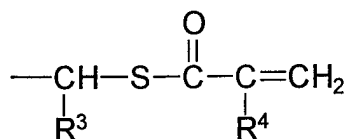


10

- (f) 2,2-bis(mercaptomethyl)-1,3-propanedithiol

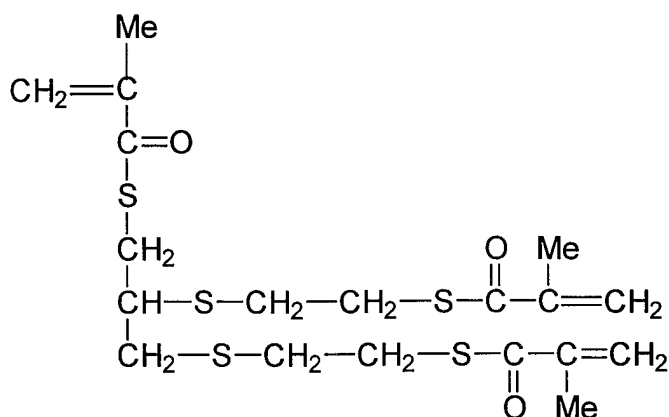


Preferably R³ and R⁴ are each hydrogen or methyl and one of R¹ and R² is



An illustrative example of an acrylic polythiol monomer is the

5 trithiomethacrylate



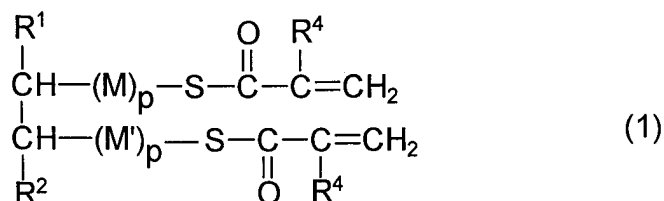
The optical article formed from the casting composition of the present invention may exhibit a refractive index in the high to very high -index range, low density and high rigidity.

By the term "high refractive index", as used herein, we mean a polymer having a refractive index of at least approximately 1.55, preferably 1.57. By the term "very high refractive index" as used herein, we mean a polymer having a refractive index of approximately 1.59 or above, preferably 1.60 or above.

By the term "low density", as used herein, we mean a density in the range
15 of approximately 1.15 to 1.25 g cm⁻³.

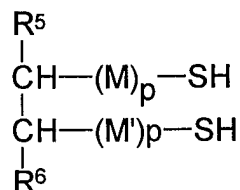
By the term "high rigidity" as used herein, we mean a polymer having a glass transition temperature (T_g) of at least approximately 65°C, preferably approximately 70°C, more preferably approximately 75°C or above.

In a further aspect of the present invention, there is provided a method for
20 preparing an acrylic or methacrylic di- or polythiol monomer of the formula



which method includes

providing a di- or polythiol of the formula



5 wherein

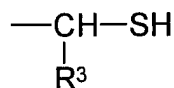
M and M' are each spacer groups as defined above,

p is an integer of 0 or 1,

R⁵ and R⁶, which may be the same or different, are selected from hydrogen, alkyl or substituted alkyl of 1 to 10 carbon atoms, alkoxy or substituted

10 alkoxy of 1 to 10 carbon atoms,

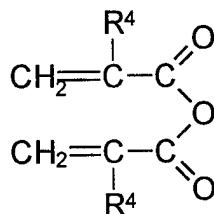
or R⁵ or R⁶ is



wherein R³ is as defined above; and

reacting the di- or polythiol with an acrylic or methacrylic anhydride of the

15 formula



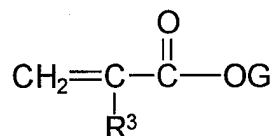
wherein R⁴ is selected from hydrogen, alkyl or substituted alkyl of 1 to 10 carbon atoms, alkoxy or substituted alkoxy of 1 to 10 carbon atoms.

Where the acrylic thio monomer is a tri thio acrylate, the method

20 according to the present invention may further include

further reacting the di- or polythiol with an acrylic or methacrylic salt of the

formula



wherein G is an alkali metal selected from sodium (Na) or potassium (K).

5 The further reaction steps may be undertaken simultaneously with, or subsequent to, the first reaction step.

It has been found that the method according to this aspect of the present invention may produce the acrylic thio monomers in high yield.

As stated above, the cross-linkable polymeric casting composition may optionally further include a polymerisable comonomer.

10 The polymerisable comonomer may be selected to improve the properties and/or processability of the cross-linkable polymeric casting composition. The polymerisable comonomer may be selected to improve tint rate, hardness, abrasion resistance and the like of the resulting polymer. The polymerisable comonomer may be an unsaturated, thiol or epoxy comonomer. The
15 polymerisable comonomer may be selected from any suitable type, e.g. methacrylates, acrylates, vinyls, vinyl ethers, allyls, epoxides, thiols and the like.

The polymerisable comonomer may preferably be selected from one or more of epoxidised monomer or oligomer, di- or polythiol, di- or poly vinyls, allylics, polyoxyalkylene glycol di-, tri-, tetra- and higher acrylates or
20 methacrylates, polymerisable bisphenol monomers, urethane monomers having 2 to 6 terminal acrylic or methacrylic groups, fluorene acrylates or methacrylates, and thioacrylate or thiomethacrylate monomers.

The polymerisable comonomer, when present, may be present in amounts of from approximately 30 to 90% by weight, preferably approximately 35
25 to 80% by weight, most preferably approximately 40% to 70% by weight, based on the total weight of the casting composition.

Where an epoxidised monomer or oligomer is included, the epoxidised monomer may function to improve curing and casting characteristics. The epoxidised monomer or oligomer may fall into one or more of the following
30 classes: internal, terminal, mono-functional, di-functional, tri-functional, tetra-

functional, aliphatic, aromatic, cyclic, structurally simple, structurally complex, esters, ethers, amines. An epoxidised soybean material may be used. The epoxidised monomer or oligomer may be selected from one or more of the following

- 5 • Epoxidised soybean oil - Triglycerides of a mixture of epoxidised a) oleic acid, b) linoleic acid, c) linolenic acid
- Propylene Oxide
- Hexanediol diglycidyl ether (HDGE)
- 1,2 epoxy butane
- 10 • Bisphenol fluorene diglycidyl ether (BPGE)
- Epolight 100MF
- AK-601
- MY 721

15 The epoxidised monomer may be present in amounts of from approximately 0.001% to 10% by weight, preferably 0.01% to 5%, more preferably approximately 0.01% to 2%, based on the total weight of the casting composition.

20 Where a di- or polythiol comonomer is included, the di- or polythiol monomer may be of any suitable type. A di-, tri- or tetra polythiol compound may be used. A tri- or tetra-polythiol comonomer is preferred. The thiol comonomer may be selected from one or more of the following:

- 4-mercaptomethyl-3,6-dithia-1,8-octanedithiol [MDO]
- Trimethylolpropane Tris (3-mercaptopropionate) [TTMP]
- Pentaerythritol Tetrakis (3-mercaptopropionate) [PTMA]
- 25 • Trimethylolpropane Tris (3-mercaptopropionate) [TTMA]
- 4-t-butyl-1,2-benzenedithiol
- Bis(2-mercaptoethyl)sulfide
- 4,4'-thiodibenzenedithiol
- benzenedithiol
- 30 • Glycol Dimercaptoacetate
- Glycol Dimercaptopropionate Ethylene bis(3-Mercaptopropionate)

- Polyethylene Glycol Dimercaptoacetates
- Polyethylene Glycol Di(3-Mercaptopropionate)
- Pentaerythritol Tetrakis (3-mercapto-propionate) [PTMP]
- Mercapto-methyl tetrahydrothiophene [MMTHT]
- 5 • Tris-(3-mercaptopropyl)isocyanurate [TMPIC]
- 2-mercaptoethyl sulphide
- 1,2,3-trimercaptopropane
- 2,2-bis(mercaptomethyl)-1,3-propanedithiol
- Dipentaerythrithiol
- 10 • 1,2,4-trimercaptomethyl benzene
- 2,5-dimercaptomethyl-1,4-dithiane
- BPHE-SH
- 4,8-bis(mercaptomethyl)-3,6,9-trithia-1,11-undecanedithiol
- 2-mercaptomethyl-2-methyl-1,3-propanedithiol
- 15 • DMDO: 1,8-dimercapto-3,6-dioxaoctane

The polythiol comonomer is preferably pentaerythritol tetrakis (3-mercapto propionate) (PTMP) or trimethylolpropane tris (3-mercapto propionate) (TTMP).

The thiol comonomer may preferably be present in amounts of from approximately 5 to 30% by weight, more preferably approximately 10 to 30% by weight, based on the total weight of the casting composition

Where a vinyl comonomer is included, the vinyl comonomer may be selected from styrene, divinyl benzene, divinyl naphthene, substituted styrenes, 3,9-divinyl-2,4,8,10-tetraoxaspiro[5.5]undecane (DTU), a divinyl ester monomer of a bi- or polycyclic compound and mixtures and derivatives thereof.

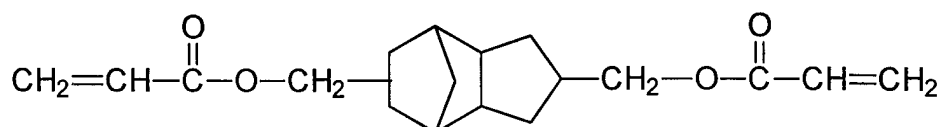
The vinyl comonomer may preferably be present in amounts sufficient to provide rigidity and high index in optical articles formed from the casting composition, but not so much as to cause brittleness or low tintability. Amounts of from approximately 5 to 50% by weight, preferably approximately 15 to 40% by weight, more preferably about 20 to 30% by weight based on the total weight of the casting composition are preferred.

Where an acrylic or methacrylic monomer is included, the acrylic or methacrylic monomer may be selected from acrylates or methacrylate derivatives

of a cycloolefin. An acrylate or methacrylate derivative of tricyclodecane is preferred.

A tricyclodecane dimethanol diacrylate or methacrylate is preferred.

5 A tricyclodecane dimethanol diacrylate or diacryloyl oxymethyl tricyclodecane of the following formula is preferred.



(DCPA)

The acrylic or methacrylic monomer may alternatively or in addition be selected from highly rigid, high Abbe No. polyfunctional acrylates or methacrylates. Pentaerythritol tetracrylate (PTA) is a preferred example.

10 The acrylic or methacrylic monomer may be present in amounts sufficient to provide high Abbe number and high rigidity, but not so much as to cause brittleness or low tintability. Amounts of from approximately 5 to 25% by weight, preferably approximately 10 to 20% by weight, more preferably approximately 15 to 20% by weight, based on the total weight of the casting composition have been
15 found to be suitable.

The urethane monomer, when present, may be a tetracyclic or higher urethane monomer.

Suitable materials falling within this definition include materials supplied under the trade names U-4H, U-4HA and U-6HA by Shin Nakamura, NF-201 and
20 NF-202 by Mitsubishi Rayon. U-4HA is preferred. These monomers may be included to improve physical toughness without causing the lens material to become too brittle. Impact resistance is improved without adversely affecting abrasion resistance.

The urethane monomer may be present in any suitable amount to provide
25 a desired level of hardness. The urethane monomer may be present in amounts of from approximately 2.5 to approximately 25% by weight, preferably approximately 5 to 10% by weight based on the total weight of the casting composition.

Where a thiodiacrylate or dimethacrylate is included, the thiodiacrylate or
30 dimethacrylates may be selected from bis(4-methacryloylthioethyl)sulfide.

(BMTES) and bis(4-methacryloylthiophenyl)sulfide (BMTS). The thioacrylate or methacrylate may be present in amounts of from 0 to approximately 20% by weight, preferably approximately 5 to 15% by weight, based on the total weight of the casting composition.

- 5 Where a fluorene diacrylate or dimethacrylate is included, the fluorene diacrylate or dimethacrylate monomer may be selected from a bisphenol fluorene dihydroxy acrylate (BFHA) or a bisphenol fluorene dimethacrylate (BFMA) or mixtures thereof.

10 The fluorene diacrylate or dimethacrylate monomer may be present in amounts of from 0 to approximately 20% by weight, preferably approximately 1 to 10% by weight.

15 The polyoxy alkylene glycol diacrylate or dimethacrylate compound according to the present invention, when present, may include ethylene oxide or propylene oxide repeating units in its backbone. A polyethylene glycol dimethacrylate is preferred. Suitable materials include dimethylacrylates where the number of repeating ethylene oxide groups is between 4 and 14. Suitable materials include those sold under the trade names NK Ester 4G, 6G, 9G or 16G. A 9G monomer is preferred.

20 The polyoxy alkylene glycol diacrylate or dimethacrylate component may be present in amounts of from 0 to approximately 20% by weight, preferably approximately 5% to 15% by weight, based on the total weight of the casting composition.

25 The high index bisphenol monomer component in the cross-linkable casting composition when present may be selected from: dimethacrylate and diacrylate esters of bisphenol A; dimethacrylate and diacrylate esters of 4,4'-bishydroxy-ethoxy-bisphenol A and the like.

30 Preferred high index bisphenol compounds include bisphenol A ethoxylated dimethacrylate and tetra brominated bisphenol A ethoxylated dimethacrylates. A bisphenol A ethoxylate dimethacrylate sold under the trade designations ATM 20 by Ancomer or NS110 by Akzo have been found to be suitable.

 The high index bisphenol monomer may be present in amounts of from 0 to approximately 45% by weight, preferably 5 to 40% by weight based on the total

weight of the casting composition.

The cross-linkable casting composition according to the present invention may include a polymerisation curing agent.

5 The polymerisation curing agent may be a radical heat cationic or radical initiator. A radical heat initiator is preferred. The compositions may be cured by a combination of UV radiation and heat.

The amount of curing agent may vary with the monomers selected. It has been possible to operate with a relatively low level of curing agent of between approximately 0.05 and 1.5%, preferably 0.4% to 1.0% by weight.

10 The following curing agents have been found to be suitable.

- AIBN (Azo radical heat initiator)
Azodiisobutyronitrile
- Trigonox TX-29 (Dialkyl Peroxide radical heat initiator)
1,1-di(-butyl peroxy-3,3,5-trimethyl cyclohexane)
- 15 • TBPEH (Alkyl Perester radical heat initiator)
t-butyl per-2-ethylhexanoate
- (Diacyl Peroxide radical heat initiator)
Benzoyl Peroxide
- (Peroxy Dicarbonate radical heat initiator)
20 Ethyl Hexyl Percarbonate
- (Ketone Peroxide radical heat initiator)
Methyl ethyl ketone peroxide
- Cyracure UV1-6974 (cationic photoinitiator)
Triaryl sulfonium hexafluoroantimonate
- 25 • Lucirin TPO (radical photoinitiator)
2,4,6-Trimethylbenzoyldiphenylphosphine oxide
- Vicure 55 (radical photoinitiator)
methyl phenylglyoxylate
- Bis(t-butyl peroxide) diisopropylbenzene
- 30 • t-butyl perbenzoate
- t-butyl peroxy neodecanoate
- Amicure DBU

- Amicure BDMA
- DABCO
- Amicure DBU and/or Amicure BDMA are preferred.

Initiator may be a single component or combination of initiator
5 components.

Other additives may be present which are conventionally used in casting compositions such as inhibitors, dyes, UV stabilisers and materials capable of modifying refractive index. Mould release agents may be added. Such additives may include:

10 UV Absorbers including

- Ciba Geigy Tinuvin P - 2(2'-hydroxy-5'-methyl phenyl) benzotriazole
- Cyanamid Cyasorb UV 531 -2-hydroxy-4-n-octoxybenzophenone
- Cyanamid Cyasorb UV5411-2(2-hydroxy-5-t-octylphenyl)- benzotriazole
- Cyanamid UV 2098 - 2 hydroxy-4-(2-acryloyloxyethoxy) benzophenone
- 15 • National Starch and Chemicals Permasorb MA - 2 hydroxy-4-(2 hydroxy-3- methacryloxy)propoxy benzophenone
- Cyanamid UV24 - 2,2'-dihydroxy-4-methoxybenzophenone
- BASF UVINUL 400 - 2,4 dihydroxy-benzophenone
- BASF UVINUL D-49 - 2,2'-dihydroxy-4,4' dimethoxy- benzophenone
- 20 • BASF UVINUL D-50 - 2,2', 4,4' tetrahydroxy benzophenone
- BASF UVINUL D-35-ethyl-2-cyano-3,3-diphenyl acrylate
- BASF UVINUL N-539-2-ethylhexyl-2-cyano-3,3-diphenyl acrylate
- Ciba Geigy Tinuvin 213

Hindered amine light stabilisers (HALS), including

- 25 • Ciba Geigy Tinuvin 765/292 - bis (1,2,2,6,6-pentamethyl-4-piperidyl)
- sebacate
- Ciba Geigy 770 - bis (2,2,6,6-tetramethyl-4- piperidiny)l sebacate

Antioxidants including

- 30 • Ciba Geigy Irganox 245 - triethylene glycol-bis-3- (3-tertbutyl-4-hydroxy-5-methyl phenyl)propionate
- Irganox 1010 -2,2-bis[[3-[3,4-bis(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropoxy]methyl]-1,3-propanediyl 3,5-bis(1,1-dimethyl ethyl)-4-hydroxy

benzene propanoate Irganox 1076 - octadecyl 3-(3',5'-di-tert-butyl(-4'-hydroxyphenyl) propionate

Anticolouring agents including

- 9, 10 dihydro-9-oxa-10-phosphaphenanthrene-1-oxide

5 Cure modifiers including

- Dodecyl mercaptan
- Butyl mercaptan
- Thiophenol
- Nitroso compounds such as Q1301 from Wako
- 10 • Nofmer from Nippon Oils and Fats

Other monomeric additives can be present in amounts up to 10% by weight as viscosity modifiers, and include monomers such as methacrylic acid, vinyl silanes, and other functional monomers. Other monomeric additives may be included to improve processing and/or material properties, these include:

- 15 • methacrylic acid, maleic anhydride, acrylic acid
- adhesion promoters/modifiers such as Sartomer 9008, Sartomer 9013, Sartomer 9015 etc.
- dye-enhancing, pH-adjusting monomers like Alcolac SIPOMER 2MIM
- a charge-reducing cationic monomer to render the material more
- 20 antistatic, example Sipomer Q5-80 or Q9-75
- mould release agents such as Phosphoric acid esters, e.g. octyl acid phosphate, etc, Alkyl quaternary ammonium salts, e.g. cetyl trimethyl ammonium bromine, etc., Zonyl Series, e.g. Zonyl FSO 100, Zonyl FSN 100, etc., Zelec Series, e.g. Zelec DP, Zelec UN, etc., and Unidain DS
- 25 Series, e.g. DS 401, DS 202, etc.

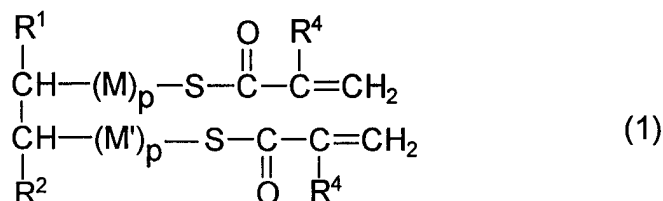
The crosslinkable polymeric casting composition according to the present invention may be utilised in the preparation of an optical article. The optical article may be characterised by having an increased very high refractive index relative to known prior art articles. The optical article may exhibit excellent colour

30 and low density.

In a preferred aspect of the present invention there is provided a method for preparing a polymeric article which method includes

providing

a cross-linkable polymeric casting composition including an effective amount of an acrylic or methacrylic di- or polythiol monomer of the formula



wherein

p is an integer of 0 or 1

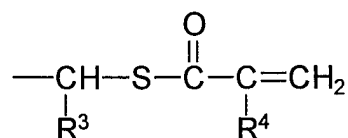
M and M' are each spacer groups selected from one or more of the following



wherein

m is an integer of 0 or 1 and n is an integer of 0 to 3,

R¹, R², R³ and R⁴, which may be the same or different, are selected from hydrogen, alkyl or substituted alkyl of 1 to 10 carbon atoms, alkoxy or substituted alkoxy of 1 to 10 carbon atoms, or R¹ or R² is



a heat and/or UV curing agent;

and optionally; a polymerisable comonomer.

mixing the polymeric casting composition and curing agent; and

subjecting the mixture to a cross-linking step.

The casting composition may be formed into a suitable article by mixing in a convenient vessel the components making up the material, and then adding the curing catalyst. The mixed material may then be degassed or filtered. As the curing time is substantially reduced, the casting process may be undertaken on a continuous or semi-continuous basis.

In a further aspect of the present invention there is provided a polymeric article prepared by the method as described above.

The polymeric article may be an optical article. The optical article may provide characteristics equal to or greater than those achievable with articles made from diethylene glycol bis(allyl carbonate) but with a considerably reduced cure time and substantially increased throughput.

The optical article may be an optical lens. The optical lens may be further characterised by having reduced weight and/or thickness relative to the prior art, excellent optical properties provided by the high rigidity, very low Yellowness Index and low density, whilst retaining good abrasion resistance and impact resistance.

The overall refractive index may be in the high to very high refractive index range of approximately 1.58 to 1.70, preferably 1.59 to 1.65.

The optical articles prepared by the method of this invention include camera lenses, ophthalmic lenses and video discs.

The chemicals 1,2-bis(2-mercaptoethyl thio)-3-mercaptopropane or 4-mercaptopomethyl-3,6-dithia-1,8-octanedithiol are abbreviated to MDO.

The present invention will now be more fully described with reference to the accompanying examples. It should be understood, however, that the description following is illustrative only and should not be taken in any way as a restriction on the generality of the invention described above.

Figure 1

Infrared spectrum of monomer MDO trithiomethacrylate in Example 1.

Figure 2

Infrared spectrum of homopolymer for MDO trithiomethacrylate in Example 2.

Figure 3

The water uptake comparison of Example 2 material with that of commercial UV curable middle index material.

Figure 4

Infrared spectrum of copolymer for MDO trithiomethacrylate and DCPA in Example 3.

Figure 5

The water uptake comparison of Example 3 material with that of commercial UV curable middle index material.

EXAMPLE 1**5 Preparation of MDO Trithiomethacrylate**

20.8 g (0.08 ml) MDO dissolved into 100 ml 10% (w/w) NaOH aqueous solution was added into 400 ml methyl tert-butyl ether (MTBE) solution of 40.66 g (0.264 mol, 10% excess) methacrylic anhydride and 0.8 g 2,6-di-ter-butyl-methyl phenol (BHT) at 0°C. After adding the solution was stirred at 0°C for further three
10 hours. The organic layer was separated and washed successively with 200 ml 0.1% NaOH aqueous solution three times and NaCl saturated aqueous solution two times. Dried over anhydrous MgSO₄, the solvent was removed, the remaining methacrylic anhydride in the product was removed by distillation or washing with methanol. After drying under vacuum, 30 g (80% yield) of
15 colourless, clear viscous liquid was obtained. The infrared spectrum of this product is shown in Figure 1.

EXAMPLE 2

The monomer synthesised in Example 1 was mixed with 0.8% (w/w) photoinitiator Vicure 55, then was used to fill the space between a pair of glass
20 moulds separated by a plastic gasket at their periphery and held together by a clip. The mould was then passed two times (speed 55) under a UV lamp, kept at 100°C for 45 minutes, passed another two times (speed 33) under UV lamp, then kept at 100°C for one hour. Total curing time was about two hours. A clear, colourless and hard plastic was obtained. The infrared spectrum of this material
25 is shown in Figure 2. The properties of this homopolymer are summarised in Table 1. The water uptake is lower than that of commercial UV curable middle index material (Figure 3)

TABLE 1**The properties of the material in Example 2**

MDOMA	Refractive Index	Abbe Number	Tg	Hardness (Bar-col)	Density
100%	1.635	37	68	30	1.31

EXAMPLE 3

The monomer synthesised in Example 1 was mixed with 25% DCPA and 0.8% (w/w) photoinitiator Vicure 55, then was used to fill the space between a pair of glass moulds separated by a plastic gasket at their periphery and held together by a clip. The mould was then passed two times (speed 55) under a UV lamp, kept at 100°C for 45 minutes, passed another two times (speed 33) under UV lamp, then kept at 100°C for one hour. Total curing time was about two hours. A clear, colourless and hard plastic was obtained. The infrared spectrum of this material is shown in Figure 4. The properties of this homopolymer are summarised in Table 2. The water uptake is lower than that of commercial UV curable middle index material (Figure 5).

TABLE 2**The properties of the material in Example 3**

MDOMA	DCPA	Refractive Index	Abbe Number	Tg	Hardness (Bar-col)	Density
75%	25%	1.609	41	92	39	1.29

EXAMPLE 4

The monomer synthesised in Example 1 was mixed with 1% (w/w) heat curing initiator TBPO, then was used to fill the space between a pair of glass moulds separated by a plastic gasket at their periphery and held together by a clip. The mould was then kept in an oven, the temperature of oven changed as following sequence, 35°C in 5 hour, 35 to 60°C in 9 hours, 60 to 85°C in 3 hours, 85 to 110°C in 2 hours, 110°C for 2 hours, 110 to 80°C in 5 minutes, 80°C for 2 hours.

Total curing time was about 23 hours. A clear, colourless and hard plastic was obtained. The properties of this homopolymer are summarised in Table 3.

TABLE 3**The properties of the material in Example 4**

MDOMA	Refractive Index	Abbe Number	Tg	Hardness (Bar-col)	Density
100%	1.635	37	68	30	1.31

EXAMPLE 5

- 5 The monomer synthesised in Example 1 was mixed with 25 % (w/w) DCPA and 1% (w/w) heat initiator TBPO, then was used to fill the space between a pair of glass moulds separated by a plastic gasket at their periphery and held together by a clip. The mould was then kept in an oven, the temperature of oven changed as following sequence, 35°C in 5 hour, 35 to 60°C in 9 hours, 60 to 85°C in 3 hours, 85 to 110°C in 2 hours, 110°C for 2 hours, 110 to 80°C in 5 minutes, 80°C for 2 hours.
- 10

Total curing time was about 23 hours. A clear, colourless and hard plastic was obtained. The properties of this homopolymer are summarised in Table 4.

15

TABLE 4**The properties of the material in Example 5**

MDOMA	DCPA	Refractive Index	Abbe Number	Tg	Hardness (Bar-col)	Density
75%	25%	1.609	41	92	39	1.29

EXAMPLE 6

- 20 The monomer MDOMA synthesised in Example 1 was formulated with different comonomers and UV cured using the method described in Example 2. The detailed formulations and the properties of the lenses were listed in Table 5.

TABLE 5
UV curable formulations with MDOMA and the properties of the lenses

Composition and properties	Form. A	B	C	D	E	F	G	H	I	J	K	L
MDOMA	65	60	55	50	50	55	50	50	40	30	20	10
DCPA	15	15	15	15	0	0	20	15	15	15	15	15
NS110	5	10	15	20	40	25	20	20	10	40	50	60
MDO	10	10	10	10	10	10	10	10	30	10	10	10
U4HA	5	5	5	5	0	10	0	5	5	5	5	5
Vicure 55	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
%T	89.4	89.5	89.6	89.7	89.3	89.3	89.3	89.3	89.9	90.0	90.1	90.5
%Haze	1.07	0.97	0.98	0.83	0.42	0.55	0.96	1.06	0.7	0.69	0.80	0.36
YI	1.42	1.24	1.36	1.32	1.09	1.16	1.54	1.45	1.37	1.36	1.27	1.27
SG	1.30	1.29	1.29	1.28	1.24	1.29	1.27	1.28	1.27	1.26	1.23	1.22
Barcol	51	46	51	50	46	50	49	50	45	43	43	39
RI	1.607	1.603	1.600	1.598	1.607	1.606	1.601	1.599	1.590	1.587	1.578	1.572
Abbe	39	39	39	39	36	35	38	38	39	39	38	38
Tg °C	100	100	105	104	91	97	95	97	104	97	97	93

NS110 Bisphenol A Ethoxylated Dimethacrylate

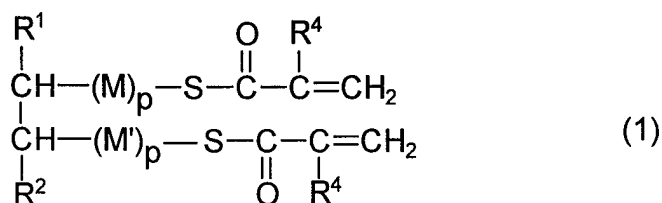
U4HA Urethane Tetracrylate

Finally, it is to be understood that various other modifications and/or alterations may be made without departing from the spirit of the present invention as outlined herein.

Claims

1. A cross-linkable polymeric casting composition including an effective amount of

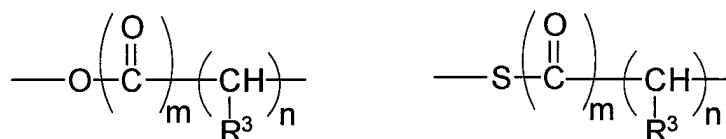
an acrylic or methacrylic di- or polythiol monomer of the formula



wherein

p is an integer of 0 or 1

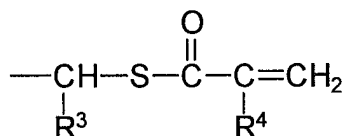
M and M' are each spacer groups selected from one or more of the following



wherein

m is an integer of 0 or 1 and n is an integer of 0 to 3,

R¹, R², R³ and R⁴, which may be the same or different, are selected from hydrogen, alkyl or substituted alkyl of 1 to 10 carbon atoms, alkoxy or substituted alkoxy of 1 to 10 carbon atoms, or R¹ or R² is



and optionally

a polymerisable comonomer.

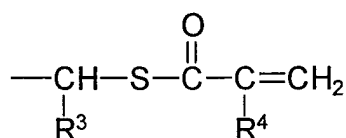
2. A cross-linkable polymeric casting composition according to Claim 1, wherein the casting composition is UV-curable.

3. A cross-linkable polymeric casting composition according to Claim 2, wherein the acrylic thiol monomer is derived from a thiol selected from one or more of the following

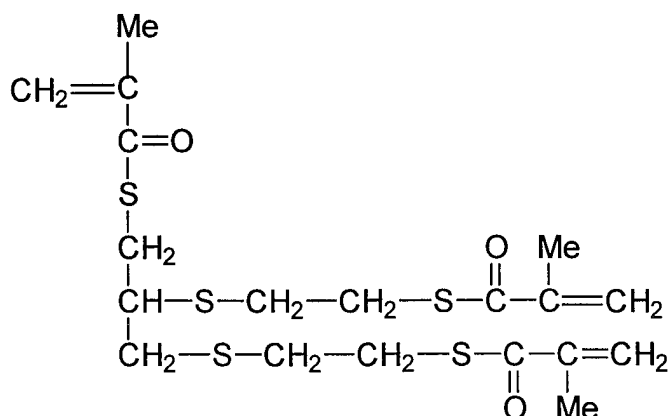
- 4-mercaptomethyl-3,6-dithia-1,8-octanedithiol [MDO]

- Glycol Dimercaptoacetate
- Glycol Dimercaptopropionate Ethylene bis(3-Mercaptopropionate)
- 1,2,3-trimercaptopropane
- 2-mercaptomethyl-2-methyl-1,3-propanedithiol
- 2,2-bis(mercaptomethyl)-1,3-propanedithiol

4. A cross-linkable polymeric casting composition according to Claim 3, wherein the acrylic polythiol monomer is an acrylic or methacrylic tri- or tetra-thiol monomer, R^3 and R^4 are each hydrogen or methyl and at least one of R^1 and R^2 is



5. A cross-linkable polymeric casting composition according to Claim 3, wherein the acrylic polythiol monomer is a trithiomethacrylate of the formula



6. A cross-linkable polymeric casting composition according to Claim 1, wherein the polymerisable comonomer is selected to improve the properties and/or processability of the cross-linkable casting composition, and is selected from one or more of the group consisting of methacrylates, acrylates, vinyls, vinyl ethers, allyls, epoxides and thiols.

7. A cross-linkable polymeric casting composition according to Claim 6, wherein the polymerisable comonomer is selected from one or more of epoxidised monomer or oligomer, di- or polythiol, di- or poly vinyls, allylics, polyoxyalkylene glycol di-, tri-, tetra- and higher acrylates or methacrylates, polymerisable bisphenol monomers, urethane monomers having 2 to 6 terminal

acrylic or methacrylic groups, fluorene acrylates or methacrylates, and thioacrylate or thiomethacrylate monomers.

8. A cross-linkable polymeric casting composition according to Claim 7, wherein the copolymerisable monomer includes approximately 5% to 60% by weight, based on the total weight of the casting composition, of an acrylic or methacrylic monomer.

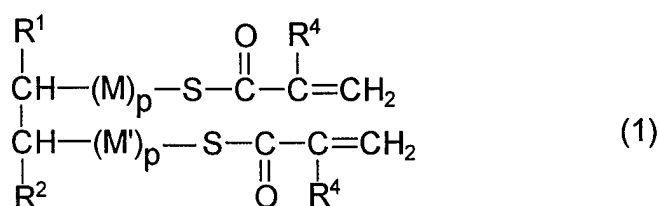
9. A cross-linkable polymeric casting composition according to Claim 8, wherein the acrylic or methacrylic monomer is an acrylate or methacrylate derivative of a cycloolefin.

10. A cross-linkable polymeric casting composition according to Claim 7, wherein the copolymerisable monomer includes approximately 5 to 30% by weight, based on the total weight of the casting composition, of a thiol monomer.

11. A cross-linkable polymeric casting composition according to Claim 7, wherein the copolymerisable monomer includes approximately 2.5% to 25% by weight, based on the total weight of the casting composition of a tetracyclic or higher urethane monomer.

12. A cross-linkable polymeric casting composition according to Claim 7, wherein the copolymerisable monomer includes approximately 5 to 60% by weight, based on the total weight of the casting composition, of a bisphenol A ethoxylated dimethacrylate.

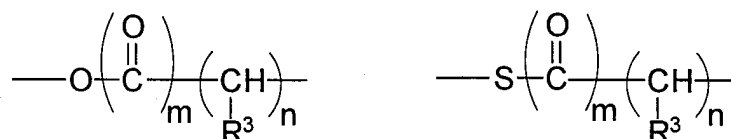
13. A method for preparing an acrylic or methacrylic di- or polythiol monomer of the formula



wherein

p is an integer of 0 or 1

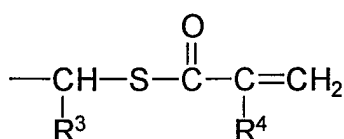
M and M' are each spacer groups selected from one or more of the following



wherein

m is an integer of 0 or 1 and n is an integer of 0 to 3,

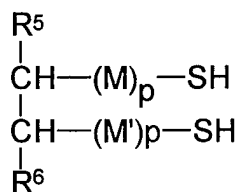
R¹, R², R³ and R⁴, which may be the same or different, are selected from hydrogen, alkyl or substituted alkyl of 1 to 10 carbon atoms, alkoxy or substituted alkoxy of 1 to 10 carbon atoms, or R¹ or R² is



and optionally

a polymerisable comonomer,

which method includes providing a di- or polythiol of the formula

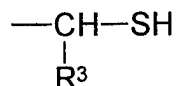


wherein

M and M' are each spacer groups as defined above,

p is an integer of 0 or 1,

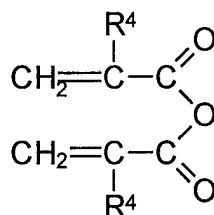
R⁵ and R⁶, which may be the same or different, are selected from hydrogen, alkyl or substituted alkyl of 1 to 10 carbon atoms, alkoxy or substituted alkoxy of 1 to 10 carbon atoms, or R⁵ or R⁶ is



wherein R³ is as defined above; and

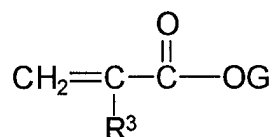
reacting the di- or polythiol with an acrylic or methacrylic anhydride of the formula

- 25 -



wherein R⁴ is selected from hydrogen, alkyl or substituted alkyl of 1 to 10 carbon atoms, alkoxy or substituted alkoxy of 1 to 10 carbon atoms.

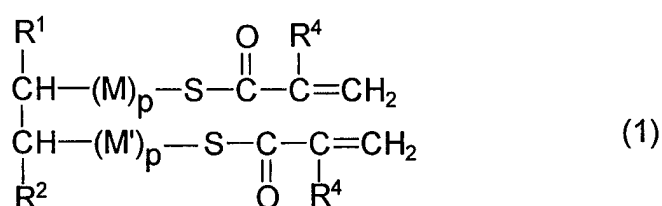
14. A method according to Claim 13, wherein the acrylic thio monomer is a tri
 5 thio acrylate, the method further including
 further reacting the di- or polythiol with an acrylic or methacrylic salt of the
 formula



wherein G is an alkali metal selected from sodium (Na) or potassium (K).

- 10 15. A method for preparing a polymeric article which method includes
 providing

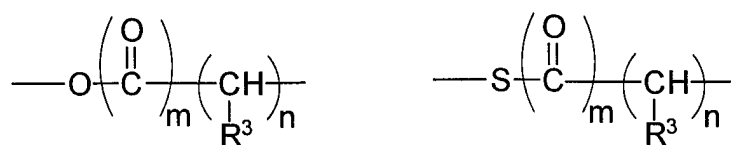
a cross-linkable polymeric casting composition including an
 effective amount of an acrylic or methacrylic di- or polythiol monomer of
 the formula



wherein

p is an integer of 0 or 1

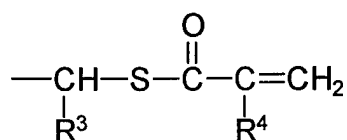
M and M' are each spacer groups selected from one or more of
 the following



wherein

m is an integer of 0 or 1 and n is an integer of 0 to 3,

R^1 , R^2 , R^3 and R^4 , which may be the same or different, are selected from hydrogen, alkyl or substituted alkyl of 1 to 10 carbon atoms, alkoxy or substituted alkoxy of 1 to 10 carbon atoms, or R^1 or R^2 is



5

a heat and/or UV curing agent;

and optionally a polymerisable comonomer.

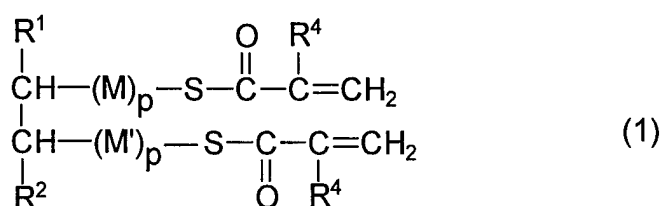
mixing the polymeric casting composition and curing agent; and

subjecting the mixture to a cross-linking step.

10 16. A polymeric article prepared by the method according to Claim 15.

17. A polymeric article formed from a cross-linkable polymeric casting composition including an effective amount of

an acrylic or methacrylic di- or polythiol monomer of the formula

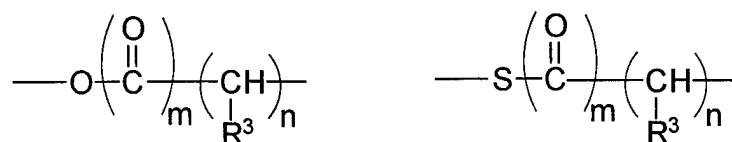


15

wherein

p is an integer of 0 or 1

M and M' are each spacer groups selected from one or more of the following



20

wherein

m is an integer of 0 or 1 and n is an integer of 0 to 3,

and optionally

a polymerisable comonomer,

wherein the polymeric article is an ophthalmic lens element having an overall

25 refractive index in the range of approximately 1.58 to 1.70.

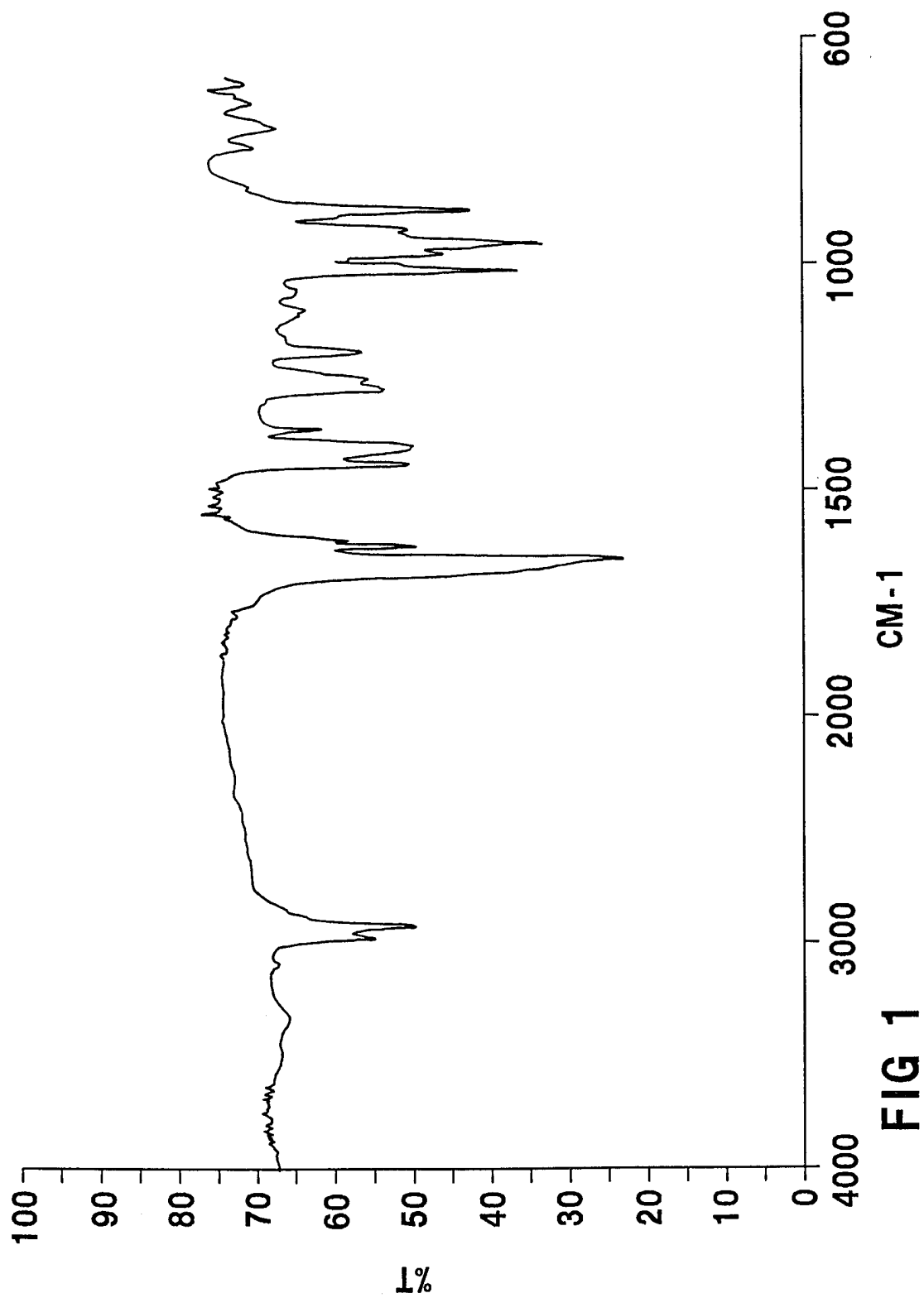
18. An ophthalmic lens element according to Claim 17 wherein the polymerisable comonomer includes an effective amount of an acrylate or methacrylate derivative of a cycloolefin.

5 19. An ophthalmic lens element according to Claim 18 wherein the cycloolefin derivative is present in amounts of from approximately 5 to 60% by weight, based on the total weight of the casting composition.

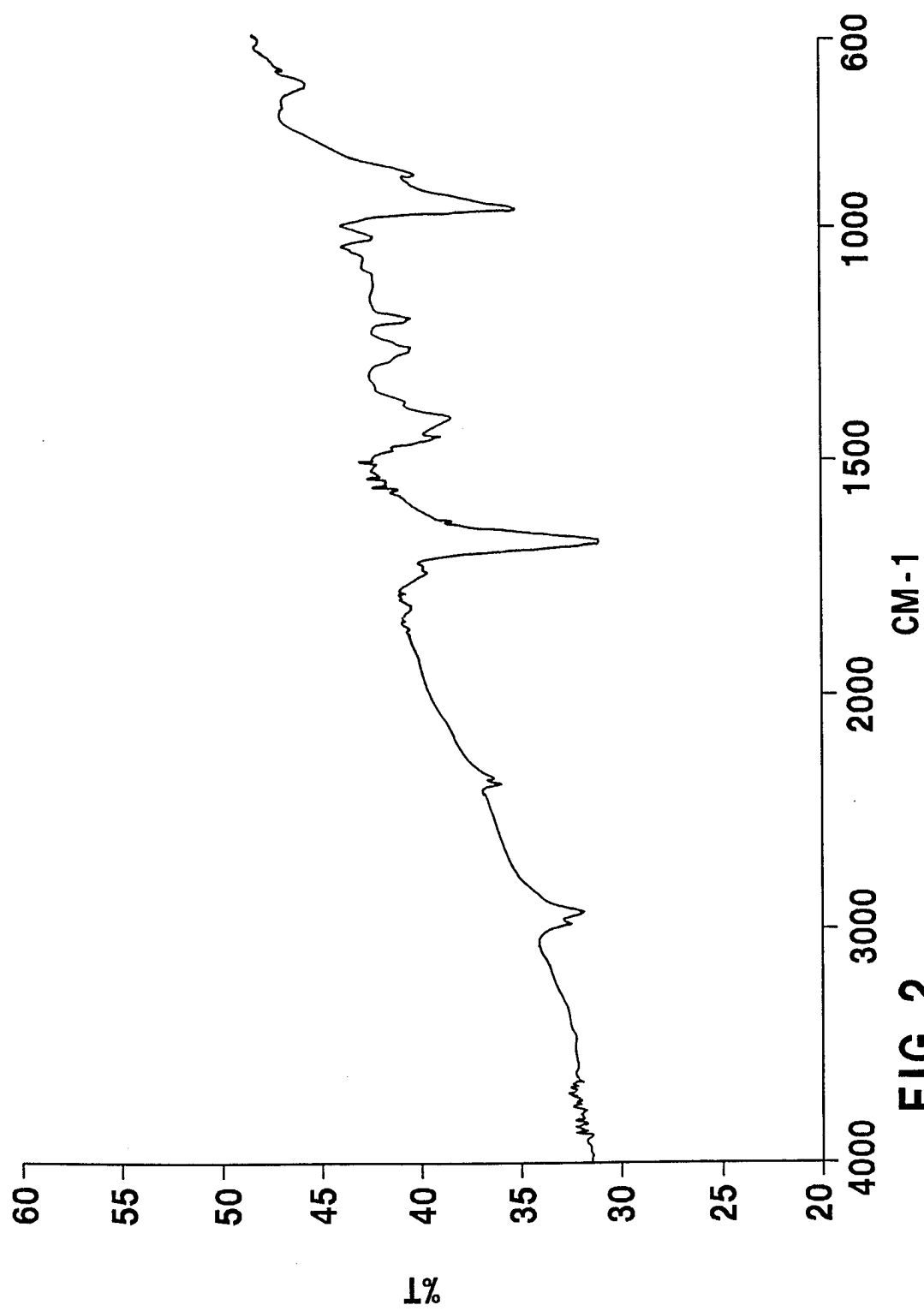
20. An ophthalmic lens element according to Claim 18, wherein the polymerisable comonomer further includes an effective amount of a thiol monomer.

10 21. An ophthalmic lens element according to Claim 20 wherein the thiol monomer is present in amounts of from approximately 5 to 30% by weight, based on the total weight of the casting composition.

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**FIG 1**

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3/5

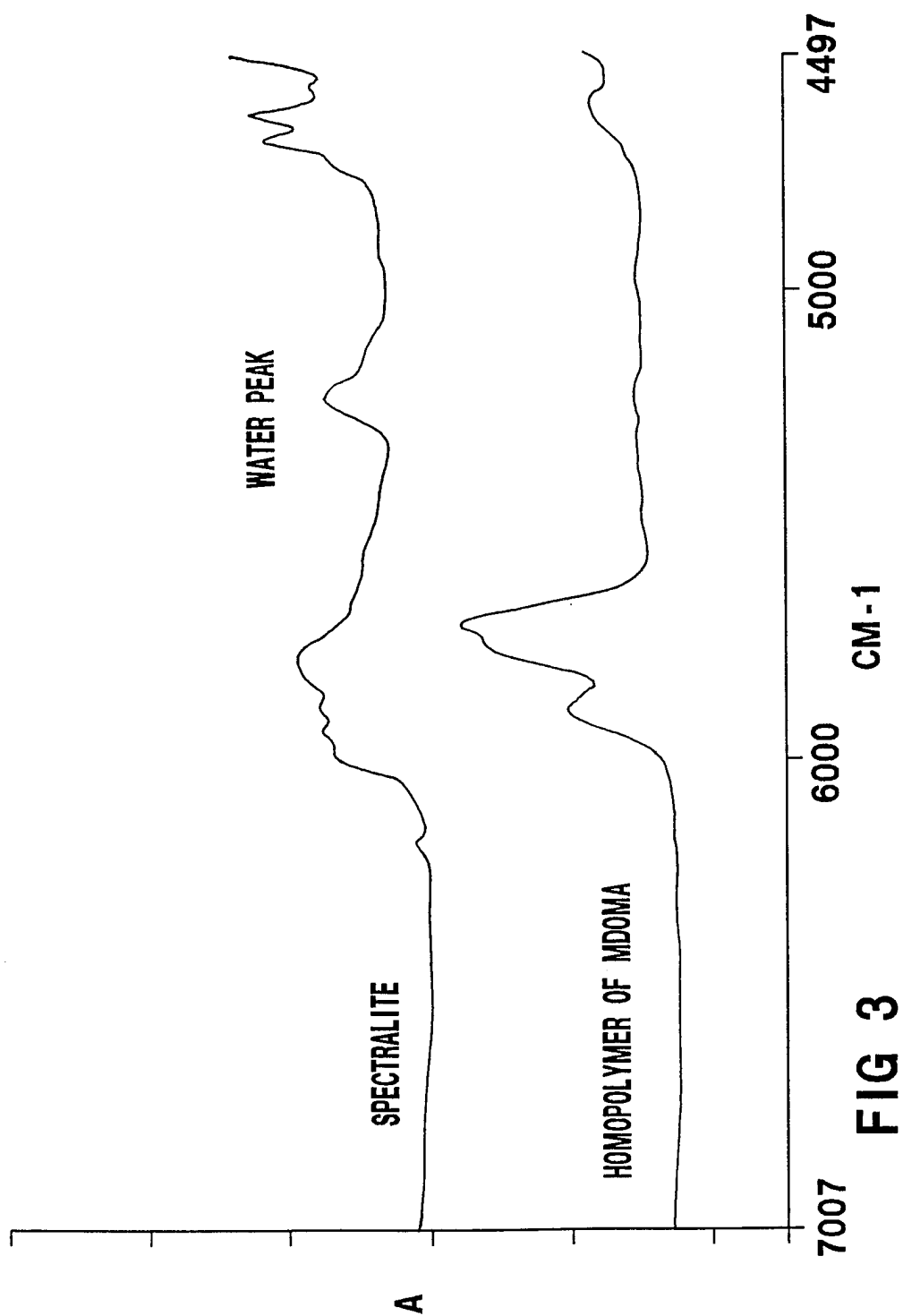
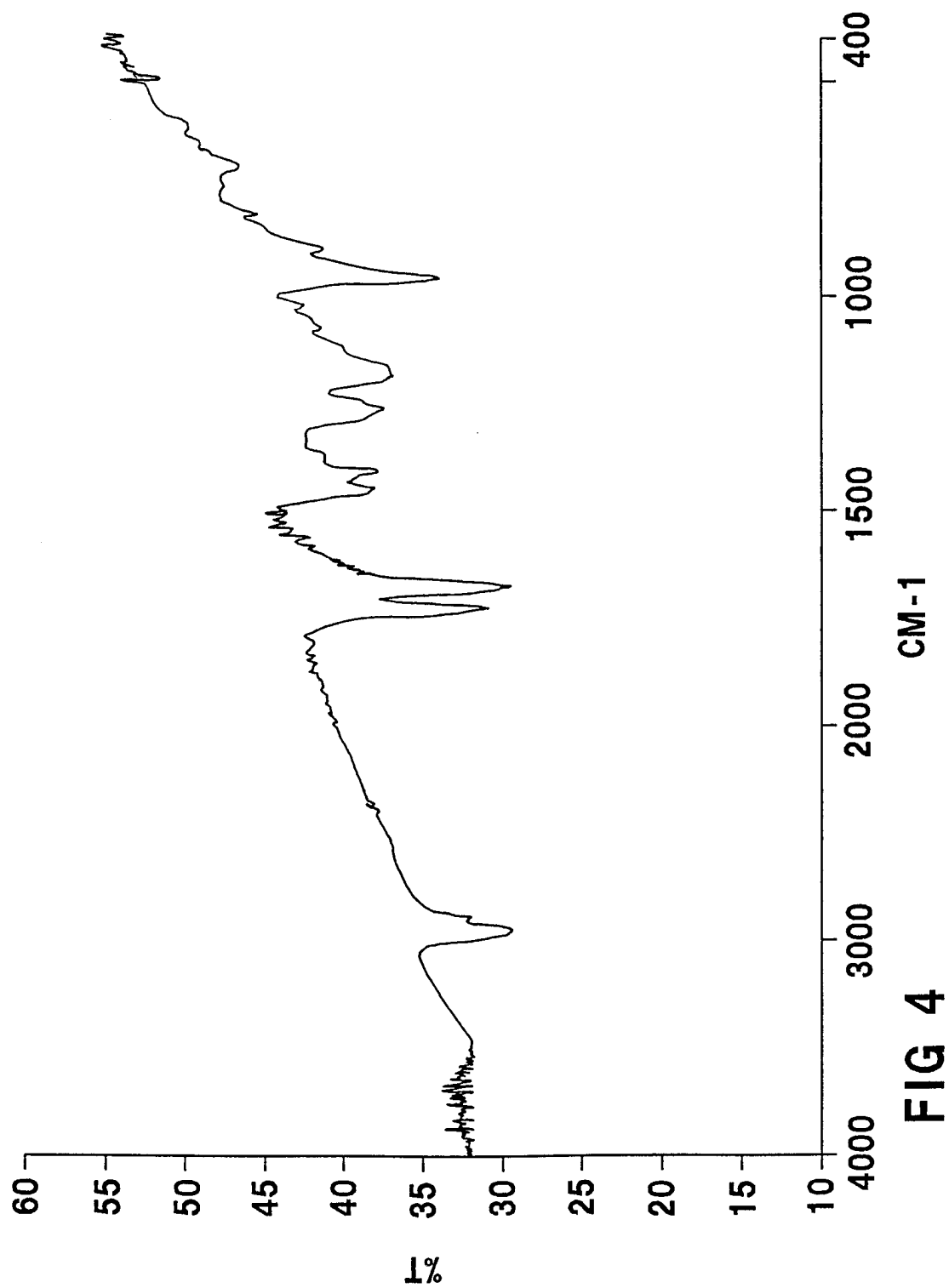


FIG 3

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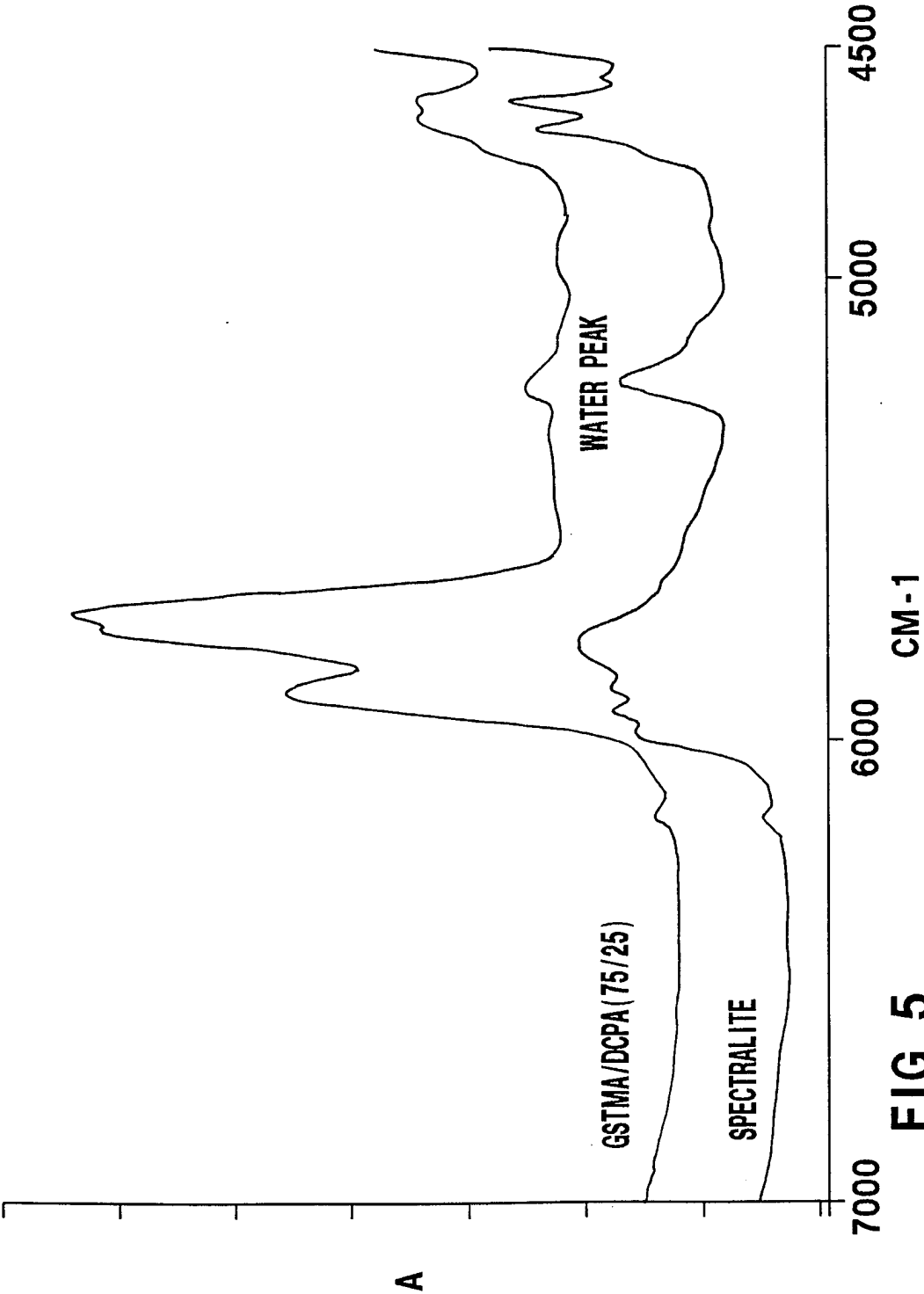


FIG 5

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/AU 97/00816

A. CLASSIFICATION OF SUBJECT MATTER		
Int Cl ⁶ : C07C 327/22, 327/28; C08F 20/38, 22/24, 28/02, 120/38, 122/24, 220/38, 222/24, 228/02; G02B 1/04		
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)		
IPC: C07C 153/07, 153/09, 153/11, 327/22, 327/28; C08F 20/38, 22/24, 28/02, 120/38, 122/24, 220/38, 222/24, 228/02		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
AU: IPC as above		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
DERWENT, WPAT AND JAPIO: ACRYL: OR METHACRYL: OR METH(W)ACRYL D1(W)THIO: OR POLY(W)THIO: OR THIO:		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	Derwent WPAT Online Abstract Accession No. 97-328466/30, Class P81, JP,A, 9132563 (MITSUI TOATSU CHEM INC) 20 May 1997 See Abstract	1-21
A	Derwent WPAT Online Abstract Accession No. 94-273853/34, Class A12 A89, JP,A, 6202049 (TOKYO KEIKAKU KK) 22 July 1994 See Abstract	1-21
A	US,A, 5384379 (MARTINA BADER et al) 24 January 1995 See column 2; Claims 1 to 3	1-21
☒ Further documents are listed in the continuation of Box C ☒ See patent family annex		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 19 January 1998		Date of mailing of the international search report 03 FEB 1998
Name and mailing address of the ISA/AU AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No.: (02) 6285 3929		Authorized officer B CROUCH Telephone No.: (02) 6283 2060

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A, 5488128 (MARTINA BADER et al) 30 January 1996 30 January 1996 See Column 1, line 53-column 3, line 60; Claims 1 to 6	1-21
A	Derwent Online Abstract Accession No. 90-249730/33, Class A41 E17, JP,A, 2172969 (MITSUI TOATSU CHEM INC) 4 July 1990 See Abstract	1-21
A	Derwent Online Abstract Accession No. 88-260508/37, Class A41 E17, JP 63188660 (MITSUI TOASTU CHEM INC) 4 August 1988 See Abstract	1-21
A	AU 82945/87 (603404) B (NIPPON SHOKUBAI K K CO LTD) 30 June 1988 See page 3-page 6; page 12; Claims 1 to 16	1-21

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/AU 97/00816

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
AU	82945/87	AT	54909	AT	85626	AU	82869/87
		AU	593416	AU	603404	CA	1267909
		DE	3763968	DE	3784152	EP	273661
		EP	273710	JP	63162671	JP	3059060
		US	4810812	US	4931521	JP	1031759
		JP	3059061	JP	1110666	JP	3059062
		JP	1026613	JP	6025232		
US	5488128	AT	139527	DE	4234253	DE	59303006
		EP	593974	JP	6234733		
US	5384379	DE	4234251	EP	592935	JP	6199963
JP	9132563	NONE					
JP	63188660	JP	7091262				
JP	2172969	JP	8025991				
JP	6202049	NONE					