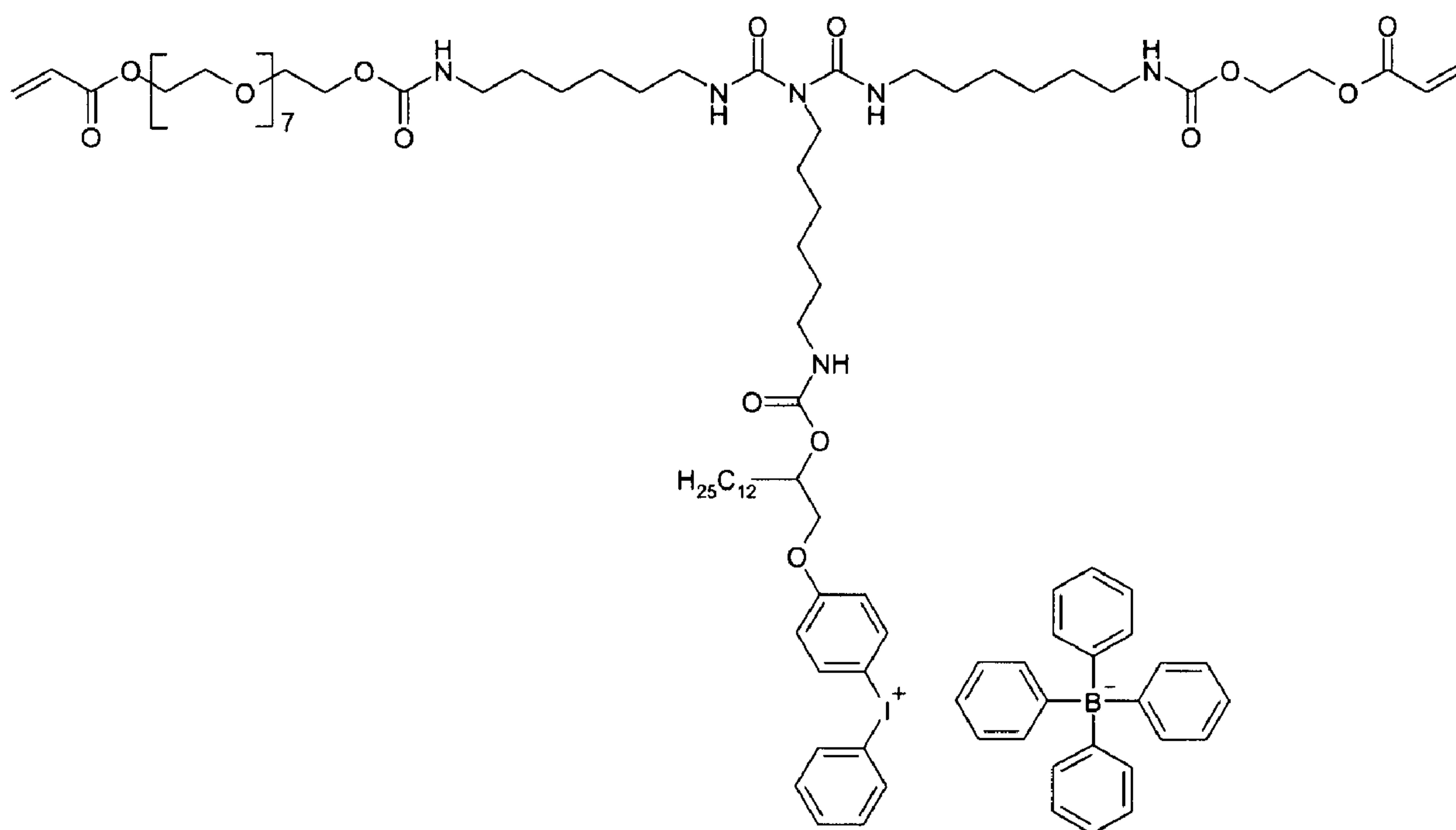




(86) Date de dépôt PCT/PCT Filing Date: 2007/05/09
(87) Date publication PCT/PCT Publication Date: 2007/11/22
(45) Date de délivrance/Issue Date: 2012/07/10
(85) Entrée phase nationale/National Entry: 2008/11/14
(86) N° demande PCT/PCT Application No.: CA 2007/000820
(87) N° publication PCT/PCT Publication No.: 2007/131336
(30) Priorité/Priority: 2006/05/17 (US60/747,474)

(51) Cl.Int./Int.Cl. *C07C 275/62* (2006.01),
B41C 1/10 (2006.01), *B41N 1/14* (2006.01),
C07C 271/08 (2006.01), *C07F 5/02* (2006.01),
C08B 11/193 (2006.01), *C08F 220/00* (2006.01),
C08G 61/02 (2006.01), *G03F 7/004* (2006.01)
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(54) Titre : NOUVEAUX MATERIAUX POUR REVETEMENTS DE PLANCHES LITHOGRAPHIQUES, PLANCHES LITHOGRAPHIQUES ET REVETEMENTS CONTENANT CEUX-CI, PROCEDES DE PREPARATION ET UTILISATION
(54) Title: NEW MATERIALS FOR LITHOGRAPHIC PLATES COATINGS, LITHOGRAPHIC PLATES AND COATINGS CONTAINING SAME, METHODS OF PREPARATION AND USE



(57) Abrégé/Abstract:

This invention relates to iodonium salts, acetal copolymers and polymer binders comprising functional groups capable of undergoing cationic or radical polymerization, their method of preparation and their use in the preparation of coatings. This invention also relates to coating solutions and coatings containing the iodonium salts, acetal copolymers and/or polymer binders and to negative working lithographic printing plates comprising these coatings.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
22 November 2007 (22.11.2007)

PCT

(10) International Publication Number
WO 2007/131336 A1

(51) International Patent Classification:

C07C 275/62 (2006.01) *C08B 11/193* (2006.01)
B41C 1/10 (2006.01) *C08F 220/00* (2006.01)
B41N 1/14 (2006.01) *C08G 61/02* (2006.01)
C07C 271/08 (2006.01) *G03F 7/004* (2006.01)
C07F 5/02 (2006.01)

(21) International Application Number:

PCT/CA2007/000820

(22) International Filing Date: 9 May 2007 (09.05.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/747,474 17 May 2006 (17.05.2006) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

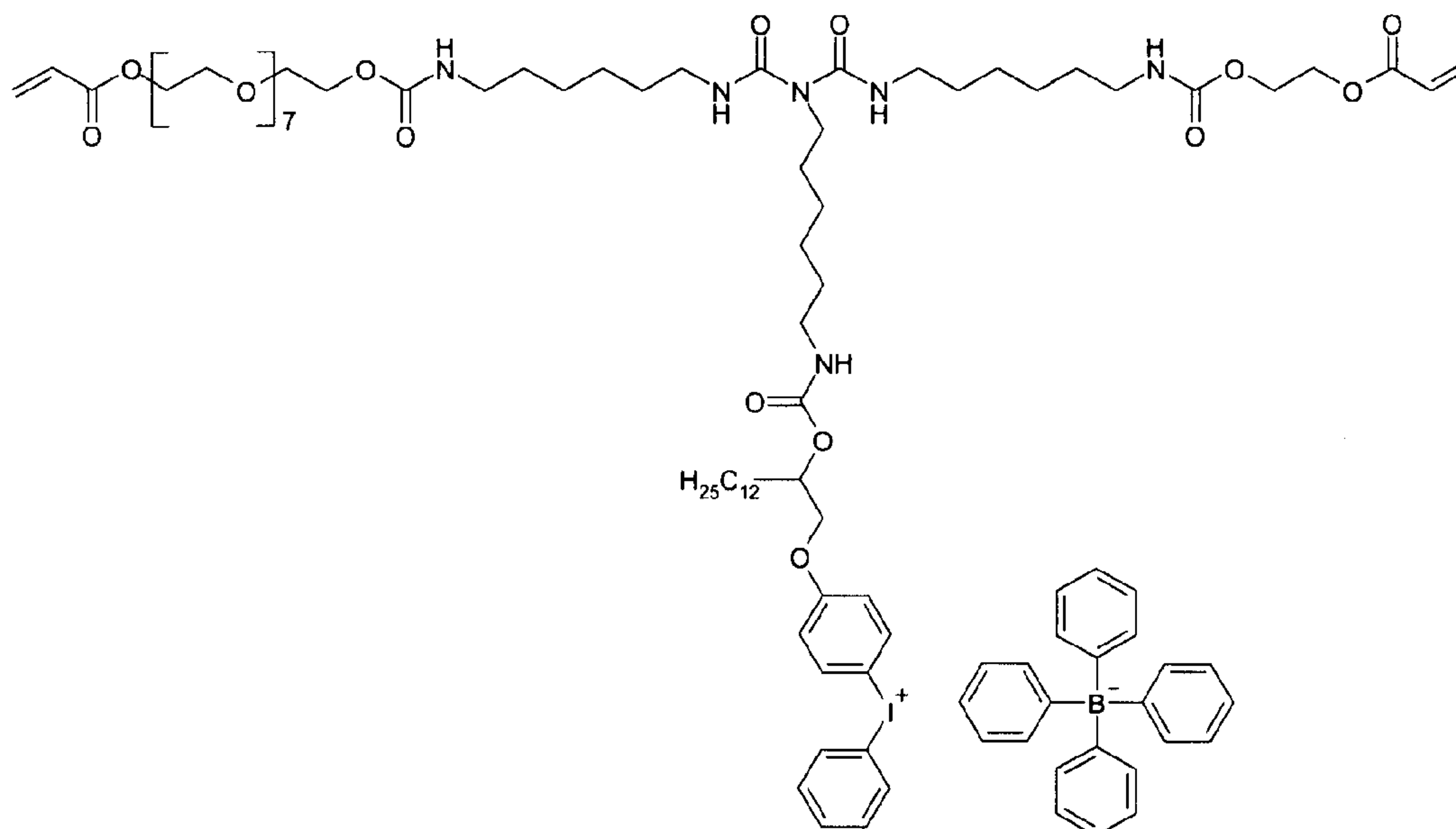
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: NEW MATERIALS FOR LITHOGRAPHIC PLATES COATINGS, LITHOGRAPHIC PLATES AND COATINGS CONTAINING SAME, METHODS OF PREPARATION AND USE



(57) Abstract: This invention relates to iodonium salts, acetal copolymers and polymer binders comprising functional groups capable of undergoing cationic or radical polymerization, their method of preparation and their use in the preparation of coatings. This invention also relates to coating solutions and coatings containing the iodonium salts, acetal copolymers and/or polymer binders and to negative working lithographic printing plates comprising these coatings.

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TITLE OF THE INVENTION

[0001] NEW MATERIALS FOR LITHOGRAPHIC PLATES COATINGS, LITHOGRAPHIC PLATES AND COATINGS CONTAINING SAME, METHODS OF PREPARATION AND USE

FIELD OF THE INVENTION

[0002] This invention relates to novel materials useful for lithographic plates coatings and to plates, coatings and coating solutions containing these materials. More specifically, these new materials and coating solutions are useful in the preparation of coatings for lithographic offset printing plates for direct digital imaging by near-infrared laser radiation.

BACKGROUND OF THE INVENTION

[0003] On-press developable negative-working lithographic offset printing plates are known in the prior art. For example, US patent No. 5,569,573 teaches lithographic printing plates comprising a laser imaging layer containing microencapsulated oleophilic materials in hydrophilic polymer binders. EP 0 770 495 A1 teaches lithographic printing plates comprising near infrared absorption materials, polymer binders and thermoplastic particles capable of coalescing under heat. US patent No. 6,983,694 teach on-press developable negative-working offset printing plates coated with near infrared sensitive coating compositions comprising thermoplastic polymer particles, such as polystyrene or poly(acrylonitrile-co-styrene) particles, non-reactive hydrophilic polymer binder and near infrared absorption dyes.

[0004] Also, US patent No. 6,261,740 teaches negative-working offset printing plates coated with near infrared sensitive coating compositions containing methoxymethacrylamide copolymers, phenolic resins, iodonium salts and near infrared absorption dyes. US patents No. 6,124,425 and 6,177,182 teach on-press developable negative-working offset printing plates coated with thermally near-infrared absorbing polymers, which undergo cross-linking reactions via cationic polymerization upon exposure to near infrared radiation. The near infrared chromophoric moieties are functionalized to the polymeric backbone via ether and ammonium bonds. US Patent No. 6,960,422 teaches negative-working offset printing plates, which contain a near infrared sensitive base-coat compositions comprising molecular near infrared dyes, radical generators, radical polymerizable urethane compounds, reactive polymer binders and other additives.

[0005] Moreover, US Patent No. 6,969,575 and 7,001,704 teach on-press developable negative-working offset printing plates having an image-forming layer, which comprise near infrared absorbing microcapsules and acid generator compound. US patent No. 6,582,882 and co-pending US patent application 2003/0157433; US patent 6,899,994 and US patent application 2005/0123853 teach on-press developable negative-working offset printing plates, which are coated with thermally imageable compositions containing polymer binders, initiator systems and polymerizable components. The described polymer binders are copolymers having non-reactive polyethylene oxide and polypropylene block, or graft copolymers having non-reactive polyethylene oxide side chains co-polymerized with acrylonitrile, styrene and other monomers. The polymerizable components are viscous liquid oligomers containing multiple acrylic functional groups. The initiator system contains near infrared absorption dyes and radical producing compounds, such as triazine and iodonium salts.

[0006] All of these coating compositions and printing plates show some disadvantages such as having a tacky surface which causes difficulties for handling and storage, exhibiting phase separation and/or surface crystallization, being difficult to prepare, requiring high laser power to achieve imaging, having poor substrate adhesion and consequently failing to provide sufficient run length on press, not being developable on-press, exhibiting poor scratching resistance, requiring an over-coating layer and/or a special substrate surface treatment and being expensive to manufacture.

[0007] There thus remains a need for new materials and new coatings for lithographic plates that would overcome some or all of the drawbacks of the prior art.

SUMMARY OF THE INVENTION

[0008] This invention relates to iodonium salts, polyvinyl alcohol acetal copolymers and polymer binders, each comprising at least one functional group capable of undergoing cationic or radical polymerization

[0009] This invention further relates to the method for preparing the iodonium salts, polyvinyl alcohol acetal copolymers and polymer binders of the invention. More specifically, one such method for preparing an iodonium salt of the invention comprises attaching a pendant group to an iodonium salt, wherein the pendant group is obtained by reacting a mono-isocyanate, a di-isocyanate or a poly-isocyanate with

an amine or an alcohol, which is terminated by one or more groups each independently selected from acrylate, methacrylate and vinyl-ether.

[0010] The present invention further relates to the use of the iodonium salts, polyvinyl alcohol acetal copolymers and polymer binders of the invention or a mixture thereof in the preparation of coating solutions and to the coatings produced using these solutions.

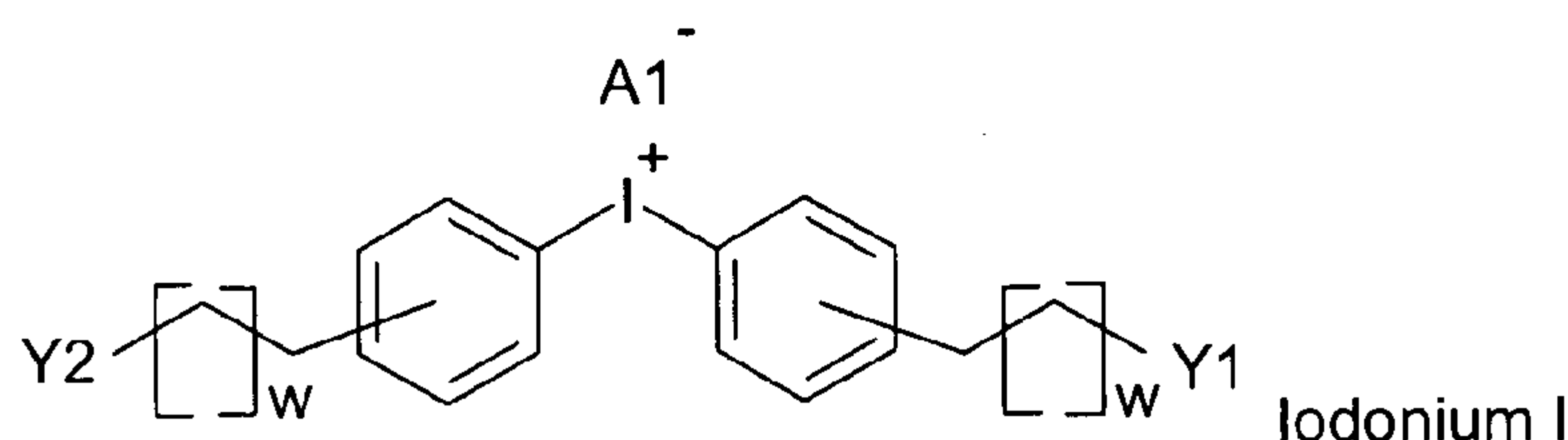
[0011] The invention also relates to coating solutions and to negative working lithographic printing plate comprising the coatings and/or the iodonium salts, polyvinyl alcohol acetal copolymers and polymer binders of the invention.

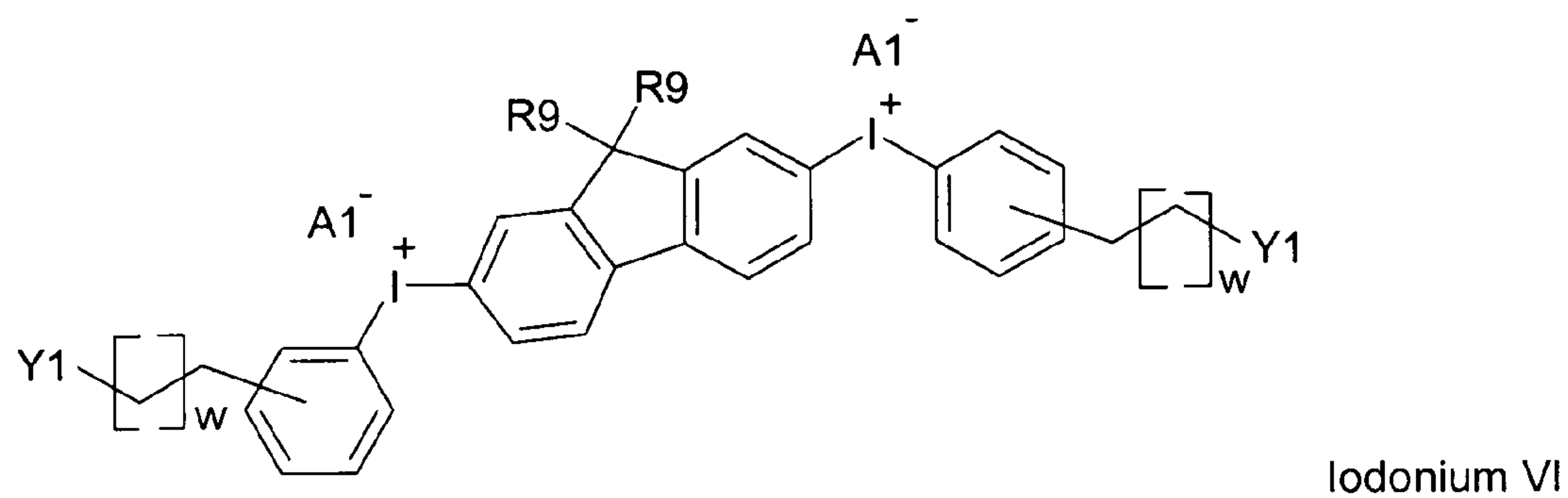
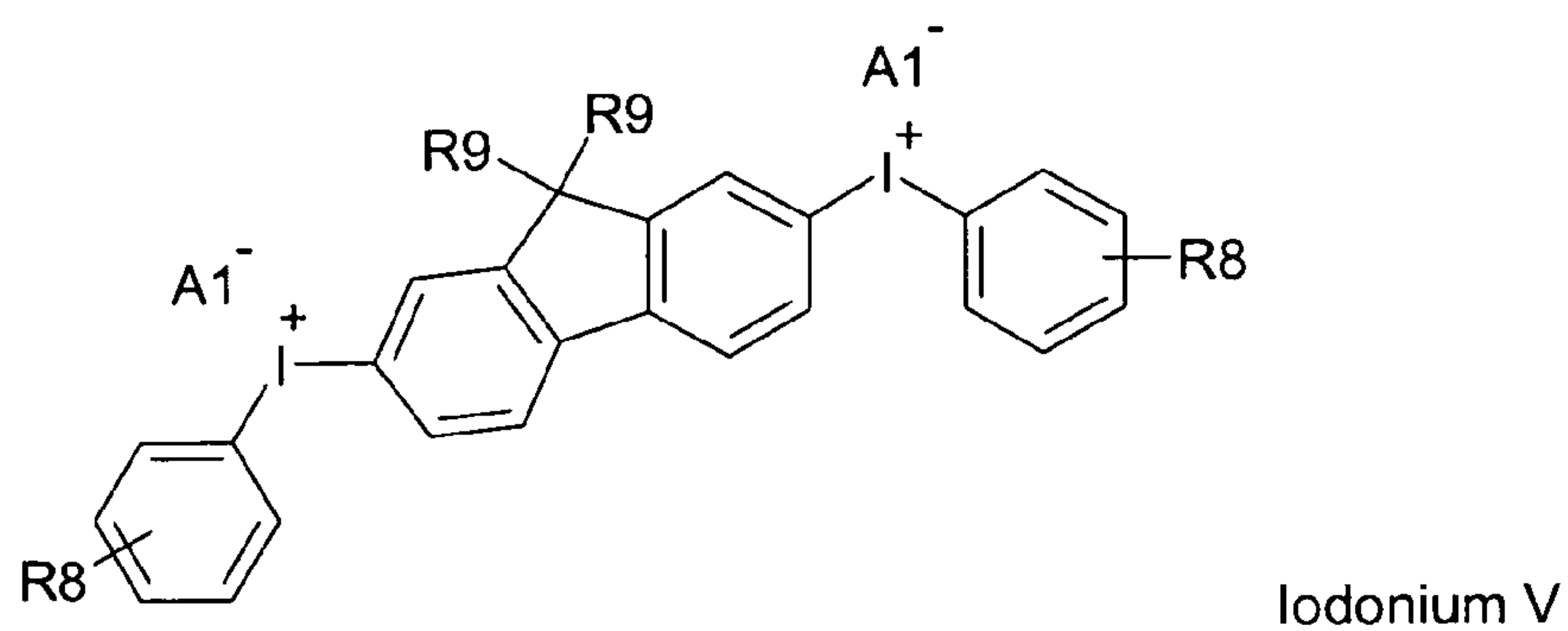
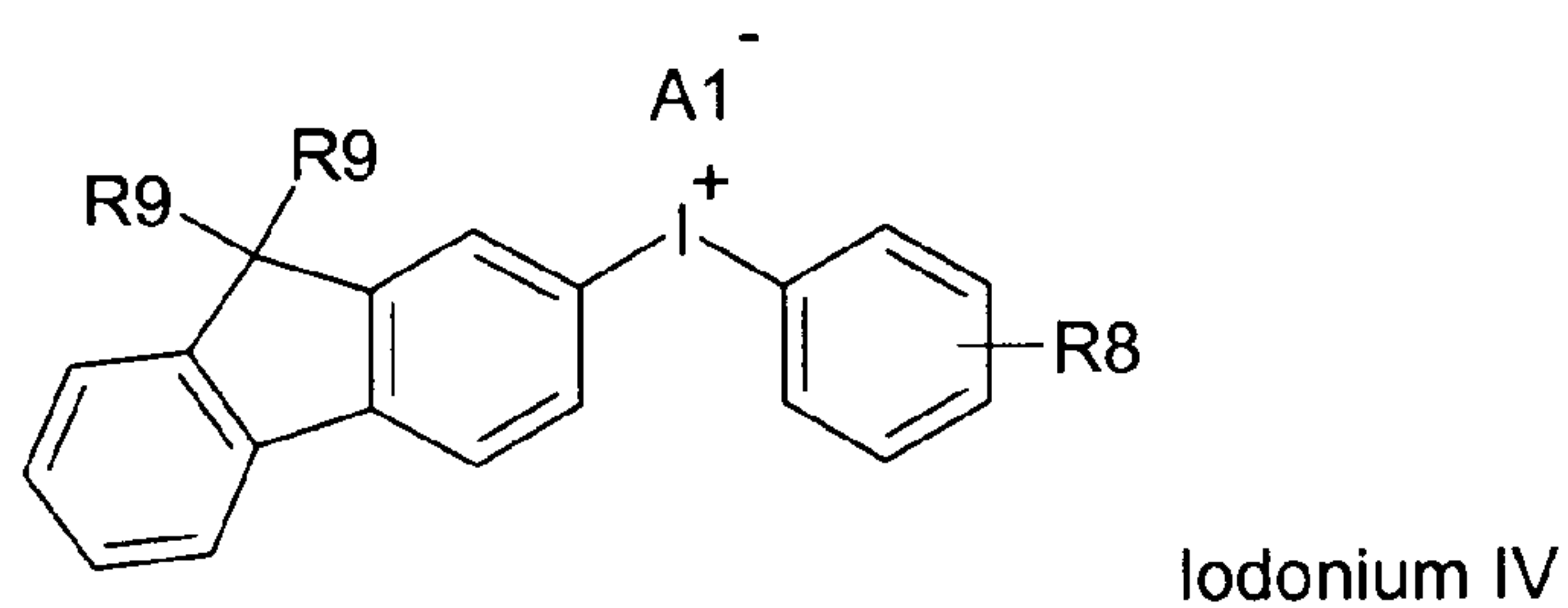
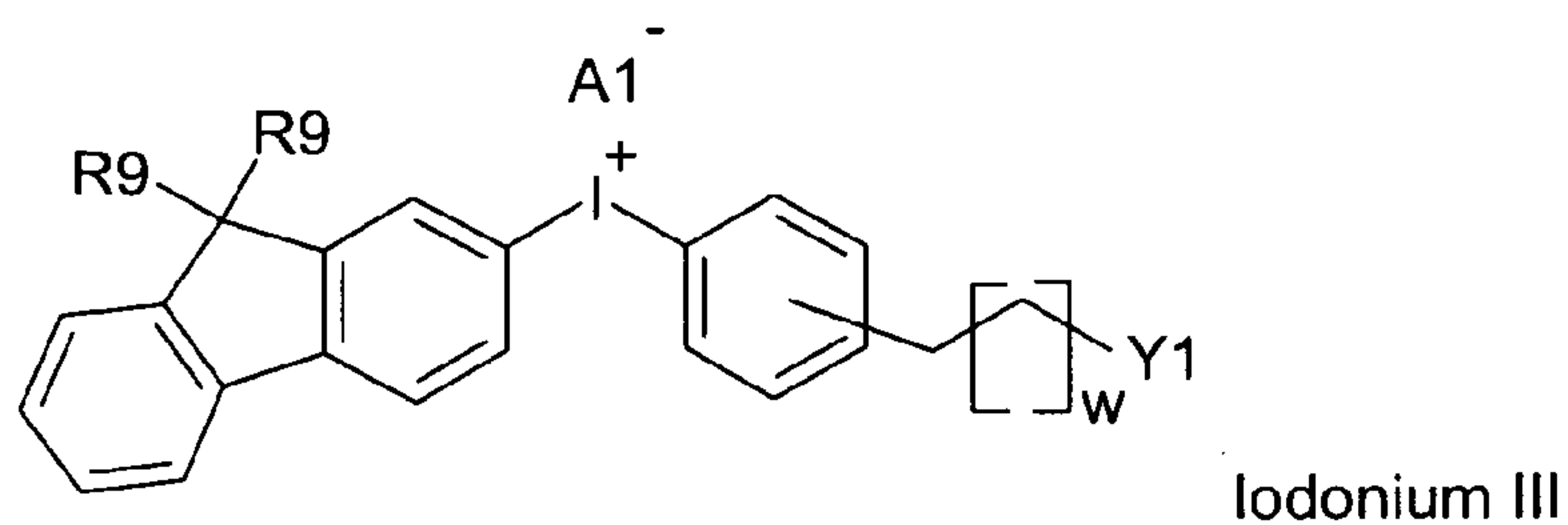
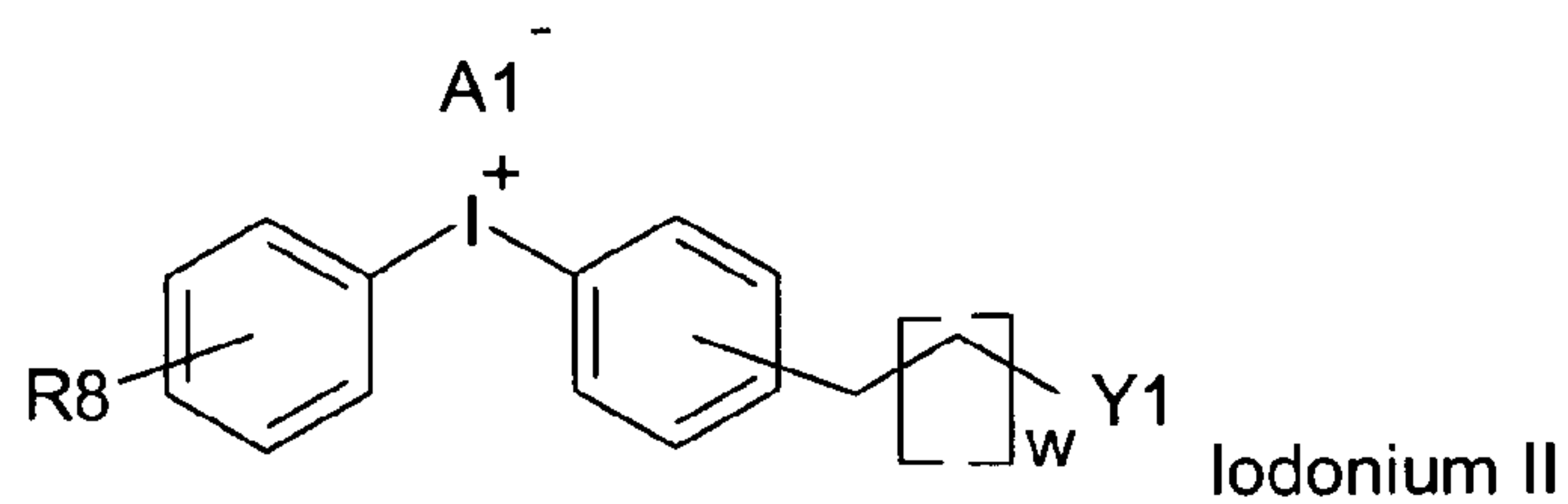
Thermally Reactive Iodonium salts

[0012] The present invention relates to iodonium salt comprising a positively charged iodine atom to which two aryl rings are attached, and a negatively charged counter ion. When exposed to near infrared radiation or heat, these salts are radical and acid generators.

[0013] The iodonium salts of the present invention comprise one or more functional groups that can undergo radical and/or cationic polymerization. Upon exposure to heat, the iodonium salt will generate radicals and acid, which will initiate the radical or cationic polymerization of these functional groups. This will contribute to the formation of a network within the irradiated area of the coating.

[0014] More specifically, the iodonium salts of the invention may contain radical polymerizable groups, such as acrylate, methacrylate and vinyl ether. These radical polymerizable groups may be pendant to the aryl rings of the salt via urethane and/or urea bonds. These salts may have the following general structures:





wherein:

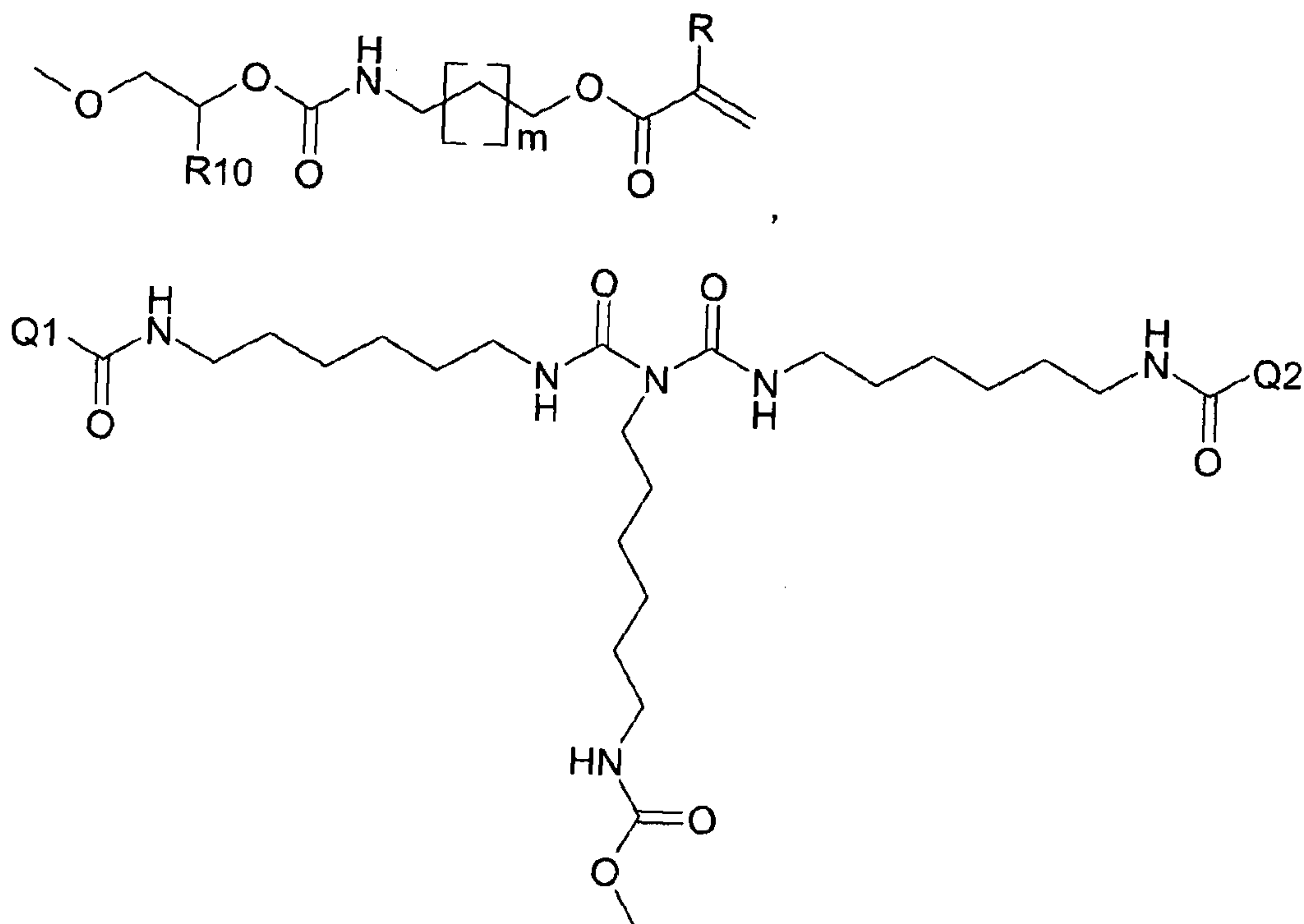
- A1 represents an anionic counter ion selected from tosylate, triflate, hexafluoroantimonate, tetrafluoroborate, tetraphenylborate and triphenyl-n-alkylborate;
- w represents the number of repeat unit and may vary between 0 and 18;
- R8 and R9 independently represent hydrogen, linear or branched C1 – C18 alkyl, alkyl oxy, poly(ethylene oxide), poly(propylene oxide) and may comprise acrylate, methacrylate and vinyl ether terminated groups (In the case of Iodoniums IV and V, either R8, R9 or both R8 and R9 do comprise such acrylate, methacrylate and vinyl ether terminated groups); and
- Y1 and Y2 independently represent urethane and/or urea containing compounds, which comprise single or multiple polymerizable functional groups, such as acrylate, methacrylate or vinyl ether.

[0015] In a more specific embodiment, Y1 and/or Y2 may be obtained by reacting a mono-isocyanate, di-isocyanate and/or poly-isocyanate with an amine or an alcohol comprising single or multiple acrylate, methacrylate and/or vinyl-ether terminated groups. These isocyanate compounds may be Desmodur™ N100, Desmodur™ N3300, Desmodur™ CB 75N, Desmodur™ I, Desmodur™ W, Desmodur™ M, Desmodur™ H and Desmodur™ TD 80, which are sold by Bayer Canada.

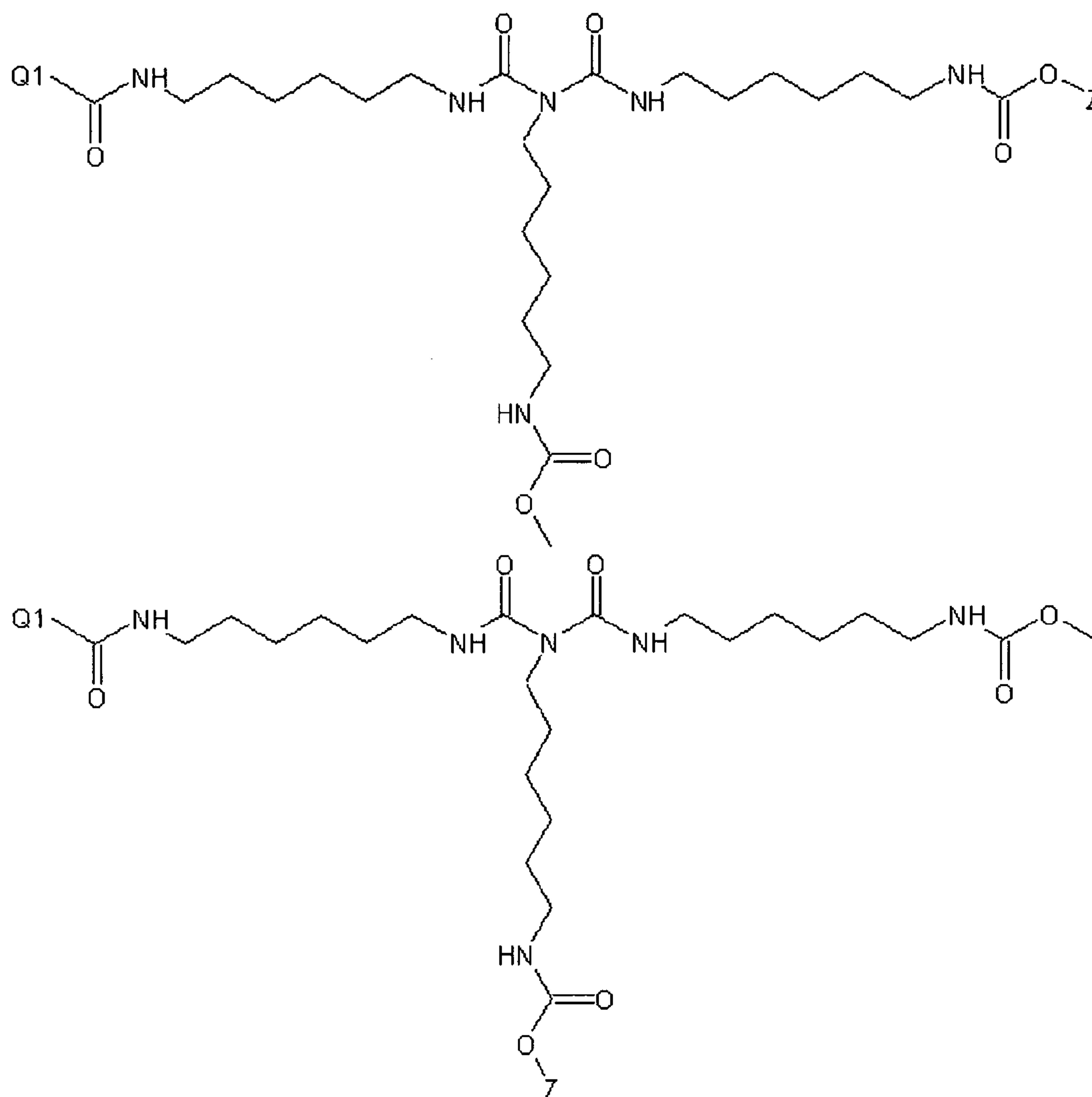
[0016] In a specific embodiment, the alcohol comprises multiple acrylate terminated groups. Such alcohol may be are obtained from Sartomer. This alcohol may be pentaerylthritol triacrylate (Trade-name SR 444) and dipentaerylthritol pentaacrylate (Trade-name SR399).

[0017] In another specific embodiment, the alcohol comprises single acrylate and methacrylate compounds and may be obtained from Sigma-Aldrich Canada. The alcohol may be 2-hydroxyethylacrylate, 2-hydroxyethylmethacrylate, 4-hydroxybutylacrylate, 4-hydroxybutylmethacrylate, 6-hydroxyhexylacrylate, 6-hydroxyhexylmethacrylate, poly(ethylene glycol) acrylate, poly(ethylene glycol) methacrylate, poly(propylene glycol) acrylate and poly(propylene glycol) methacrylate.

[0018] Y1 and Y2 may have the following chemical structures:



, or



wherein:

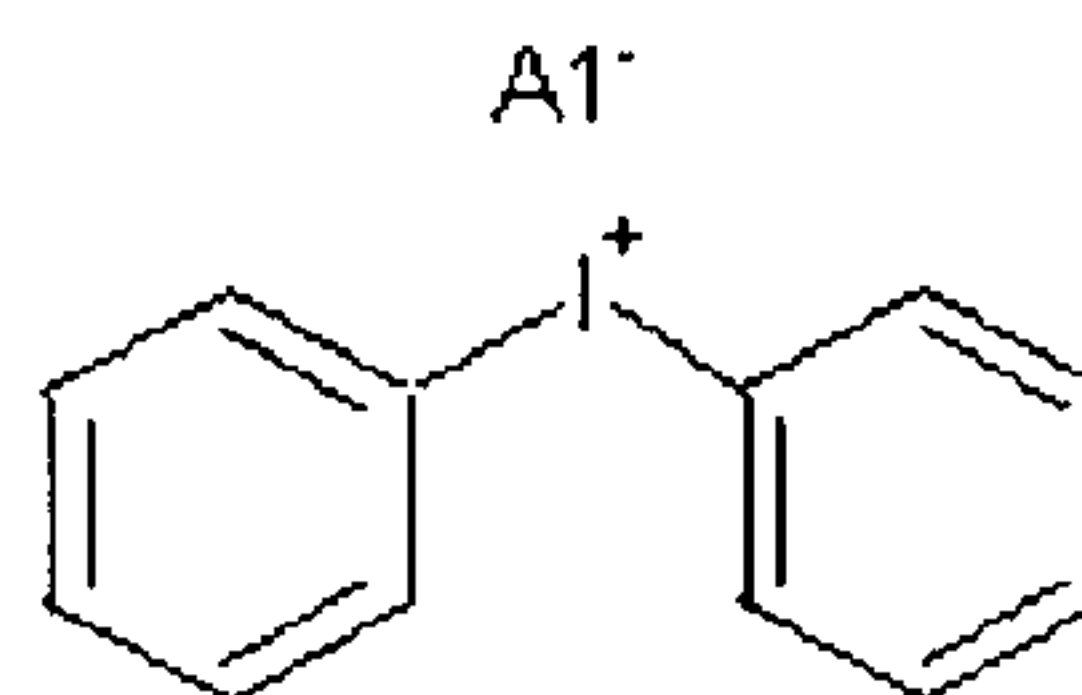
m varies between 1 and 18,

R is hydrogen or methyl

R_{10} is hydrogen or a linear or branched C1-C18 alkyl chain;

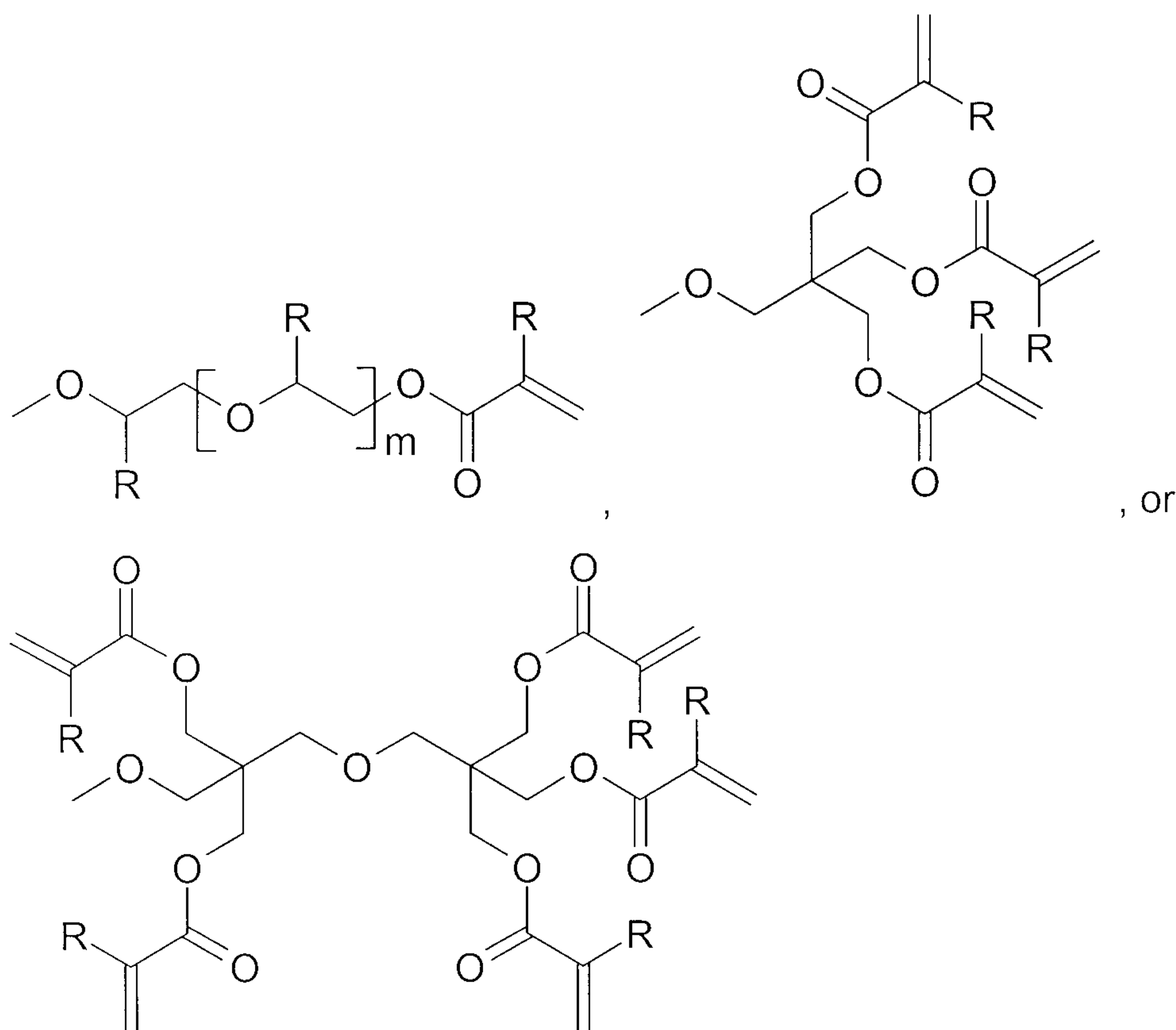
$Q1$ and $Q2$ independently represent an end compound comprising single or multiple polymerizable functional groups; and

Z represents a substituent comprising



, wherein $A1$ is

[0019] More specifically, Q1 and Q2 may independently have any of the following structures:



wherein R is hydrogen or methyl and m is as defined above, and preferably between 0 and 7.

[0020] The synthesis of urethane containing iodonium salts having no reactive (polymerizable) functional groups can be seen in US Patent No. 6,380,277.

[0021] The iodonium salt of the present invention may be used for the preparation of coating solutions and coatings. Such coating may comprise from about 5 to about 60 % by solid weight of the iodonium. The coatings are usually prepared by depositing a coating solution comprising the iodonium salt onto a substrate. These solutions comprise a solvent or a mixture of solvent allowing the formation of the coating. Any solvent known to the person of skill in the art to be appropriate for this purpose can be used. Examples of such solvents include n-propanol, water and other similar solvents.

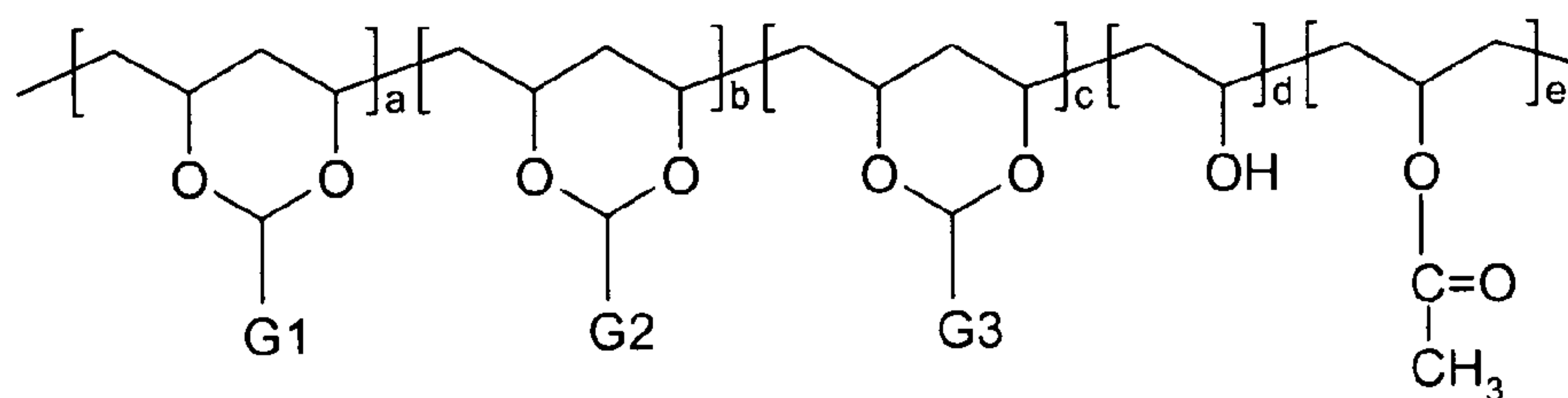
[0022] In a specific embodiment, the coating/coating solution of the present invention comprises a mixture of iodonium salts, which may ease the manufacturing process.

Near infrared absorbing dyes

[0023] The coating/coating solution of the present invention may also comprise a near infrared absorbing dye which produces heat upon exposure to near infrared radiation. More specifically, this near infrared absorbing dye may be a molecular dye, a dimeric dye, a dendrimeric dye or a polymeric dye. In a specific embodiment, this dye is an polyvinyl alcohol acetal copolymer.

[0024] This molecular dye, and more particularly this polyvinyl alcohol acetal copolymer, may have attached thereto a functional group capable of undergoing cationic or radical polymerization. Therefore, when the iodonium salt produces acid/radicals, this functional group will react with other such functional groups present in the coating, for example that of the iodonium salt, to produce a chemical link, and contribute to the formation of a network within the irradiated area of the coating.

[0025] More specifically, the near infrared absorbing polyvinyl alcohol acetal copolymers may have a molecular weight greater than about 2,000 g/mol and may either be soluble in organic solvents or in aqueous solutions. Furthermore, they may have the following general structure:

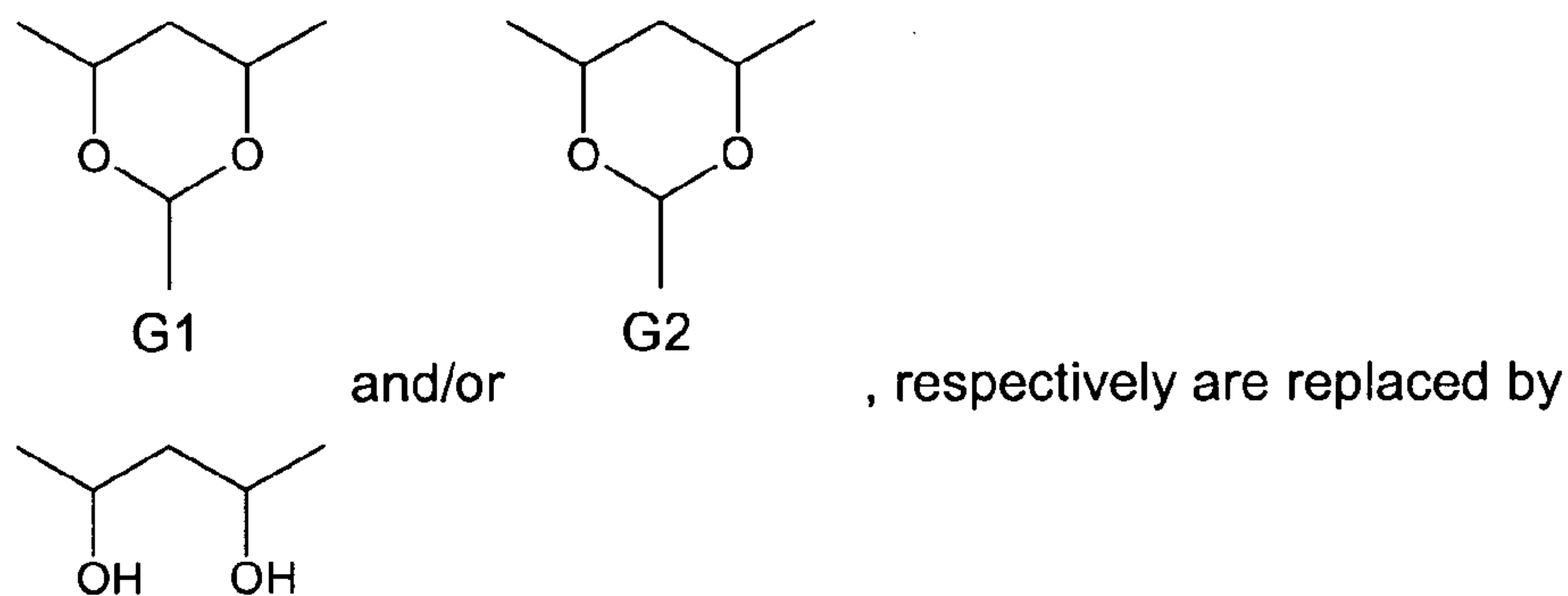


Formula 1

wherein:

- G1 represents an optional processing segment that provides solubility in organic solvents such as alcohol, ketone, and ester;
- G2 represents an optional thermal reactive segment;
- G3 represents a radiation-absorbing segment that exhibits one or more strong absorption bands between 700 and 1100 nm. Optionally, this segment may also exhibit strong absorption bands between 400 and 700 nm;

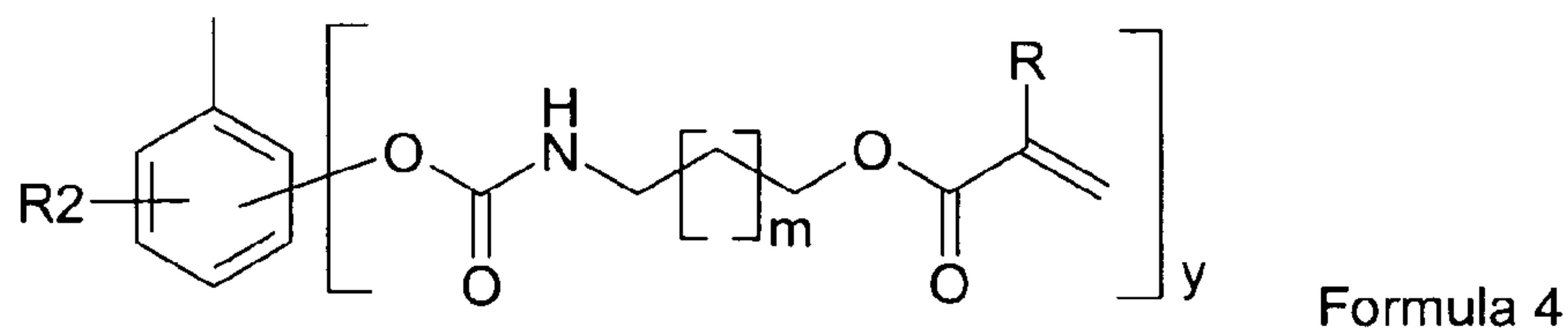
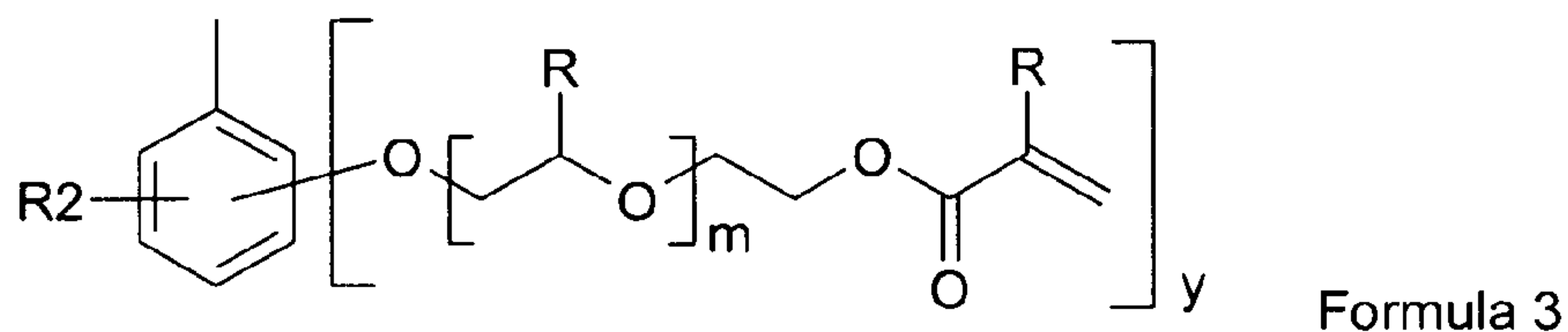
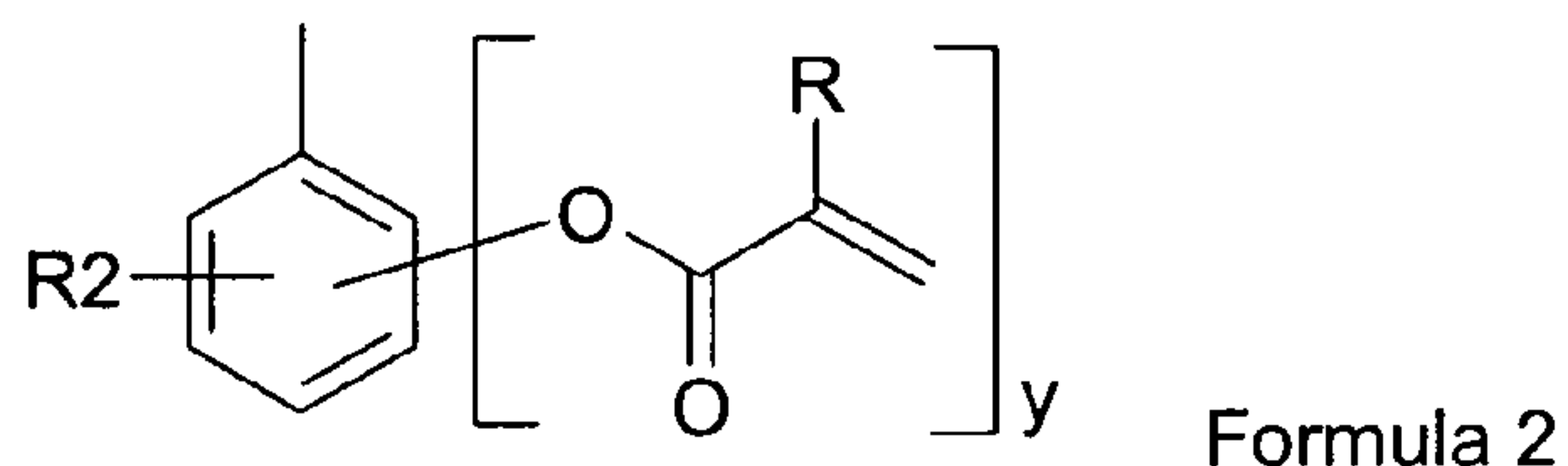
- a, b, c, d and e are molar ratios that can vary from 0.01 to 0.99; and
- when the optional G1 and/or G2 segments are not present,

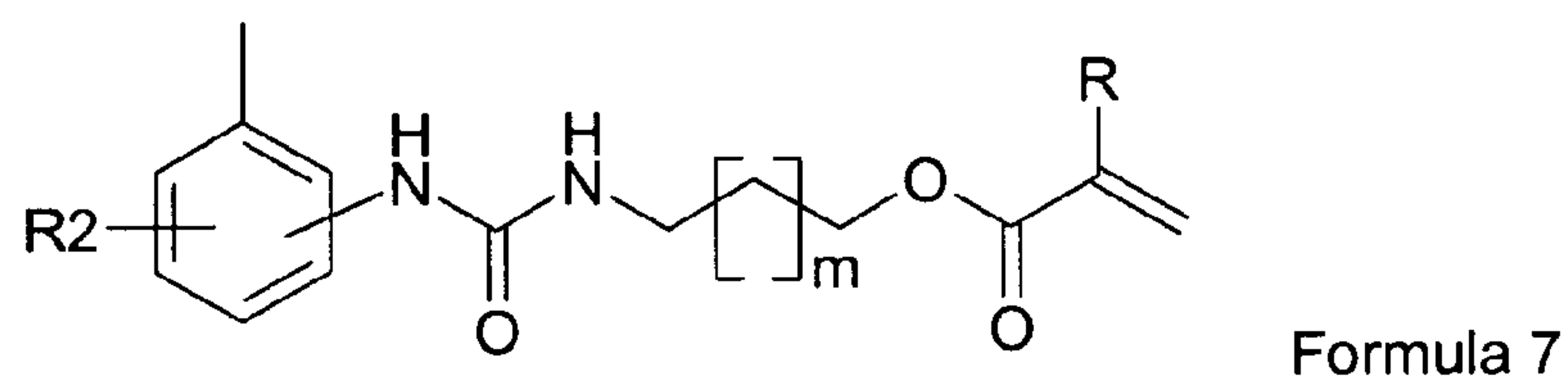
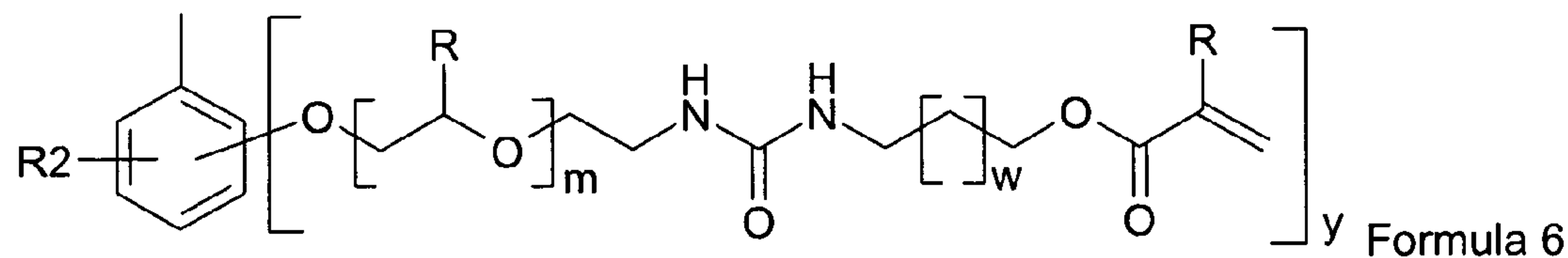
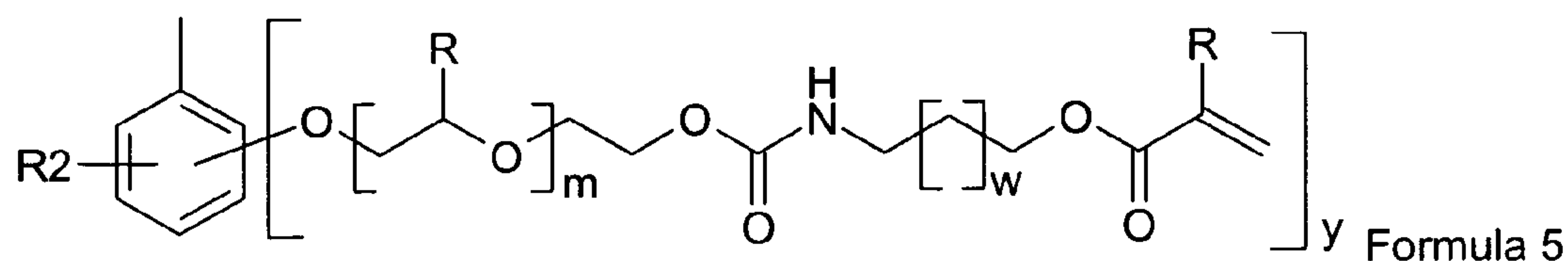


[0026] More specifically, the G1 processing segment of this invention may be a linear or branched alkyl or aryl compound containing cyano, hydroxy, dialkylamino, trialkylammonium salts, ethylene oxide, propylene oxide, methylbenzylsufonyl-carbamate or carboxylic acid and phosphoric acid functional groups.

[0027] The G2 thermal reactive segment of this invention may be a linear or branched alkyl or aryl compound and may contain a functional group capable of undergoing radical and/or cationic polymerization, such as acrylate, methacrylate, alkoxy-methyl acrylamide, alkoxy methacrylamide and vinyl ether.

[0028] The G2 thermal reactive segment may have the following structures:



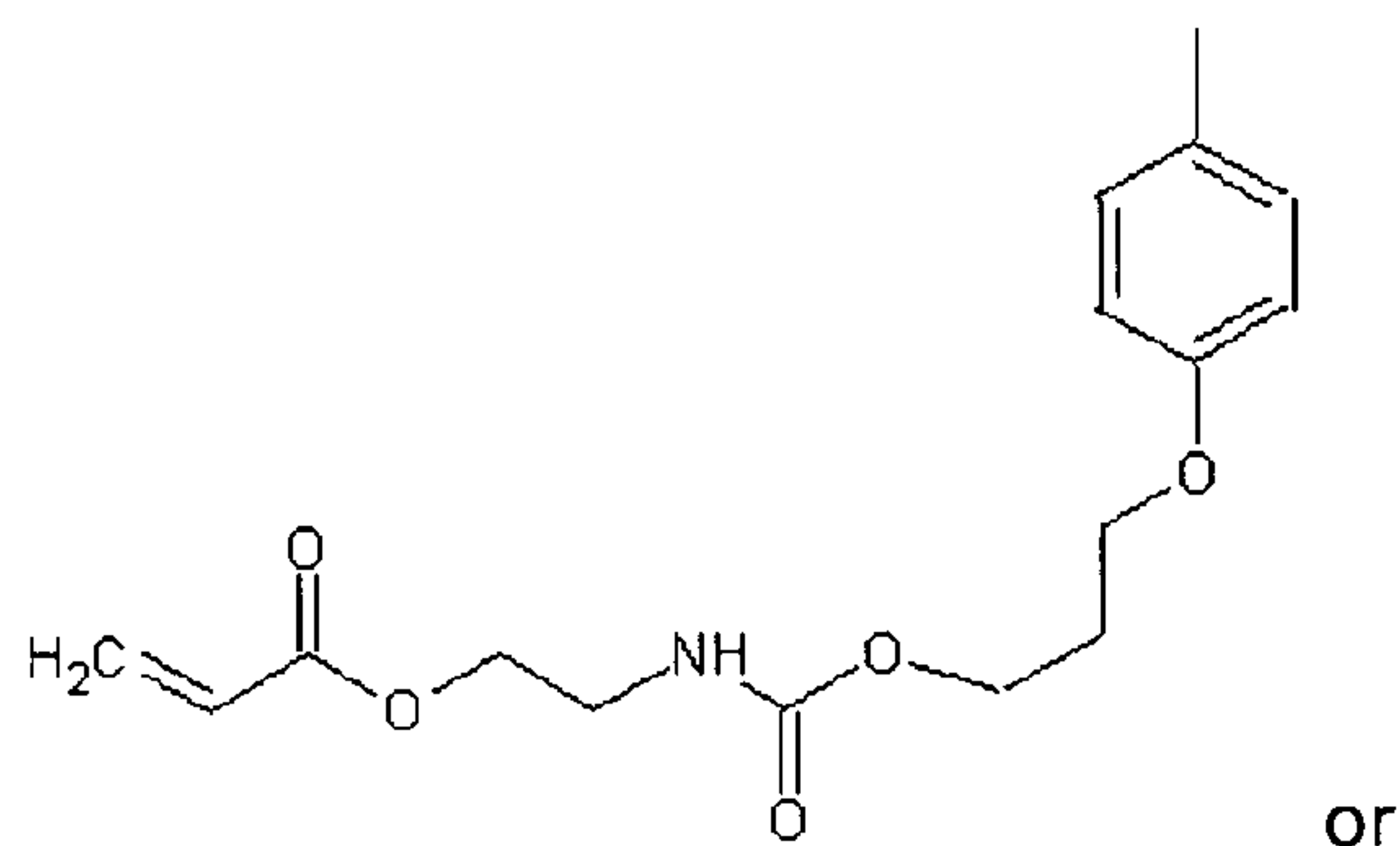


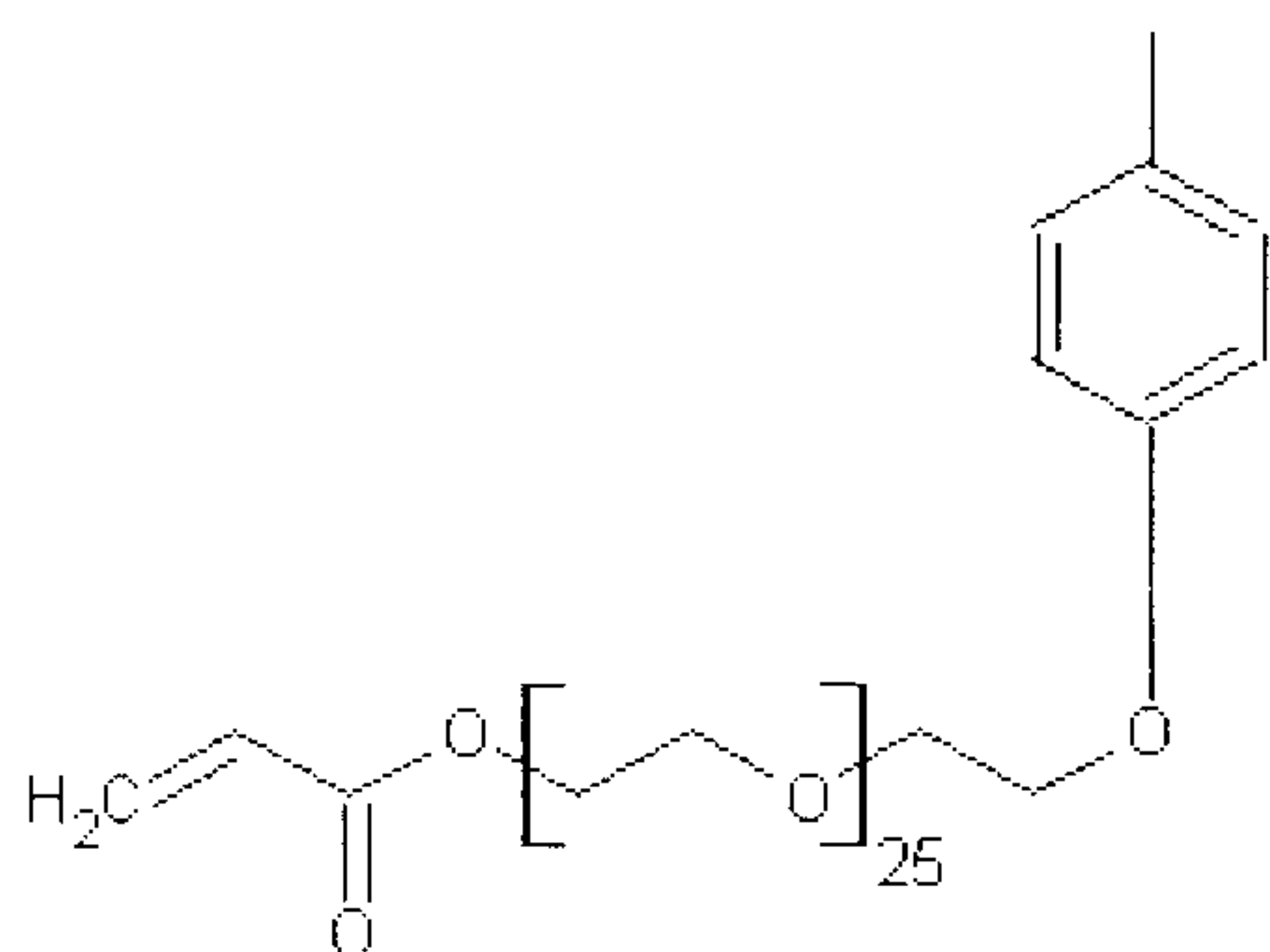
wherein:

- R is hydrogen or methyl;
- R2 is C1 – C8 alkyl or alkoxy;
- m and w represent the number of repeat and may vary between 0 and 50;
- y is 1 or 2.

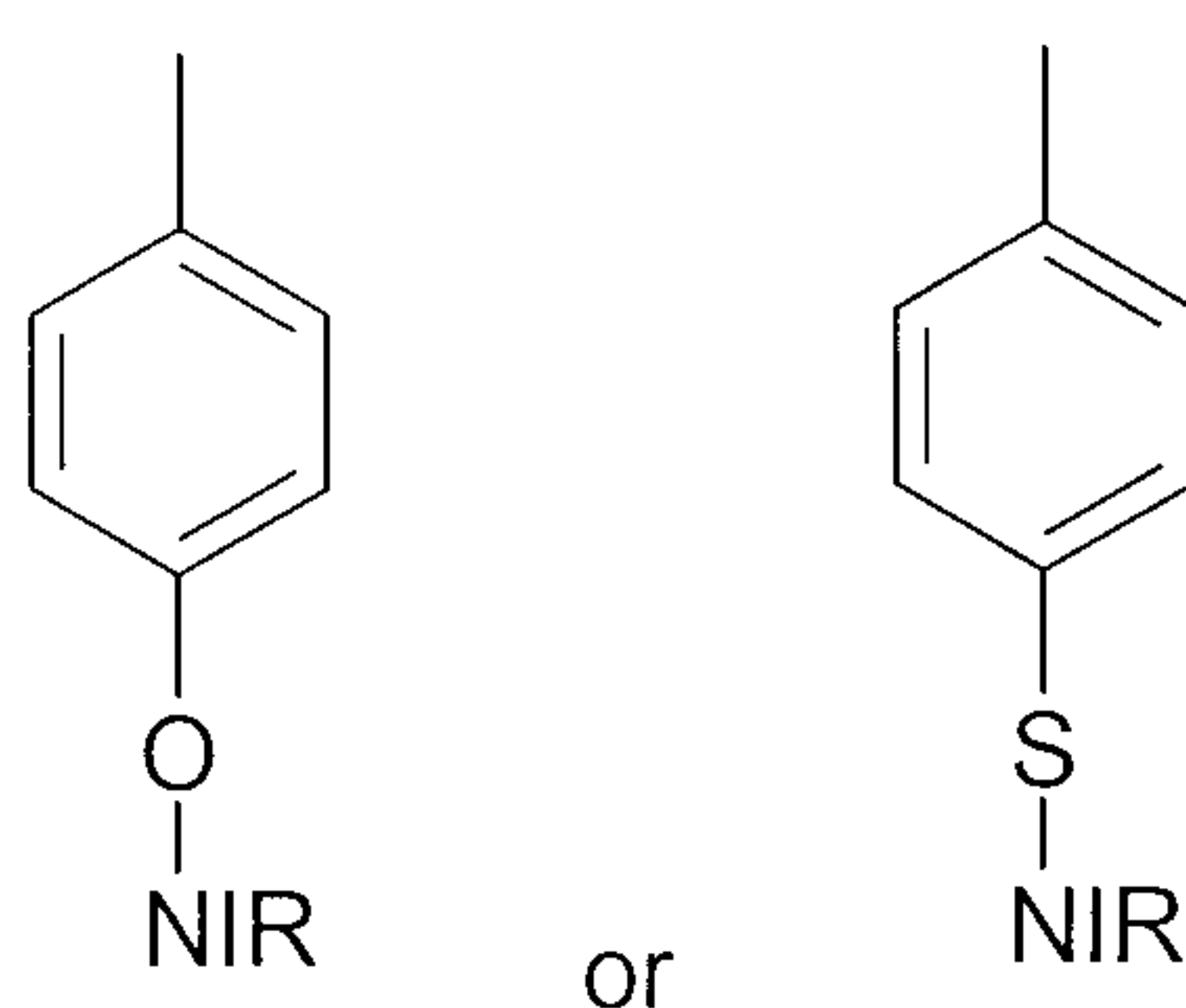
[0029] In another specific embodiment, the G2 segments may have pendant groups to those illustrated in formulas 2 to 7, but terminated with vinyl ether, alkoxy-methyl acrylamide or alkoxy methacrylamide functional groups.

[0030] In specific embodiments, G2 may be:





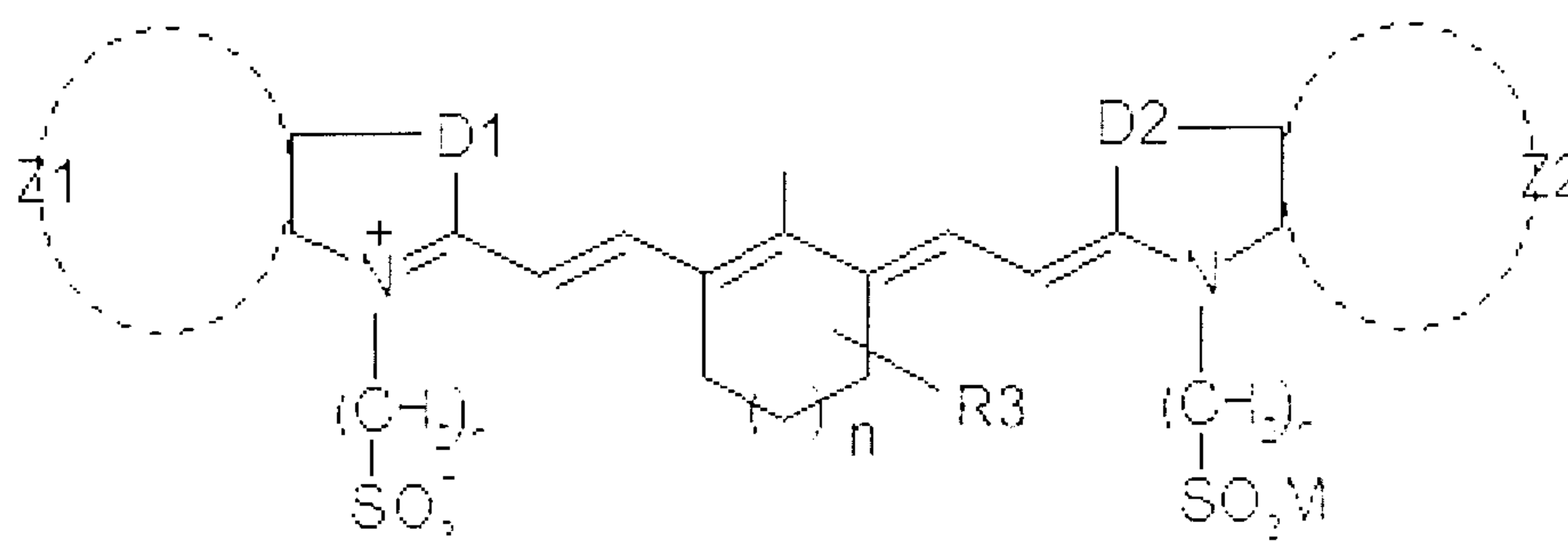
[0031] The G3 segment may be similar to that described in US Patent Application No. 2006/0275698. More specifically, the G3 segment may have the following structures:



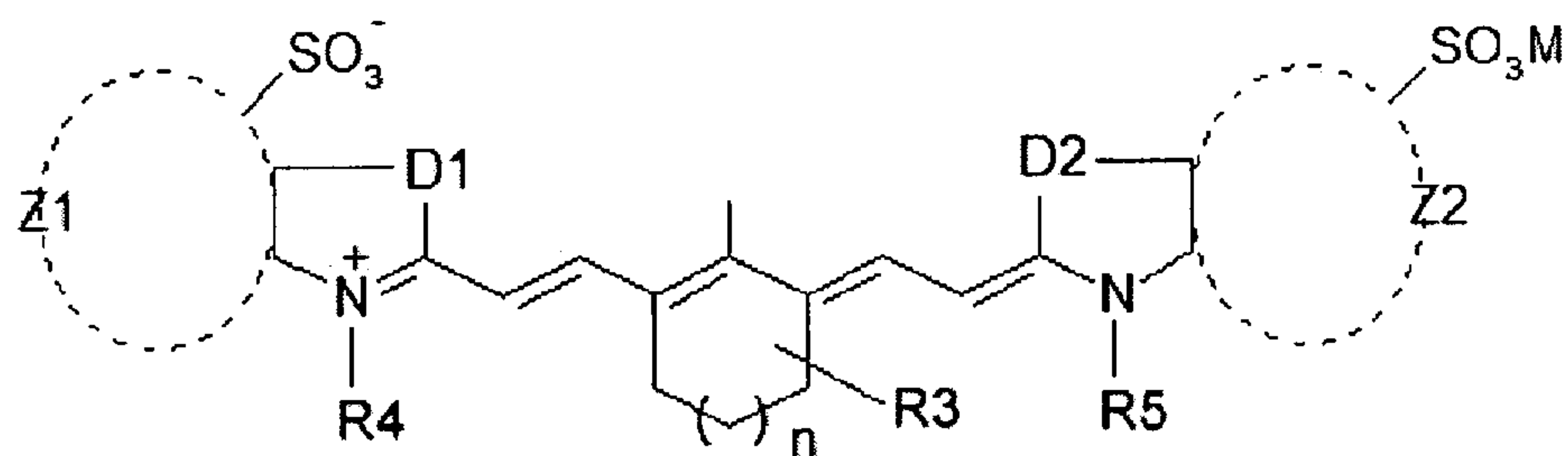
wherein NIR is a near-infrared absorbing chromophore that exhibits one or more strong absorption peaks between 700 and 1100 nm and may optionally exhibit one or more strong absorption peaks between 400 and 700 nm.

[0032] The polyvinyl alcohol acetal polymer of the invention may also comprise different G3 segments comprising different near-infrared absorbing chromophores.

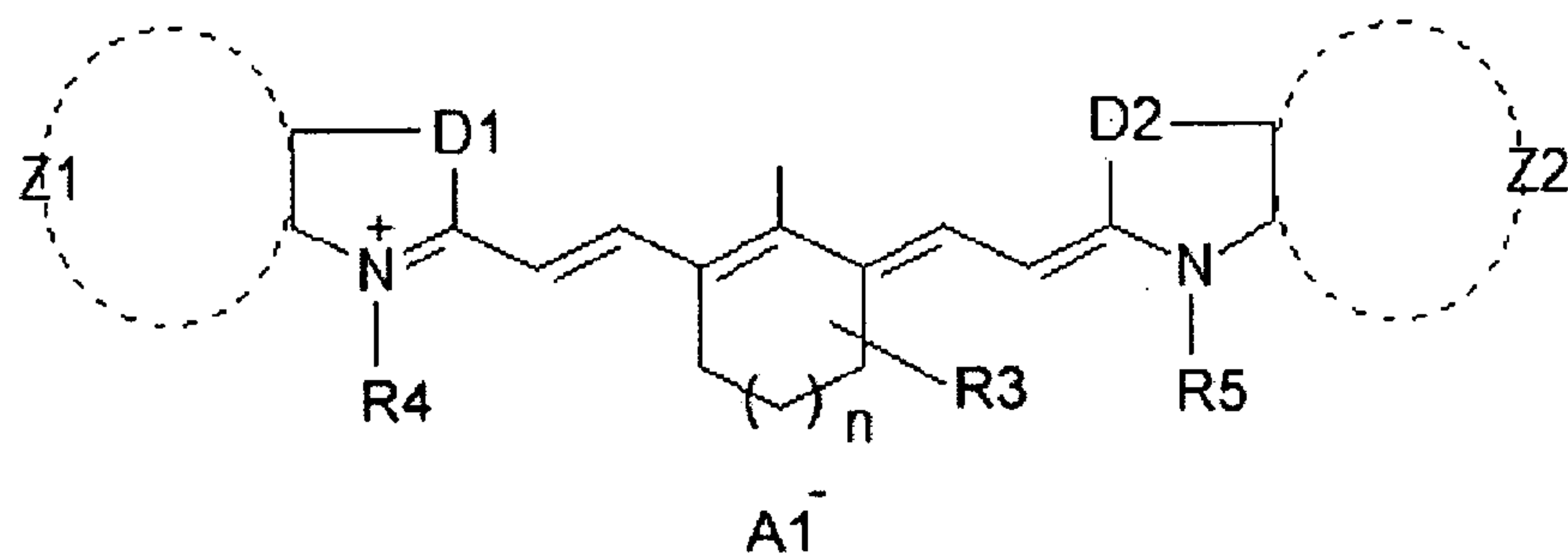
[0033] The near-infrared absorbing chromophores (NIR chromophores) may be near infrared absorbing organic compounds containing cyanine and/or arylimine functional groups. These chromophores may have the following structures:



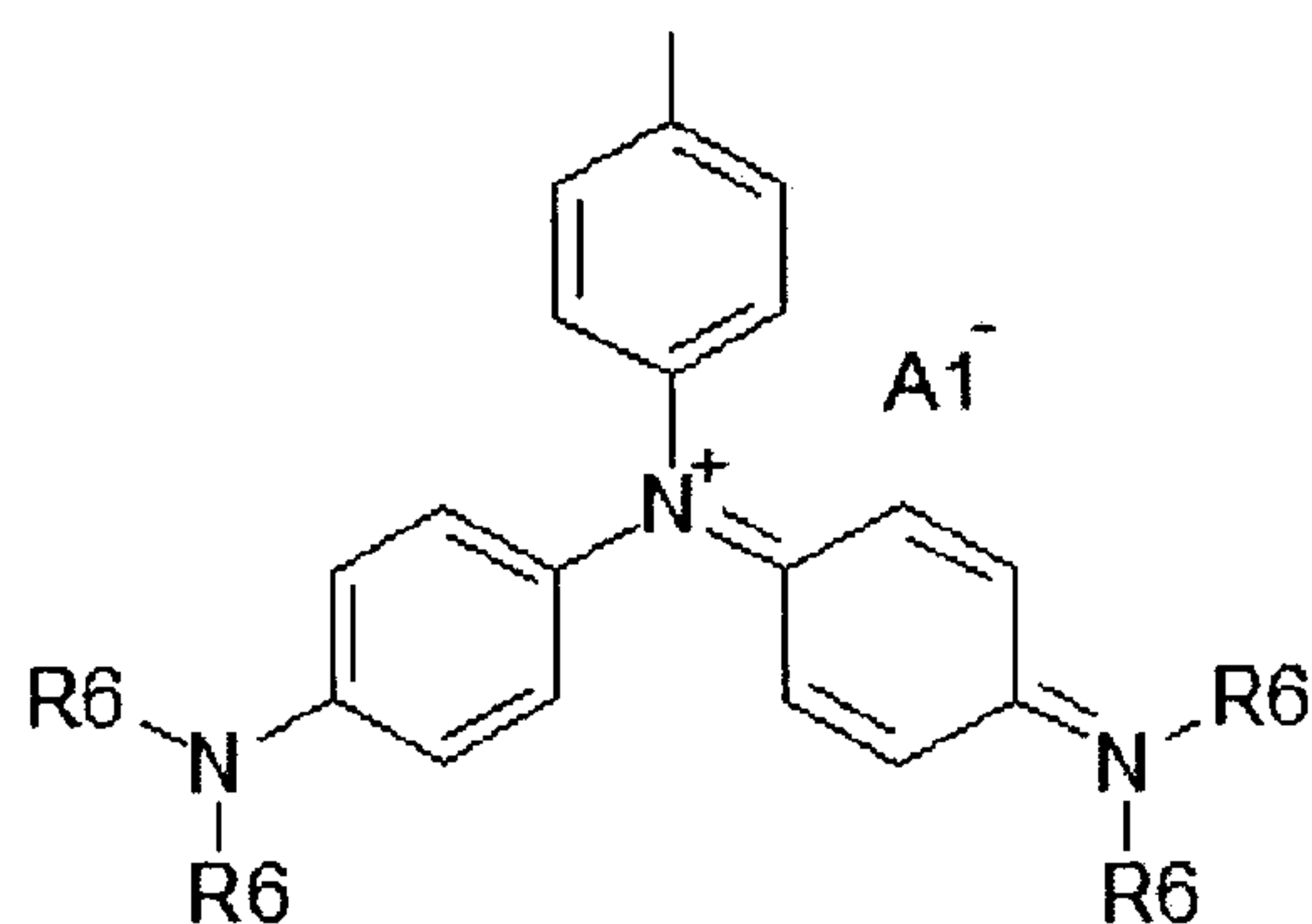
NIR Chromophore I



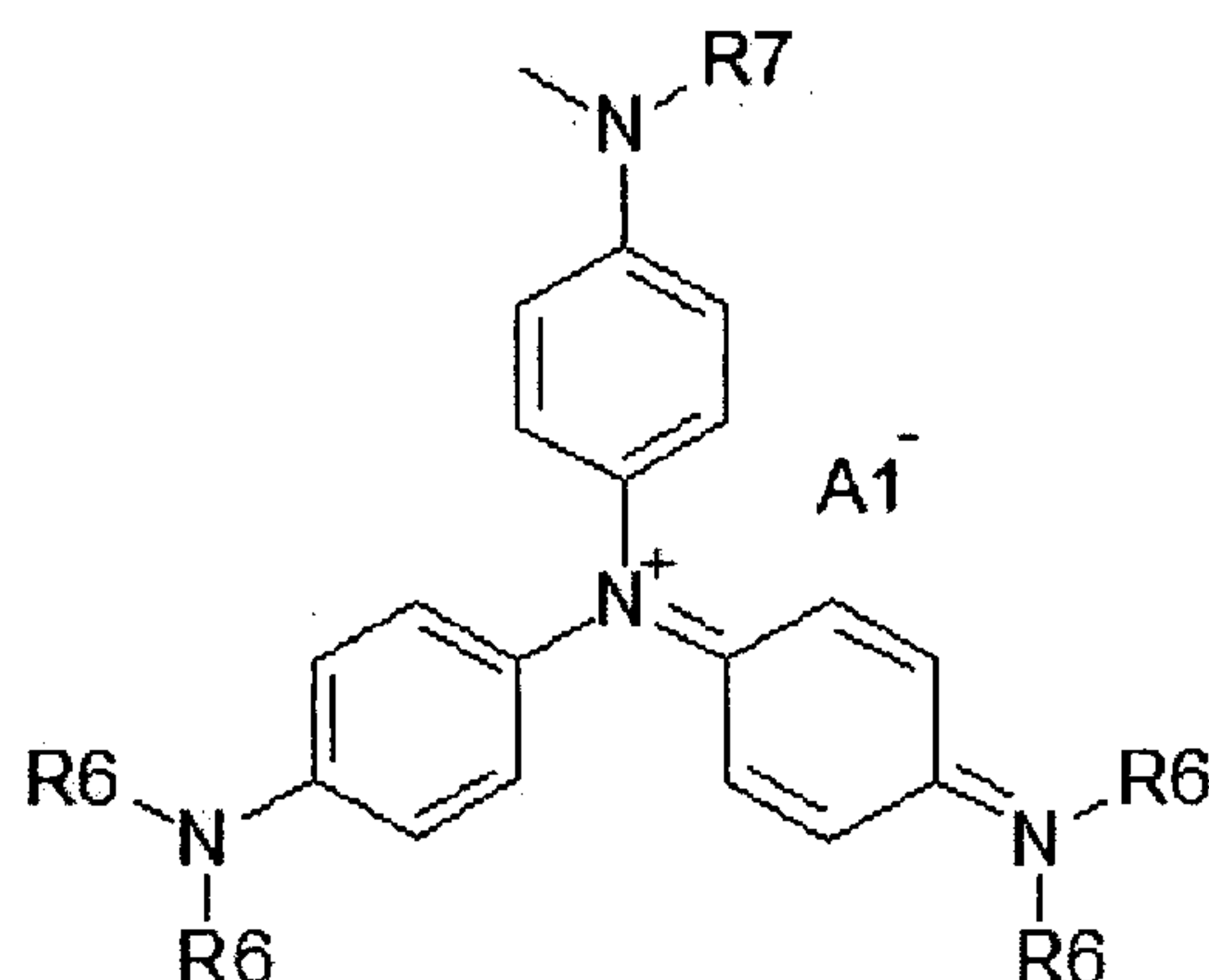
NIR Chromophore II



NIR Chromophore III



NIR Chromophore IV

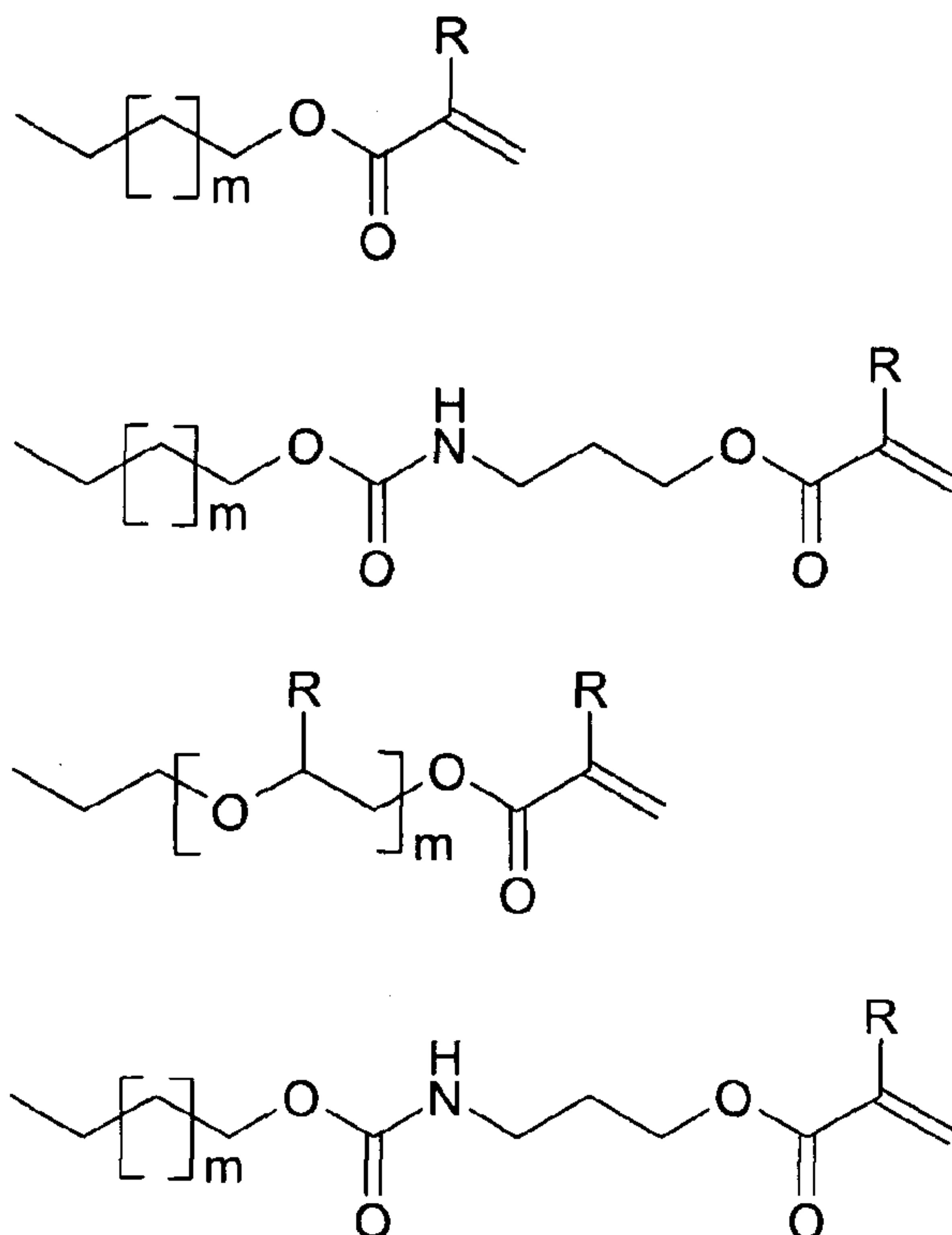


NIR Chromophore V

wherein:

- D1 and D2 are identical or different and represent -O-, -S-, -Se-, -CH = CH-, and -C(CH₃)₂;
- Z1 and Z2 are identical or different and represent one or more fused substituted or unsubstituted aromatic rings, such as phenyl and naphthyl;
- h represents integer number from 2 to 8;
- n represents 0 or 1;
- M represents hydrogen or a cationic counter ion selected from Na, K, and tetraalkylammonium salts.
- A1 represents an anionic counter ion selected from bromide, chloride, iodide, tosylate, triflate, trifluoromethane carbonate, dodecyl benzosulfonate and tetrafluoroborate, tetraphenylborate and triphenyl-n-butylborate.
- R3 and R7 represent hydrogen or alkyl; and
- R4, R5 and R6 are identical or different and represent alkyl, aryl alkyl, hydroxy alkyl, amino alkyl, carboxy alkyl, sulfo alkyl.

[0034] In a specific embodiment, R4, R5 and R6 may represent a polymerizable substituents having the following structure:



wherein:

- m is a number of $-\text{CH}_2-$ on the alkyl chain and may vary between 0 and 50; and
- R is hydrogen or methyl.

[0035] The near infrared absorbing polyvinyl alcohol acetal copolymers may be used in the coating of the present invention in quantities ranging from about 5 to 50 % by solid weight.

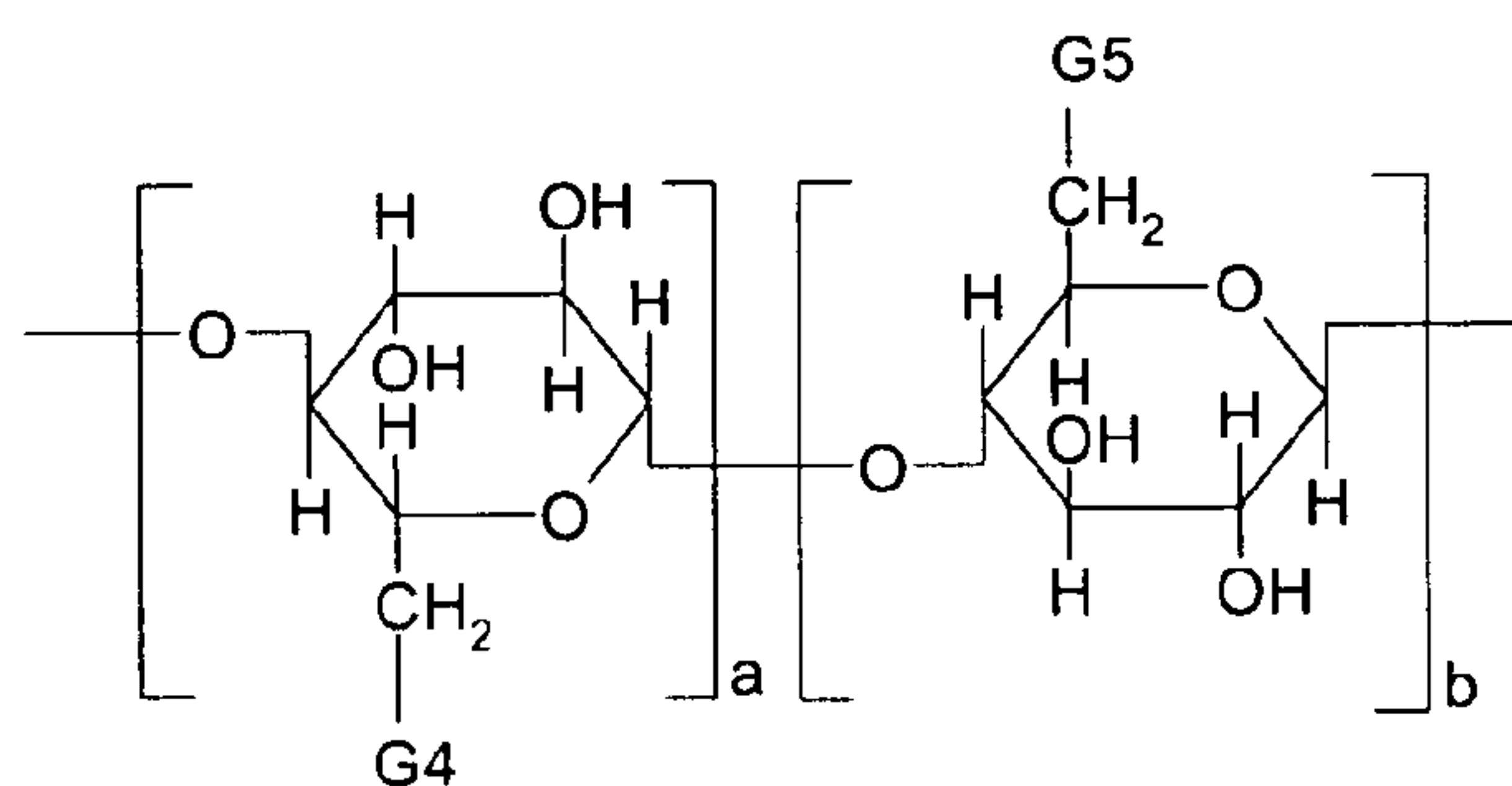
Polymer binders

[0036] The coating/coating solution of the present invention may also comprise a polymer binder. This polymer binder may be used in the coating in quantities ranging from about 1 to about 50 % by solid weight.

[0037] More specifically, the polymer binders of this invention may be polymers, copolymers or dendrimers, which may comprise functional group(s) which can undergo radical and/or cationic polymerization. Therefore, when the iodonium salt produces acid/radicals, these functional groups will react with other such functional groups present in the coating, for example that of the iodonium salt and the dye (if present), to produce chemical links, and contribute to the formation of a network within the coating.

[0038] Specifically, these functional groups may be acrylate, methacrylate, and vinyl ether. More specifically, these functional groups may be cation reactive functional groups such as hydroxy, alkoxy-methyl acrylamide, alkoxy methacrylamide, N-methoxymethylacrylamide and N-methoxymethylmethacrylamide.

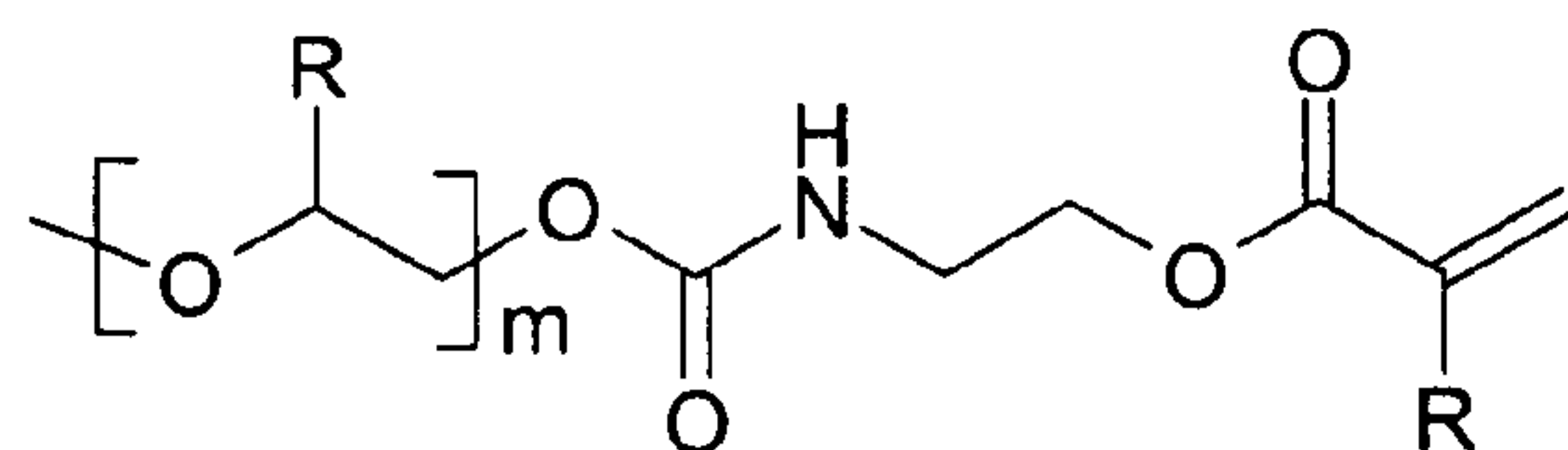
[0039] The polymer binders of the invention may be solvent- and/or water-soluble cellulose ethers comprising a functional group which can undergo radical and/or cationic polymerization. This cellulose ether may be obtained by reacting of 2-isocyanato-ethyl methacrylate with the hydroxymethyl, hydroxyethyl and hydroxypropyl group on the cellulose backbone. The cellulose ether of the invention may have the following structure:



wherein:

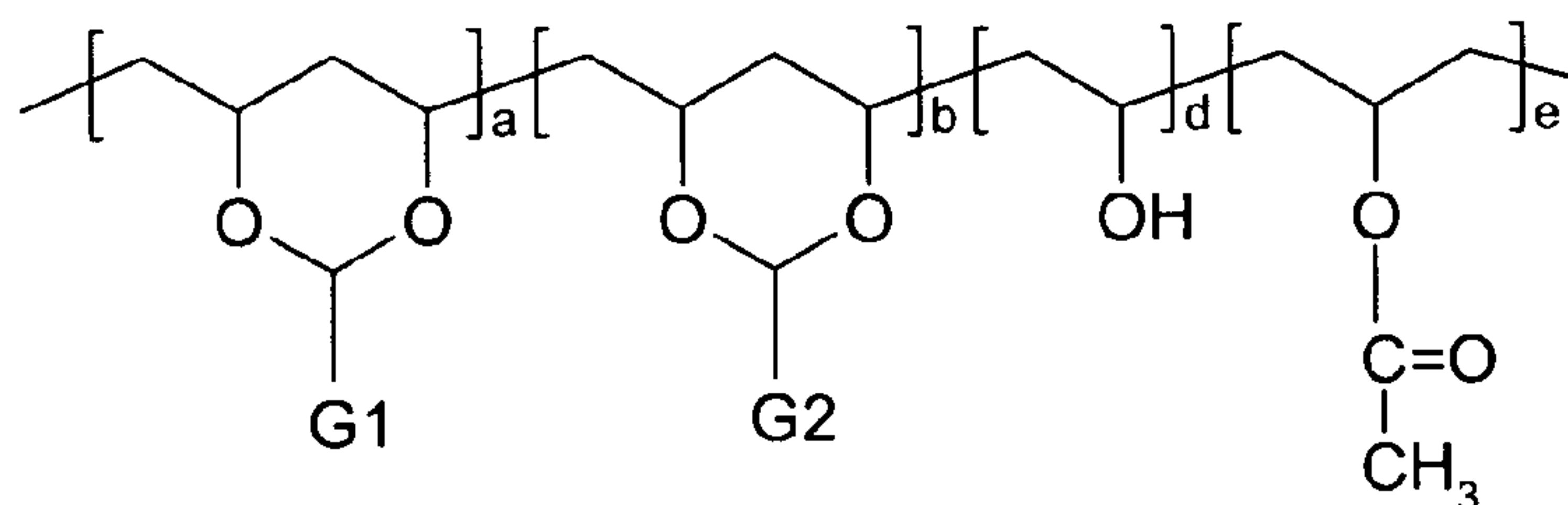
- G4 is hydroxy, hydroxyethyl and hydroxypropyl.
- G5 is the functional group which can undergo radical and/or cationic polymerization.

[0040] More specifically, the G5 groups may have the following structure

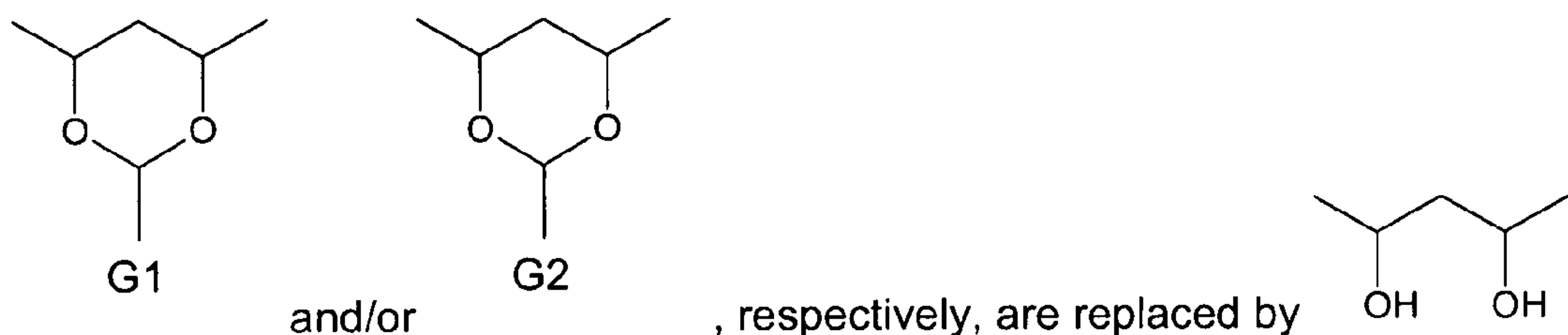


wherein m is 0 or 1 and R is hydrogen or methyl.

[0041] The polymer binder of the invention may also be an polyvinyl alcohol acetal copolymer which does not absorb near infrared radiation. More precisely, the polyvinyl alcohol acetal copolymers of this invention may have the following general structure:



wherein G1, G2, a, b, d and e are similar to those defined in Formula 1 as above and wherein when the optional G1 and/or G2 segments are not present,



[0042] The polymer binders of the invention may also be copolymers comprising a functional group which can undergo radical and/or cationic polymerization. Such copolymers can be obtained from acrylonitrile, styrene, poly(ethylene glycol) acrylate, poly(ethylene glycol) methacrylate and methoxymethylmethacrylamide monomers.

[0043] Also, copolymers of the invention may be obtained by copolymerizing at least one monomer selected from:



- m and w are represent the number of repeat unit and may vary between 0 and 50;
- R is hydrogen or methyl;
- R11 is linear and branched alkyl chain; and
- R12 is alkyl, hydroxyl and carboxylic acid.

[0044] The polyvinyl alcohol acetal copolymer of the present invention may be used in the preparation of a coating/coating solution. The coating/coating solution may also comprise the iodonium salt of the present invention and a polymer binder in the above mentioned quantities.

[0045] The polymer binder of the present invention may be used in the preparation of a coating/coating solution. The coating/coating solution may also comprise the iodonium salt of the present invention and a near-infrared absorbing moiety in the above mentioned quantities.

Colorants and stabilizers

[0046] The coatings/coating solutions of the invention may also comprise colorants to provide good image printout after laser imaging. These colorants of this invention may be the derivatives of triarylpyridine, xanthene and isobenzofuranone. These color-generating compounds may be colorless and then become colored in the presence of free radical or acid. More specifically, these compounds may be:

- 3',6'-bis[N-[2-chlorophenyl]-N-methylamino]spiro[2-butyl-1,1-dioxo[1,2-benz isothiazole-3(3H),9'-(9H)xanthene]](prepared by the method of US Patent No. 4,345,017);
- 3',6'-bis[N-[2-[methanesulfonyl]phenyl]-N-methylamino]spiro[2-butyl-1,1-dioxo[1,2-benzisothiazole-3(3H),9'-(9H)xanthene]](prepared by the method of US Patent No. 4,345,017);
- 9-Diethylamino[spiro[12H-benzo(a)xanthene-12,1'(3'H)-isobenzofuran)-3'-one] (available from BF Goodrich, Canada);
- 2'-di(phenylmethyl)amino-6'-[diethylamino]spiro[isobenzofuran-1(3H),9'-(9H)-xanthen]-3-one (available from BF Goodrich, Canada);
- 3-[butyl-2-methylindol-3-yl]-3-[1-octyl-2-methylindol-3-yl]-1-(3H)-isobenzofuranone (available from BF Goodrich, Canada);

- 6-[dimethylamino]-3,3-bis[4-dimethylamino]-phenyl-(3H)-isobenzofuranone (available from BF Goodrich, Canada);
- 2-[2-Octyloxyphenyl]4-[4-dimethylaminophenyl]-6-phenylpyridine (available from BF Goodrich, Canada); or
- Leuco lactone dyes, such as Blue-63, GN-169 and Red-40 (available from Yamamoto Chemicals Inc., Japan).

[0047] The colorants may be used in the coatings of the present invention in quantities ranging from 0.5 to 5 % by solid weight.

[0048] The coatings/coating solutions of the invention may also comprise stabilizers to prolong the shelf-life of the printing plates during storage. These stabilizers may be methoxyphenol, hydroxyphenol, phenothiazine, 3-mercapto triazol or monomethyl ether hydroquinone. These stabilizers may be used in the coatings of the present invention in quantities ranging from 0.5 to 5 % by solid weight.

Negative-working lithographic printing plates

[0049] The coating solutions of the present invention may be used in the preparation of negative-working lithographic printing plates.

[0050] This invention therefore also relates to printing plates containing the iodonium salts, the polyvinyl alcohol acetal copolymers and/or the polymer binders of the present invention. These lithographic offset printing plates may be directly imaged with near-infrared laser imaging devices in computer-to-plate and digital offset printing technologies.

[0051] More specifically, such coating solutions may be used in the production of on-press developable negative-working lithographic offset printing plates that comprise single- or multiple-layer coatings deposited on a substrate such as anodized aluminum, plastic films or paper.

[0052] The aluminum substrate may be brushed-grained or electro-grained, then anodized with acidic solutions.

[0053] The anodized aluminum substrate may be coated with a polymeric adhesion-promoting layer. The adhesion-promoting and heat insulating layer may be obtained from water solutions containing poly(acrylic acid), poly(acrylic acid-co-vinylphosphoric acid) or polyvinyl phosphoric acid, which are then dried using hot air at

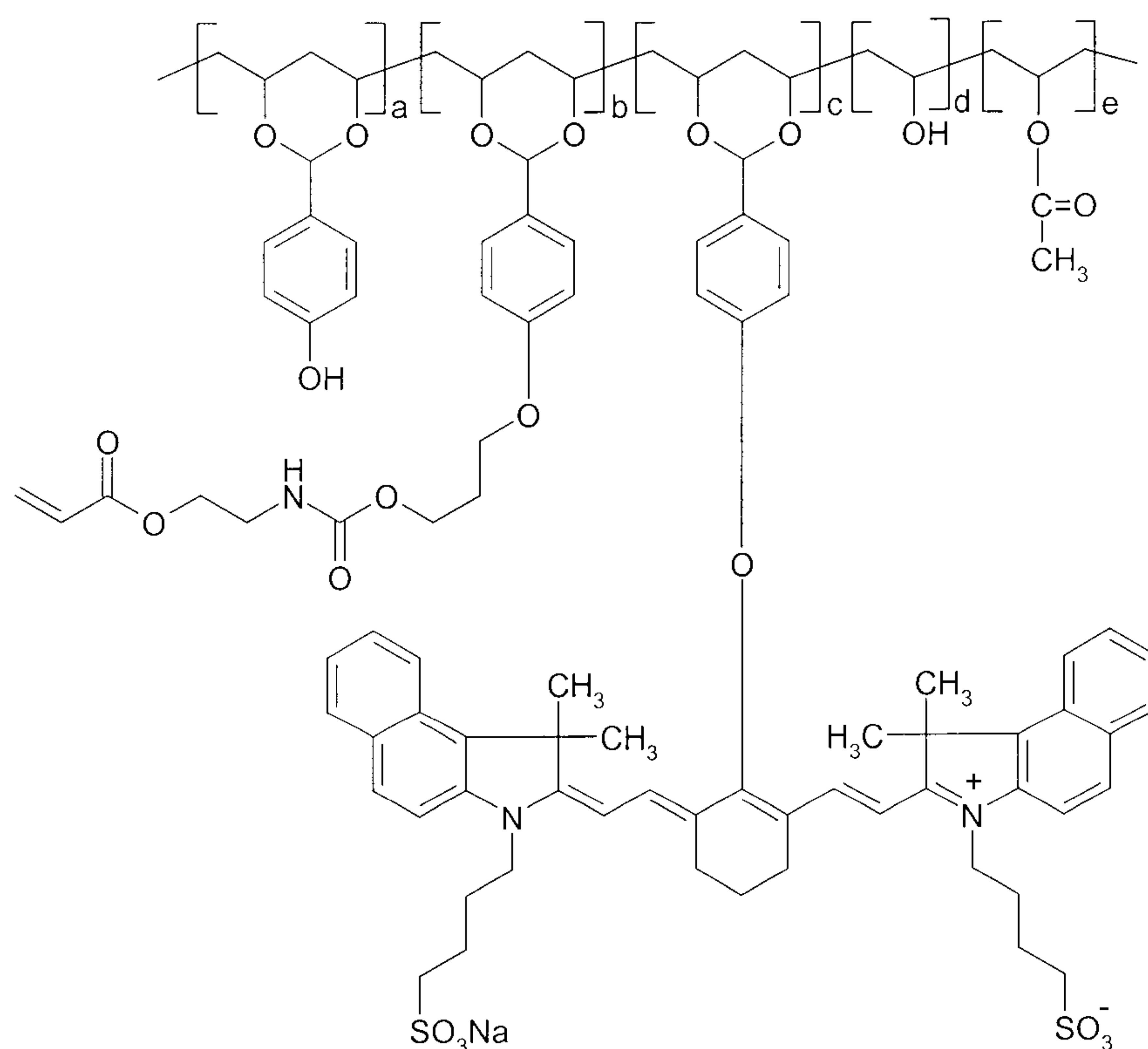
about 110°C. The coating weight of the adhesion-promoting layer may be between about 0.1 and about 1.0 g/m².

[0054] The thermally reactive coating solutions may be deposited on top of the adhesion-promoting layer and may have a coating weight between about 0.5 and about 2.5 g/m².

[0055] Other embodiments and further scope of applicability of the present invention will become apparent from the detailed description given hereinafter. It should be understood, however, that this detailed description, while indicating preferred embodiments of the invention, is given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art.

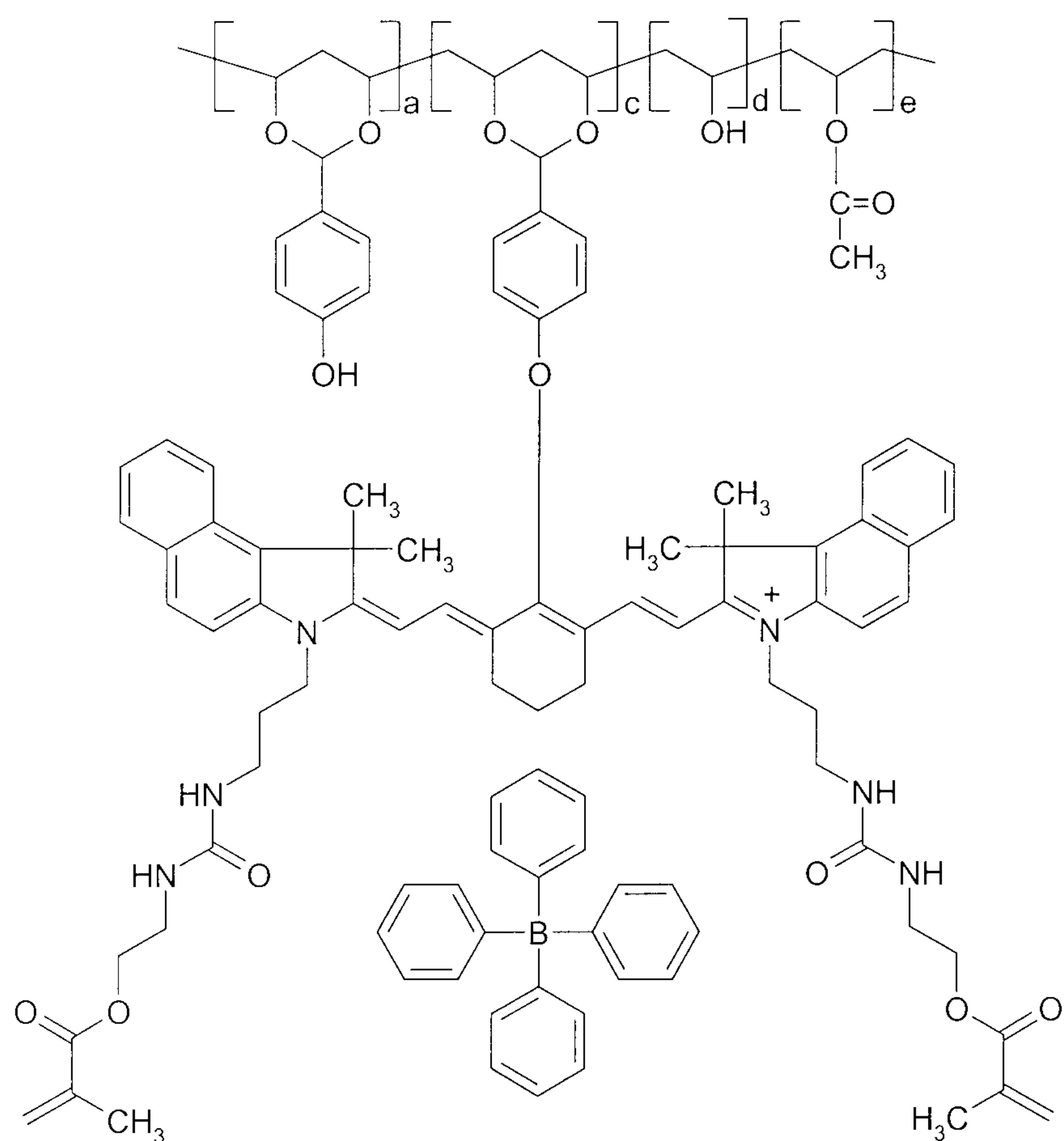
FORMULAS

[0056] Herein, Formula 1 is the ideal structure of polyvinyl alcohol acetal copolymer PVA-01:

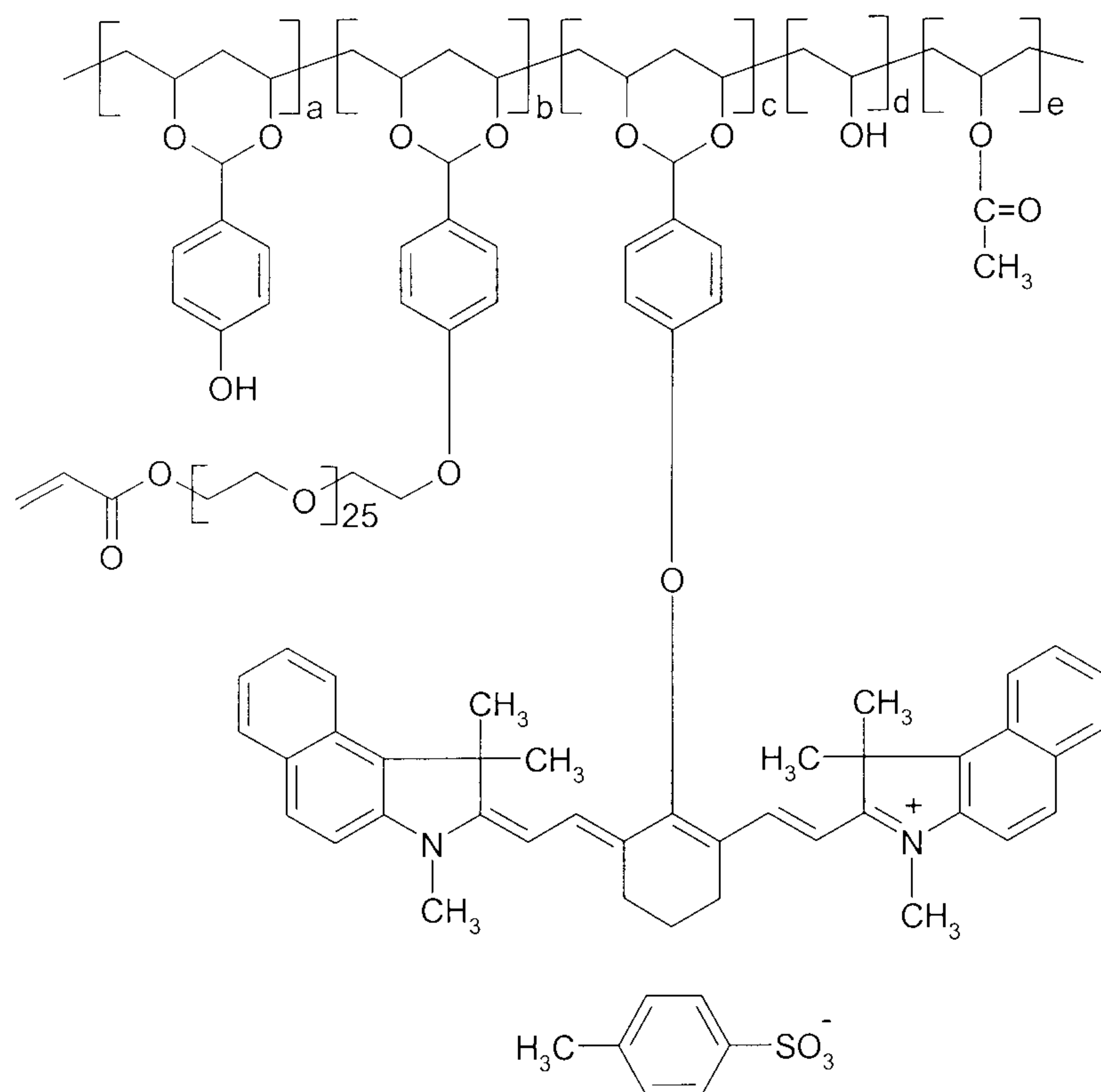


[0057] Formula 2 is the ideal structure of polyvinyl alcohol acetal copolymer PVA-02:

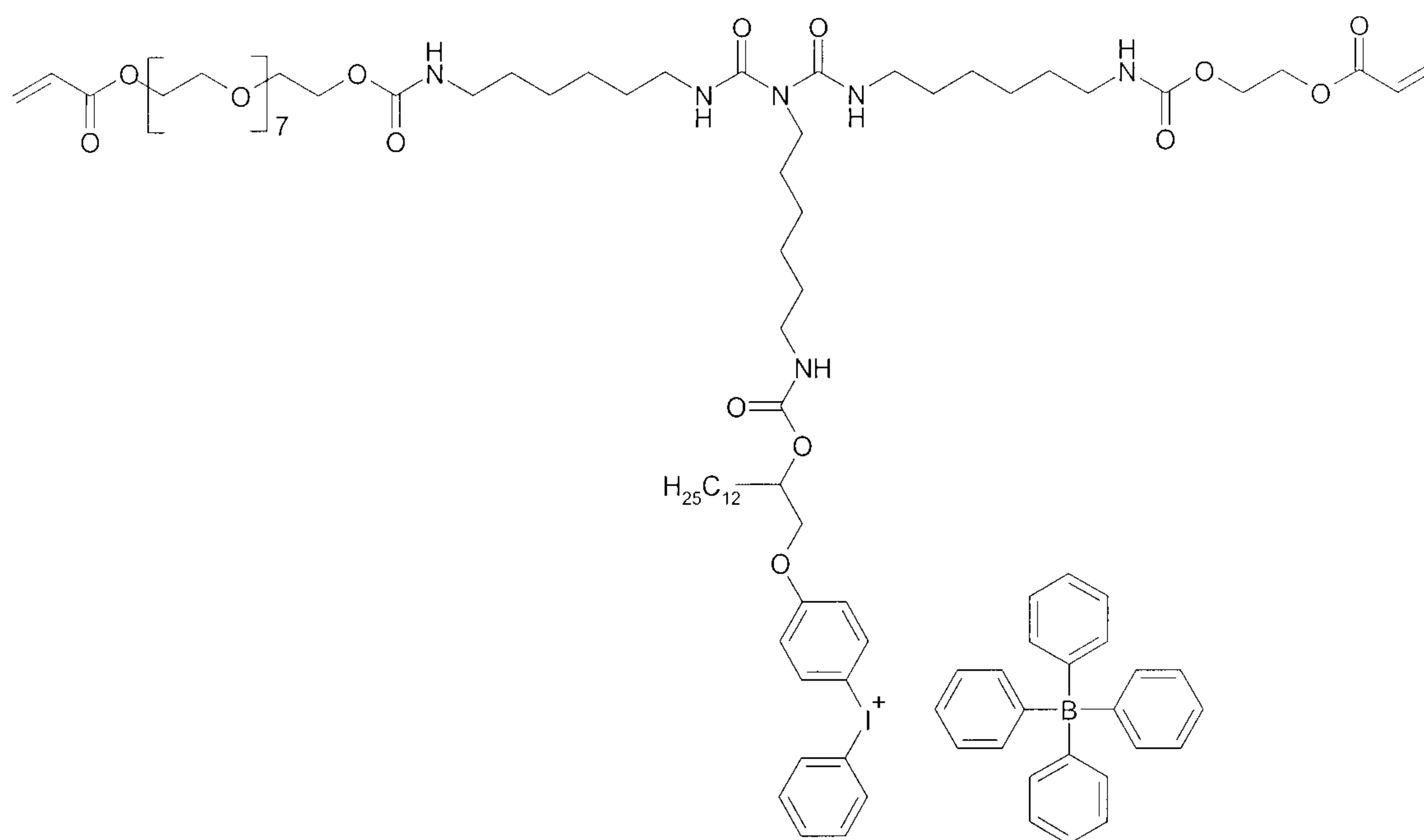
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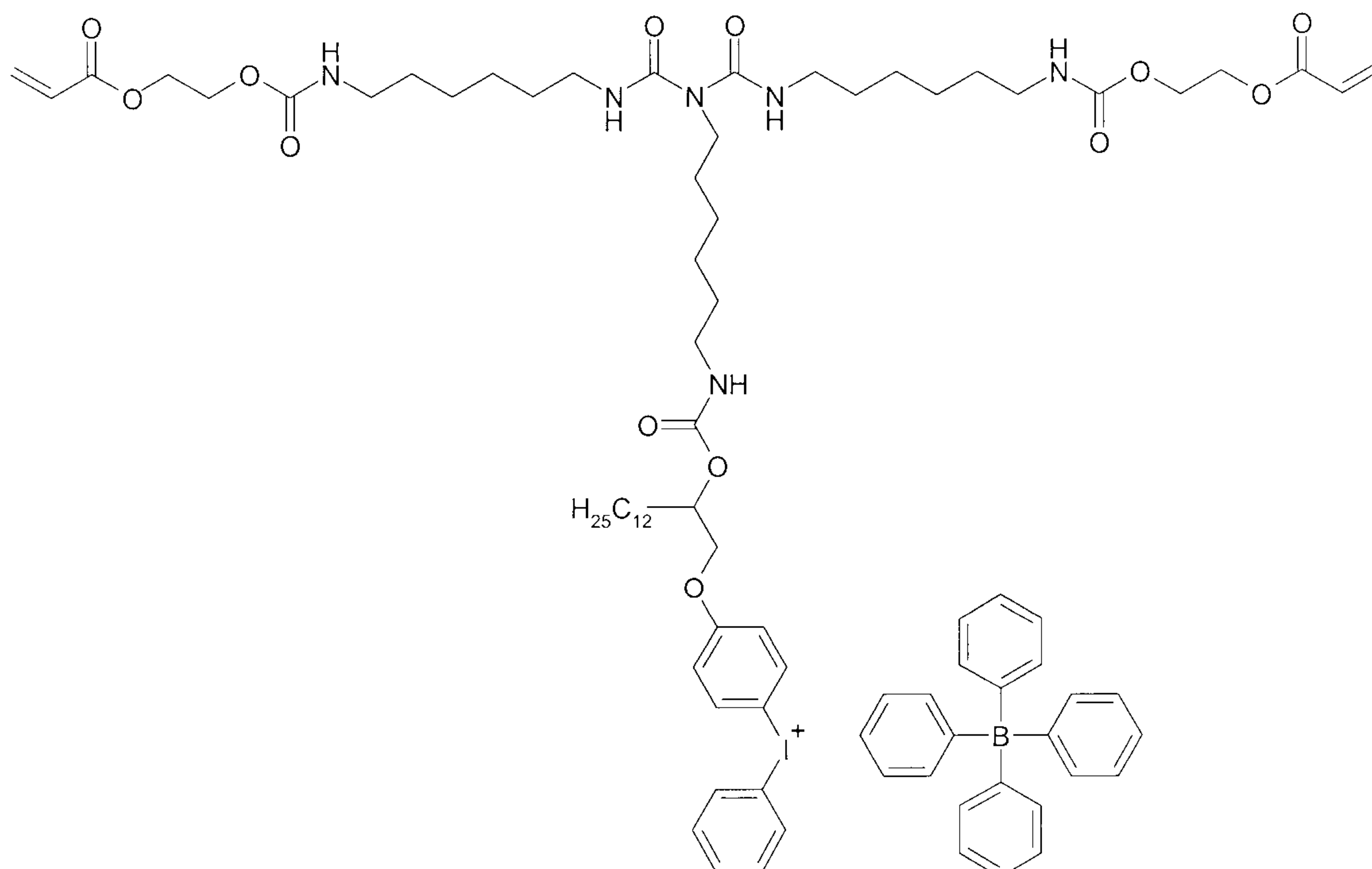
[0059] Formula 4 is the ideal structure of polyvinyl alcohol acetal copolymer PVA-04:



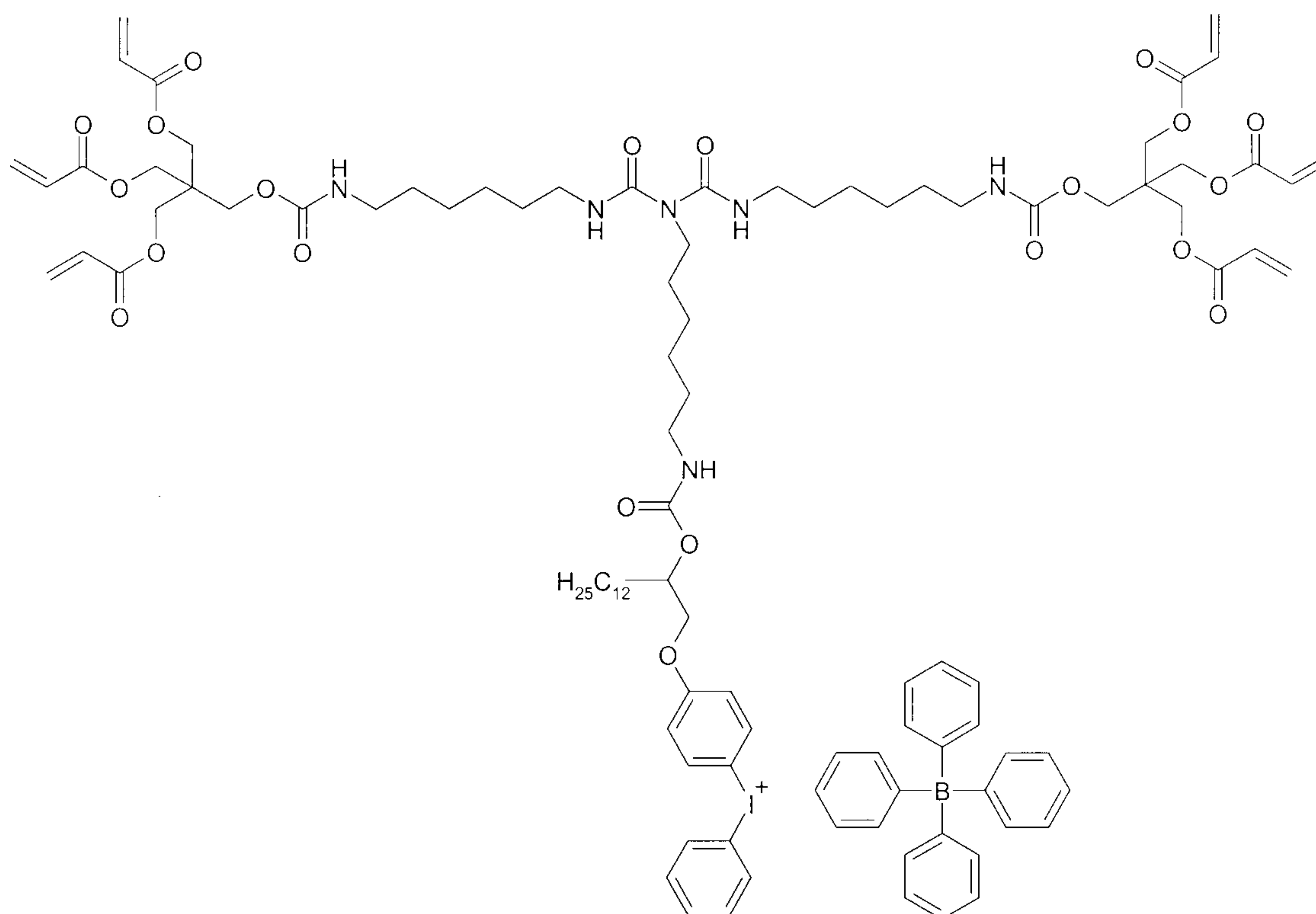
[0060] Formula 5 is the possible structure of a specific embodiment of an iodonium salt of the present invention:



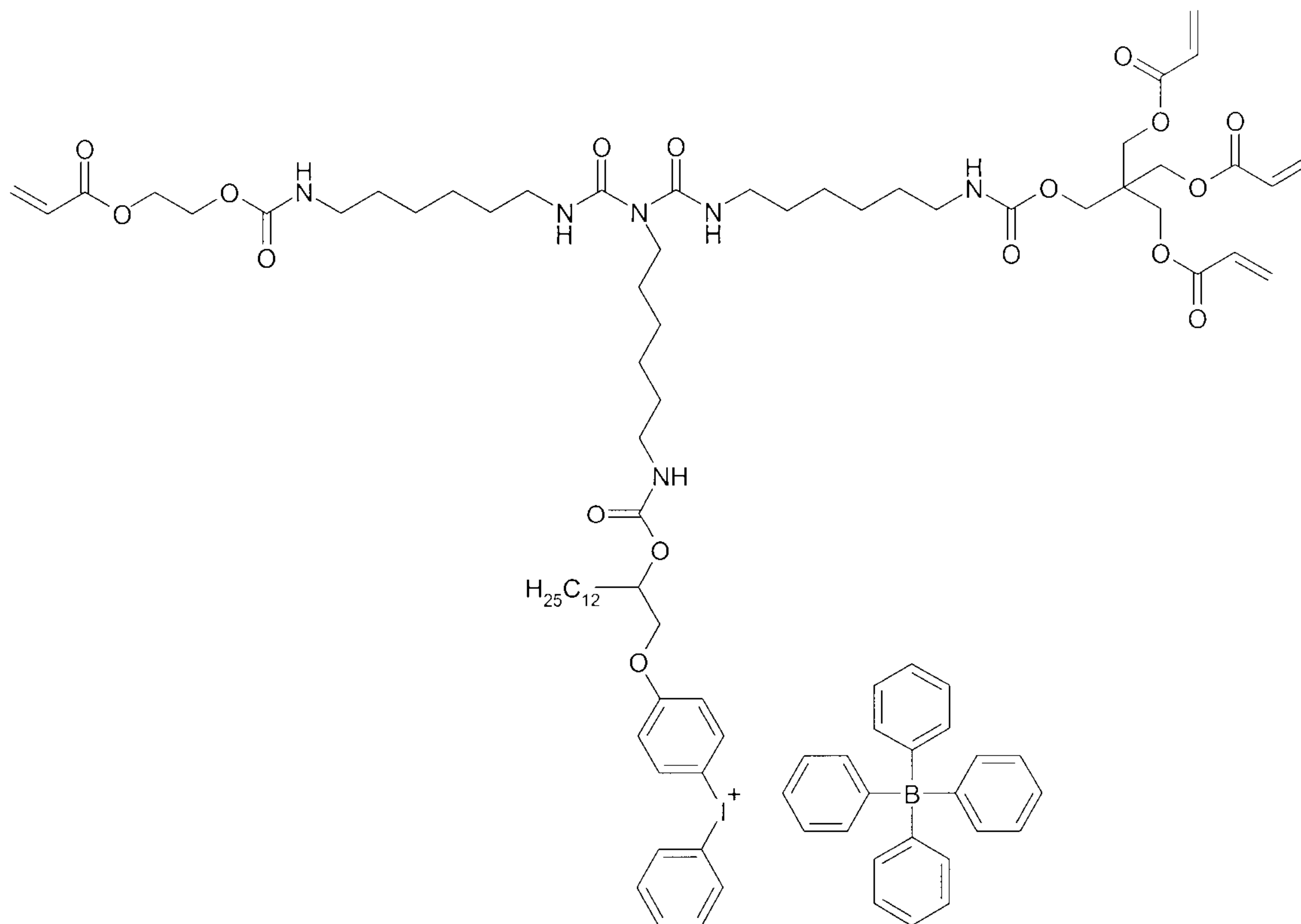
[0061] Formula 6 is the possible structure of a specific embodiment of a n iodonium salt of the present invention:



[0062] Formula 7 is the possible structure of a specific embodiment of an iodonium salt of the present invention:



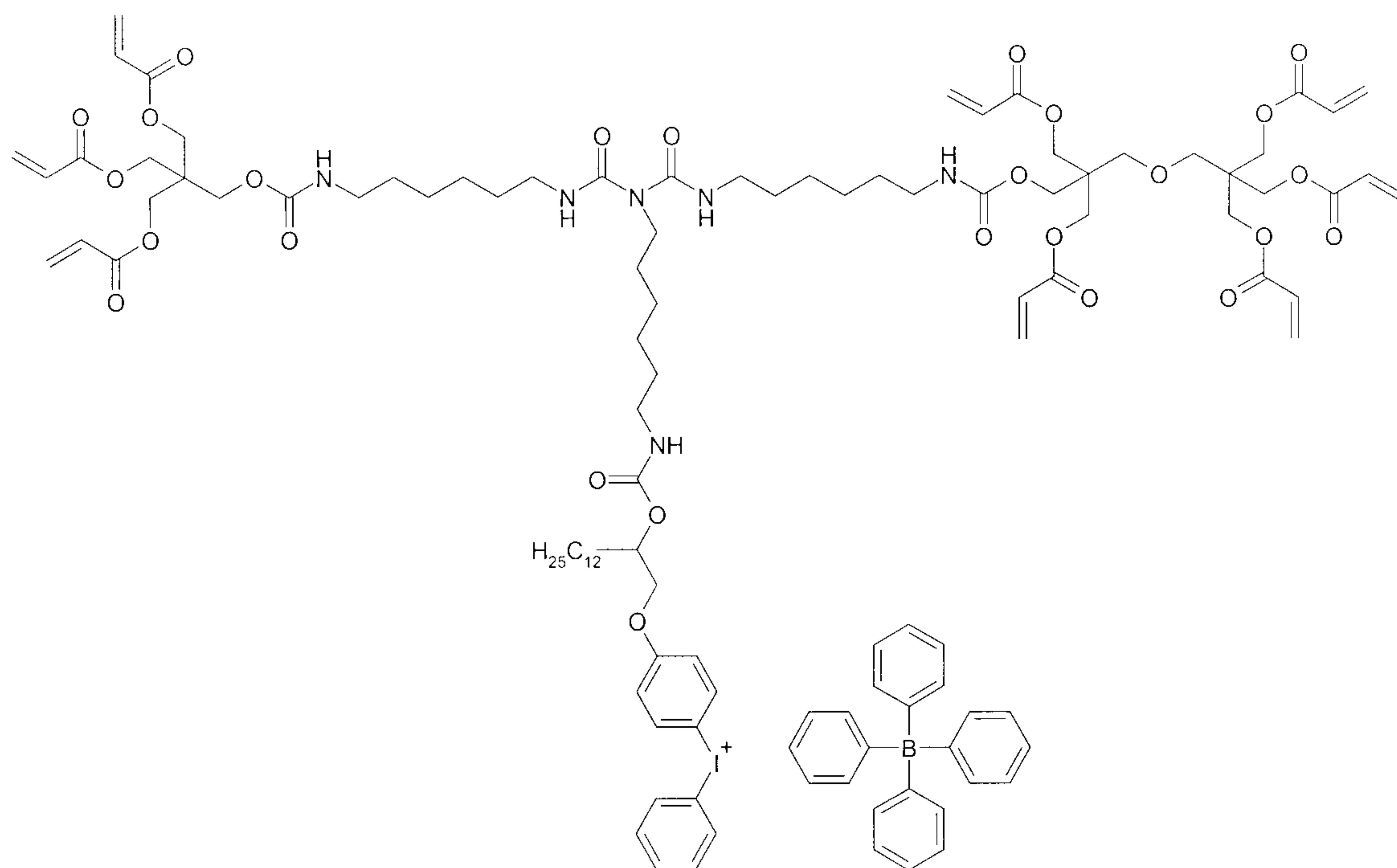
[0063] Formula 8 is the possible structure of a specific embodiment of an iodonium salt of the present invention:



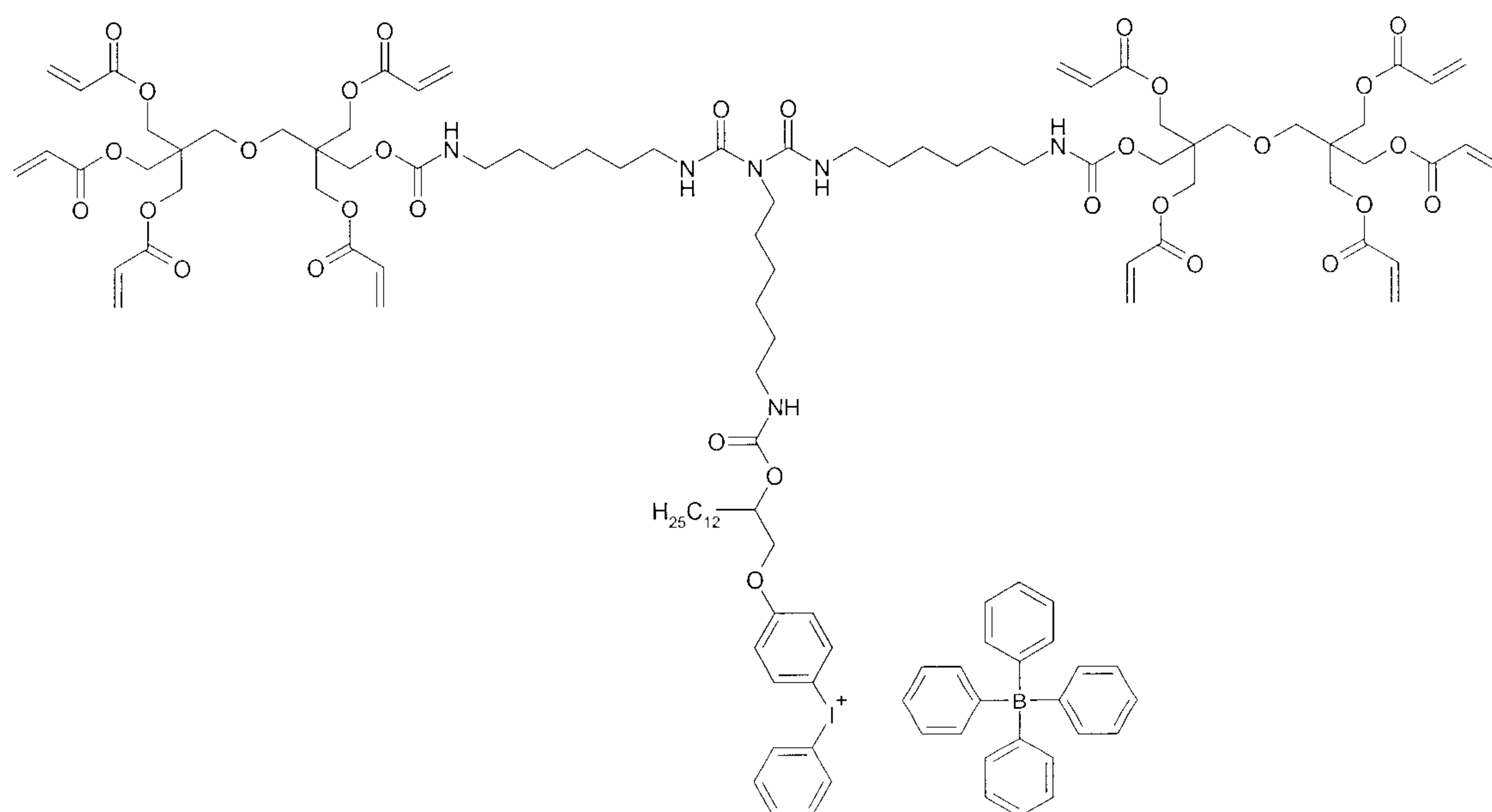
[0064] Formula 9 is the possible structure of a specific embodiment of an iodonium salt of the present invention:

C=CC(=O)OCCOCCOCCOCCOCCOCCOCCOCC(=O)NCCCCCCCCNC(=O)NCCCCCCCCNC(=O)NCCCCCCCCNC(=O)OCC(COC(=O)C=C)COC(=O)C=C
CCCCCCCCCCCCCCCCCCCCCOC(Cc1ccc(I)cc1)C(=O)NCCCCCCCCNC(=O)NCCCCCCCCNC(=O)NCCCCCCCCNC(=O)OCC(COC(=O)C=C)COC(=O)C=C
[I+](c1ccccc1)c2ccc(OCCCCCCCCCNC(=O)NCCCCCCCCNC(=O)NCCCCCCCCNC(=O)OCC(COC(=O)C=C)COC(=O)C=C)cc2
c1ccccc1B(c2ccccc2)(c3ccccc3)c4ccccc4

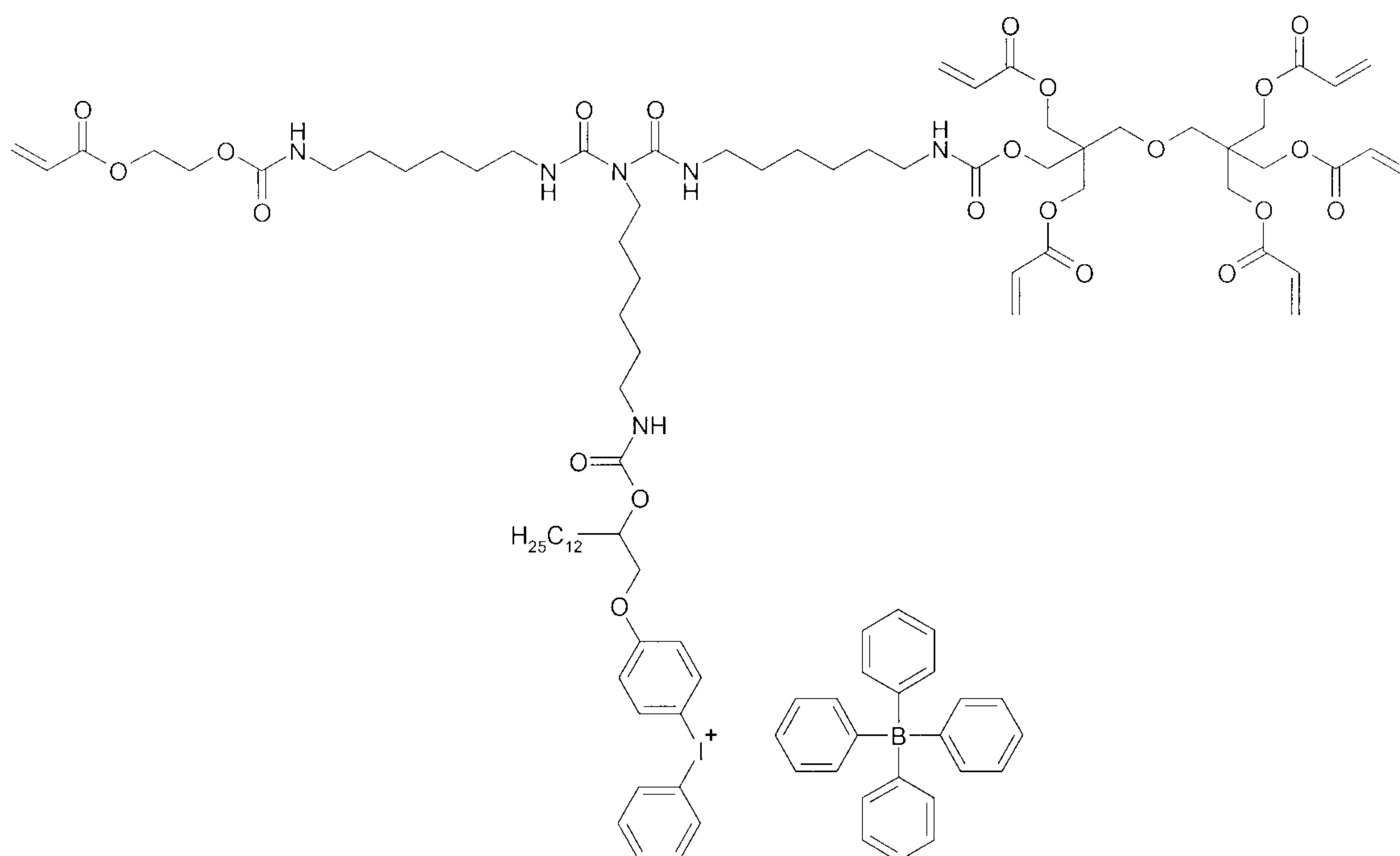
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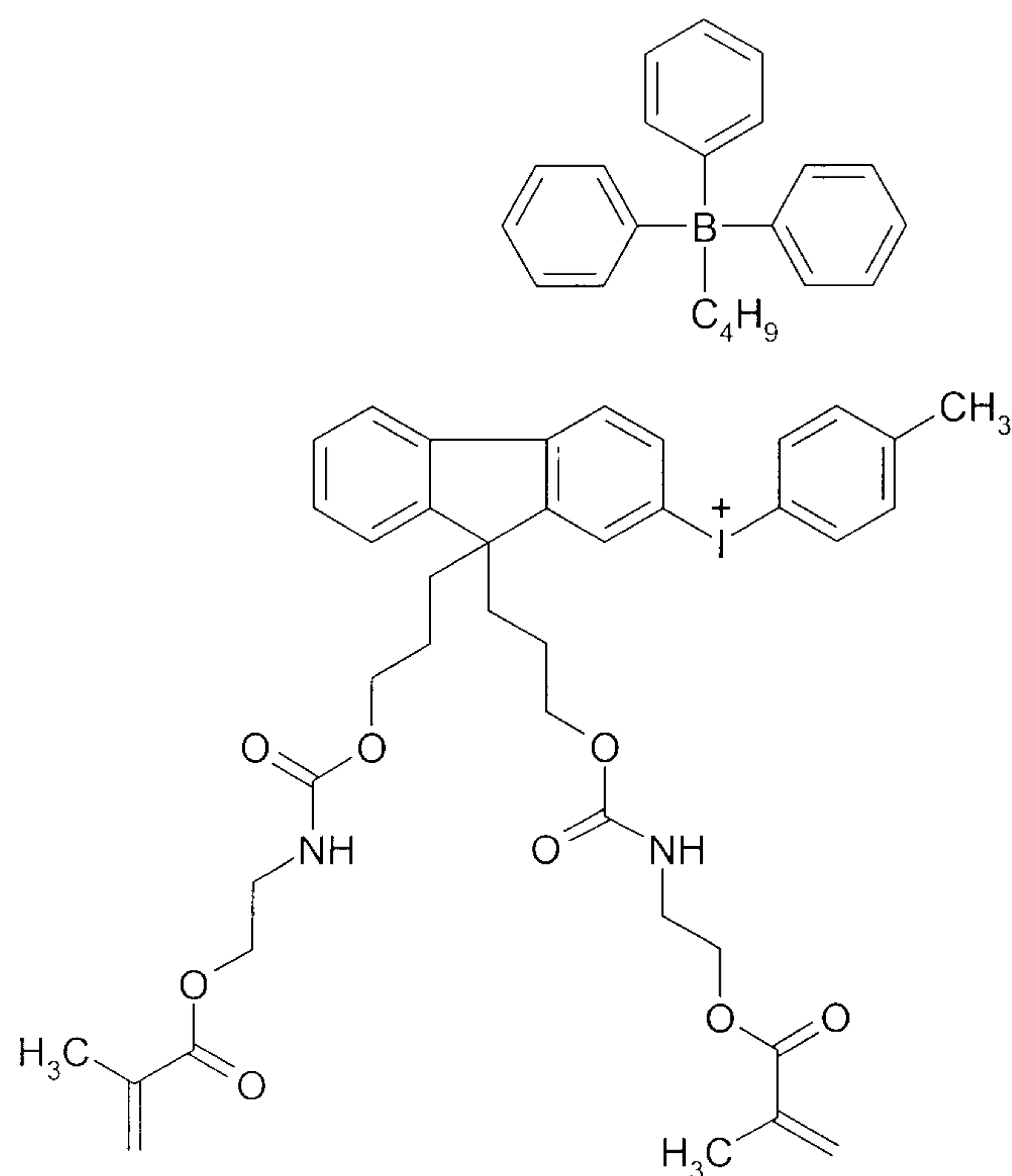
[0067] Formula 12 is the possible structure of a specific embodiment of an iodonium salt of the present invention:



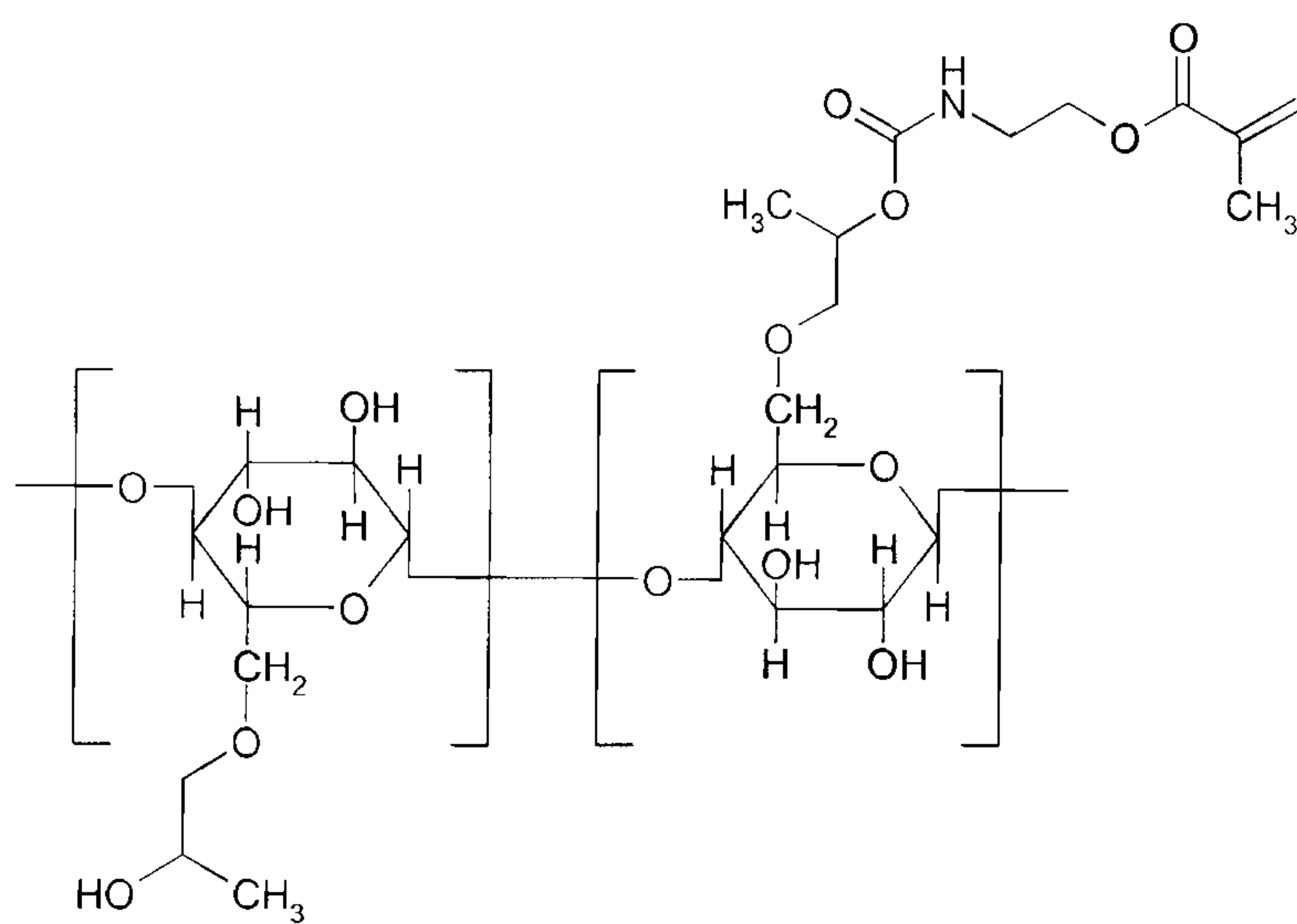
[0068] Formula 13 is the possible structure of a specific embodiment of an iodonium salt of the present invention:



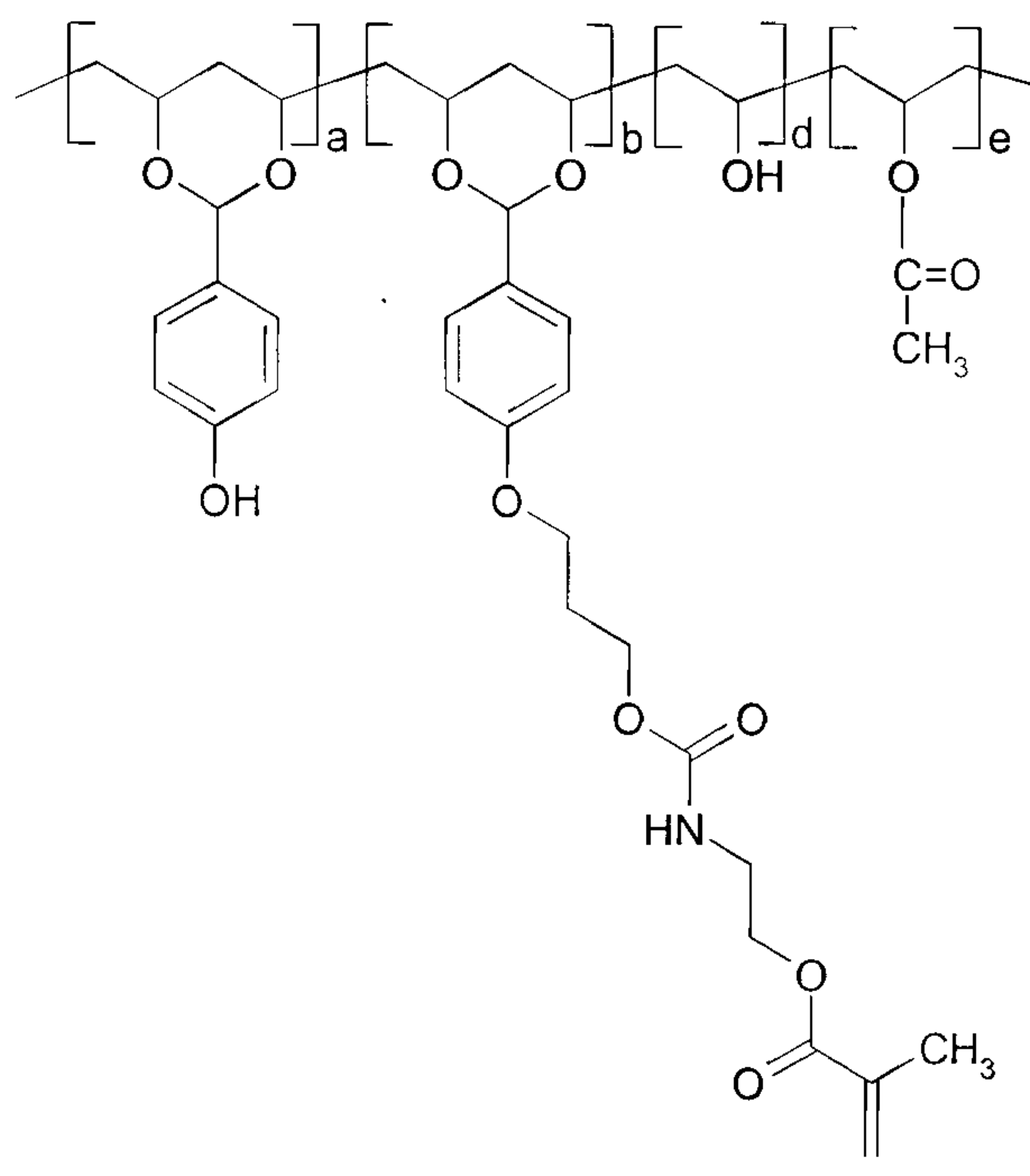
[0069] Formula 14 is the ideal structure of a specific embodiment of an iodonium salt synthesized from fluorene compound:



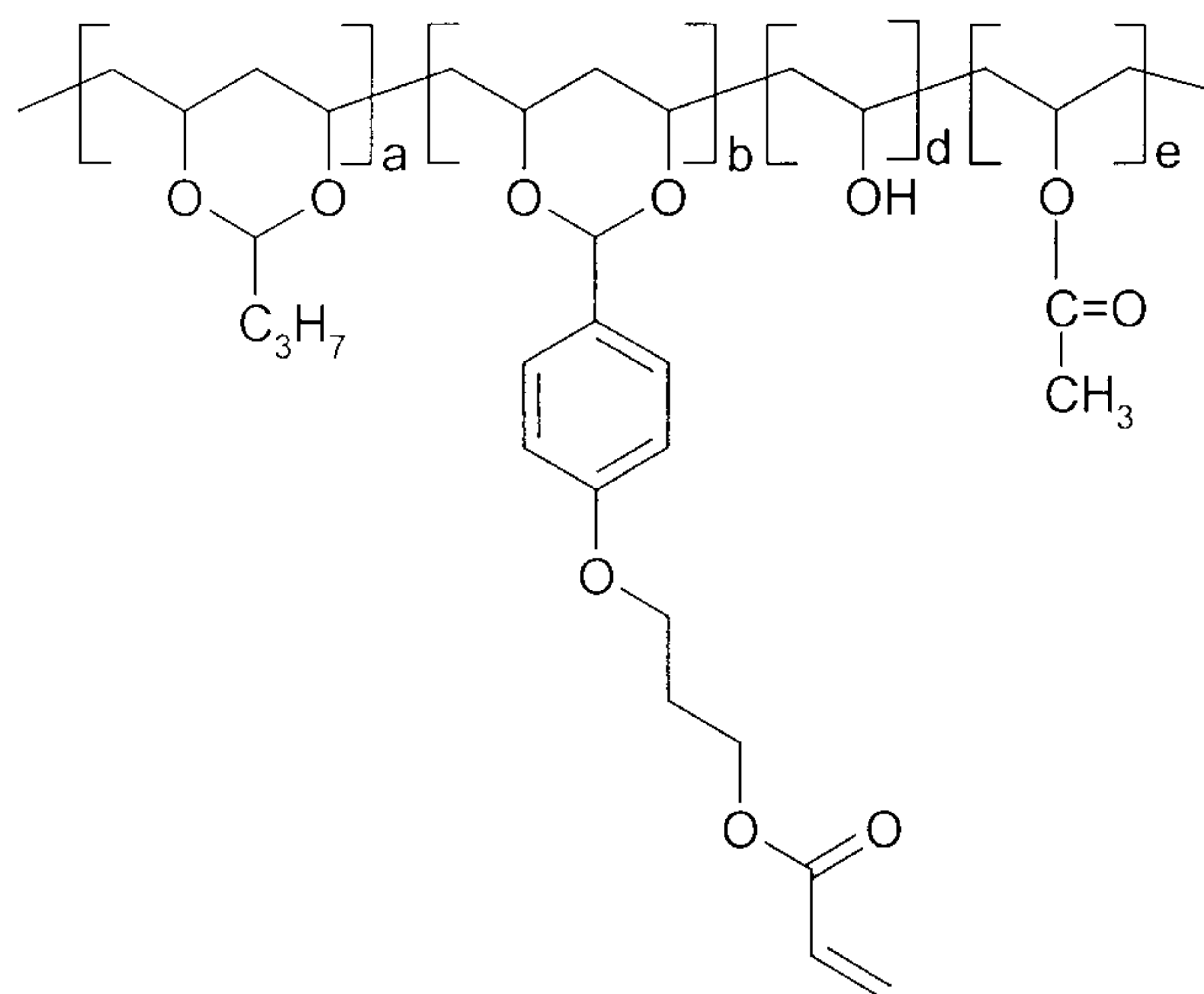
[0070] Formula 15 is the ideal structure of polymer binder RPB-01:



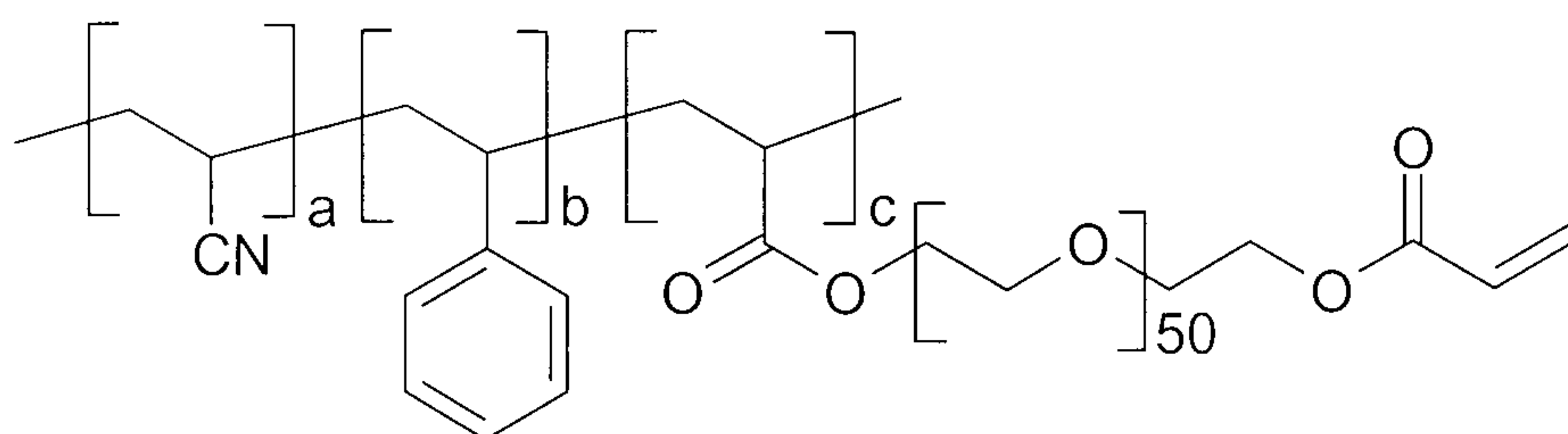
[0071] Formula 16 is the ideal structure of polymer binder RPB-03



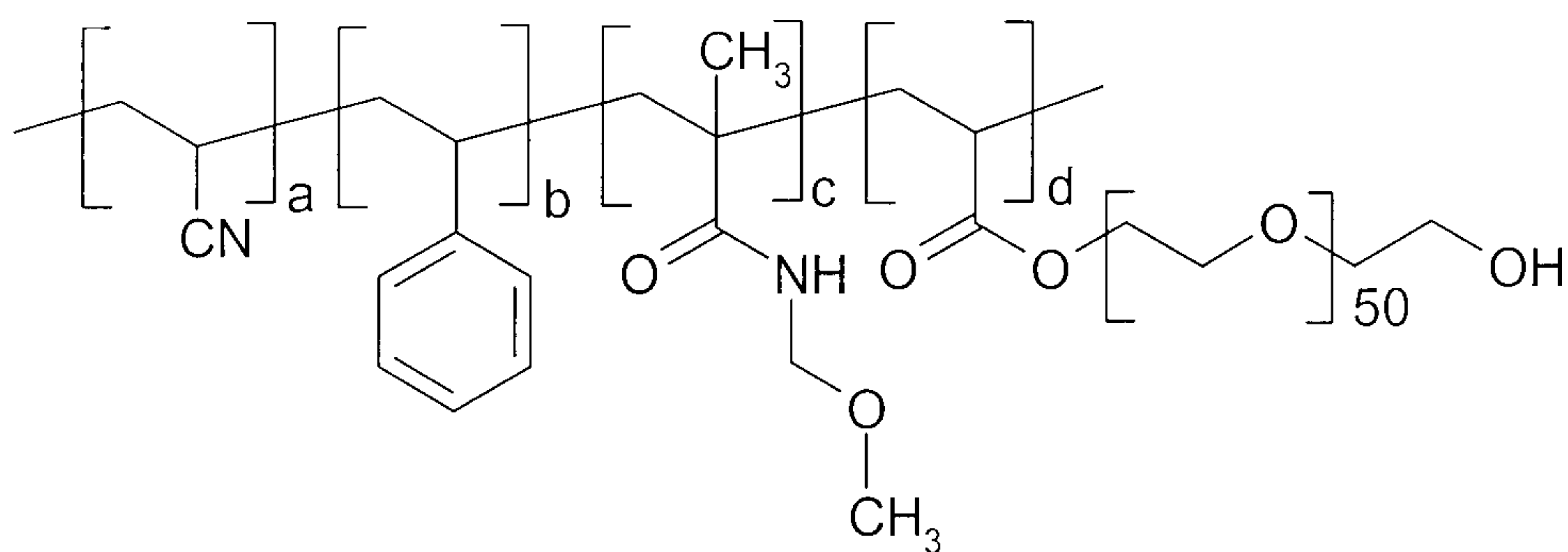
[0072] Formula 17 is the ideal structure of polymer binder RPB-04



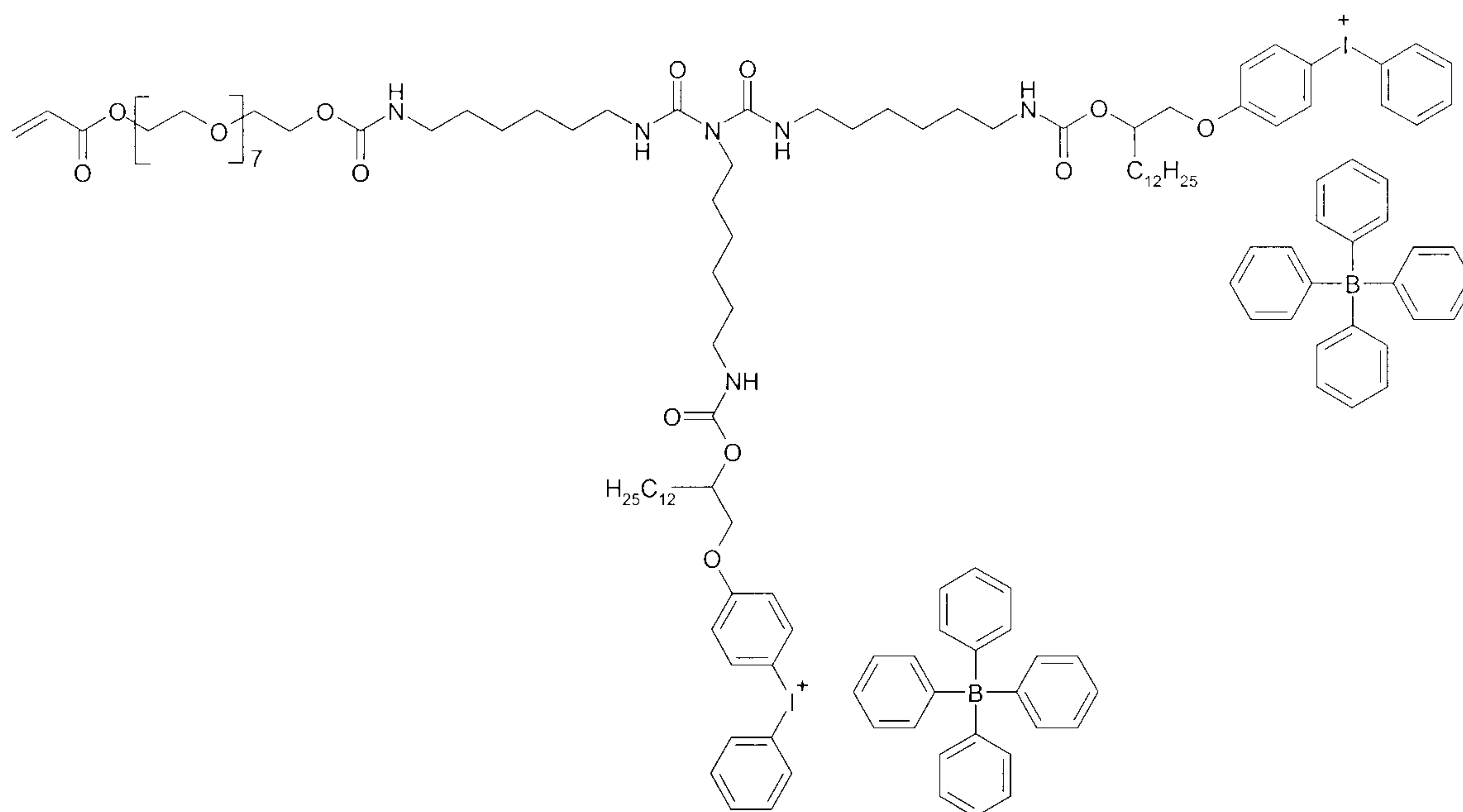
[0073] Formula 18 is the ideal structure of polymer binder RPB-05:



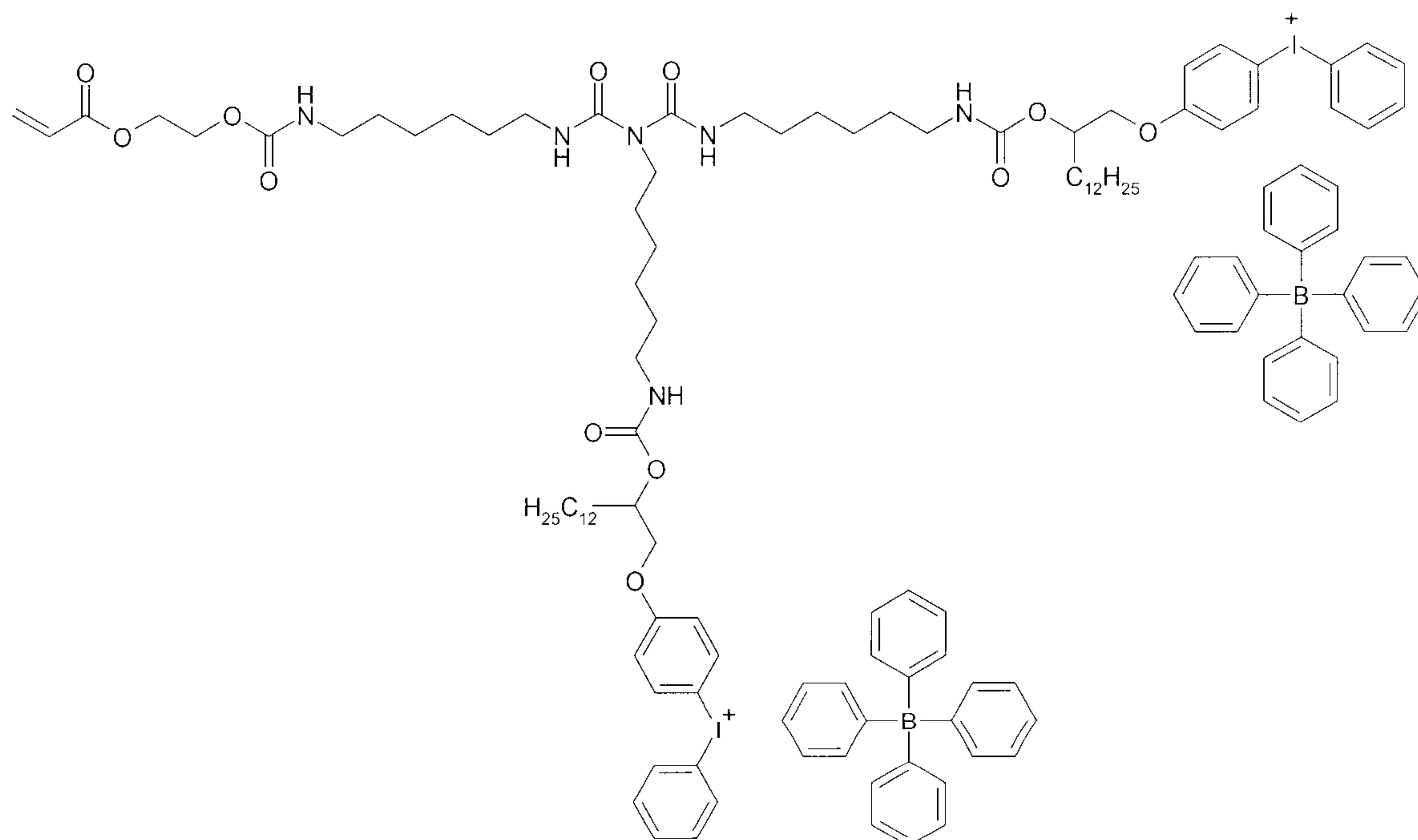
[0074] Formula 19 is the ideal structure of polymer binder RPB-06:



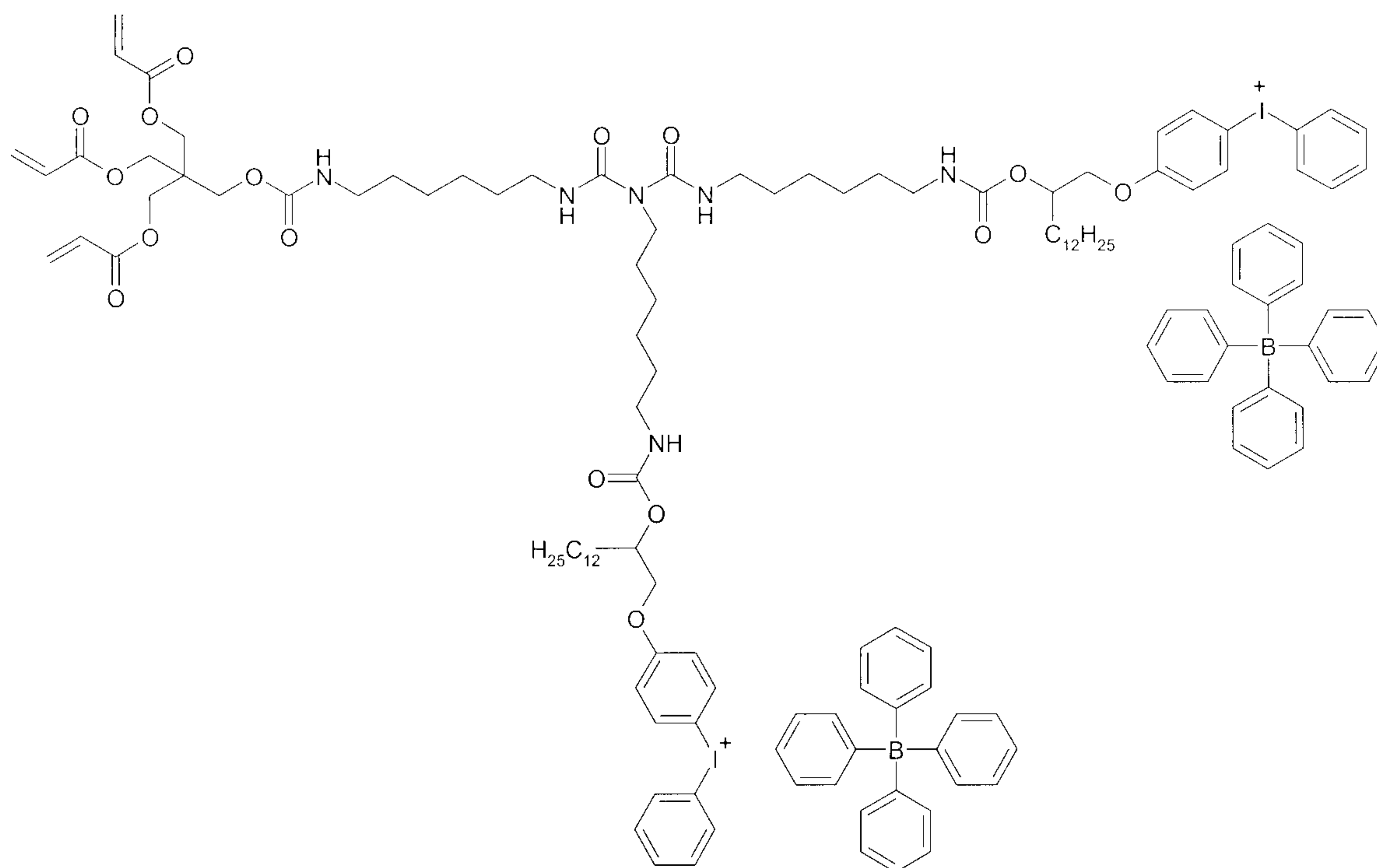
[0075] Formula 20 is the possible structure of a specific embodiment of an iodonium salt of the present invention:



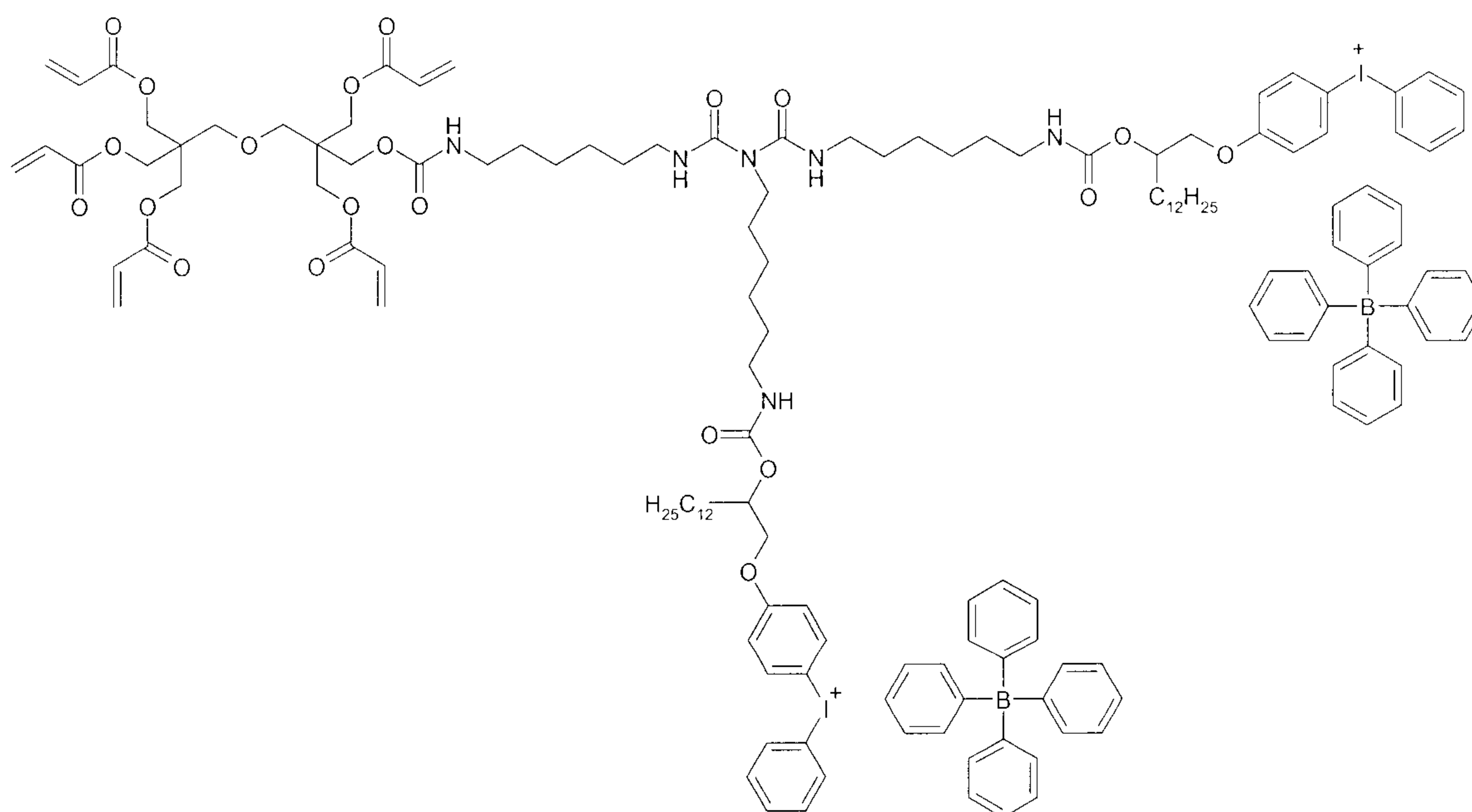
[0076] Formula 21 is the possible structure of a specific embodiment of an iodonium salt of the present invention:



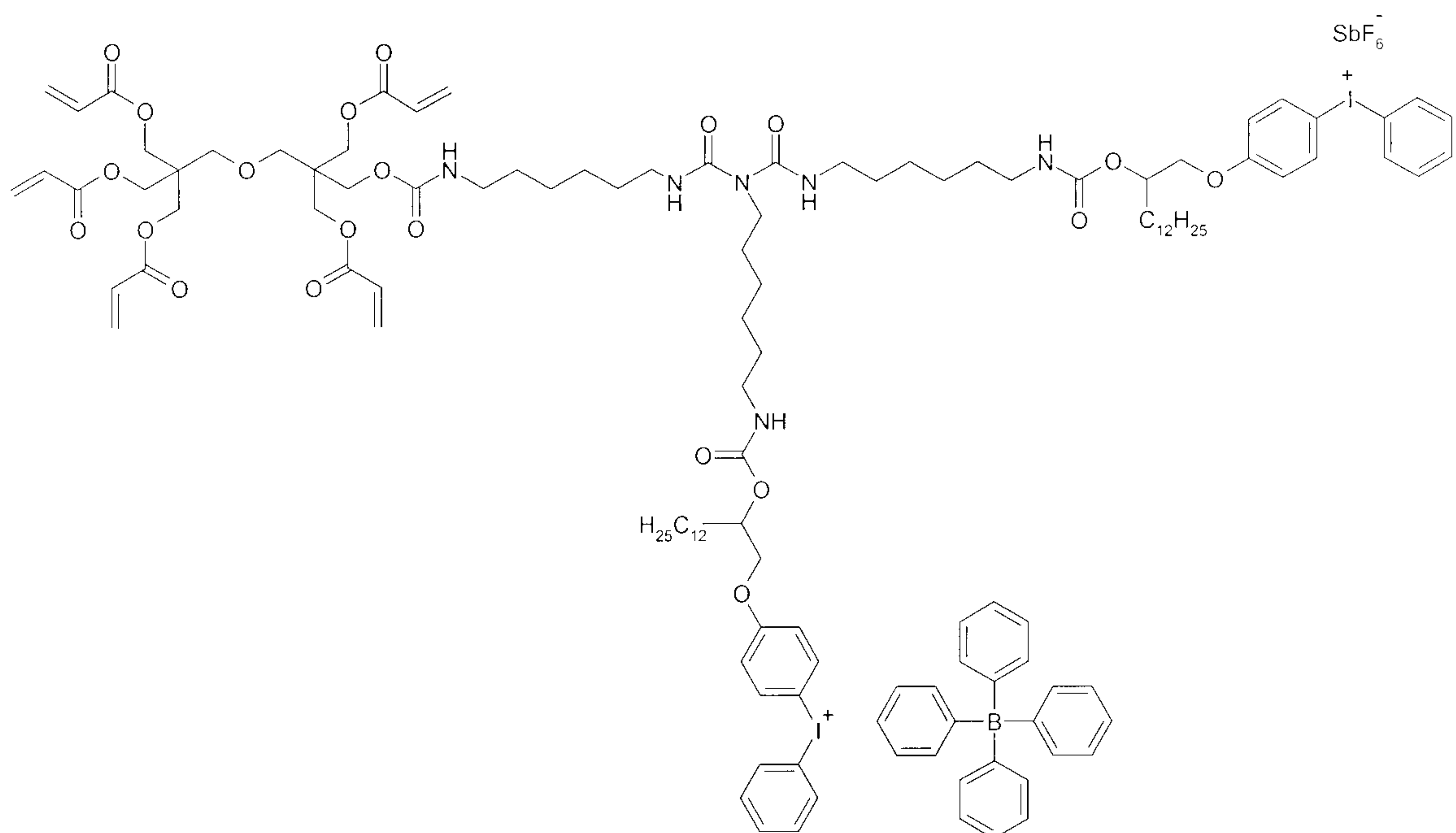
[0077] Formula 22 is the possible structure of a specific embodiment of an iodonium salt of the present invention:



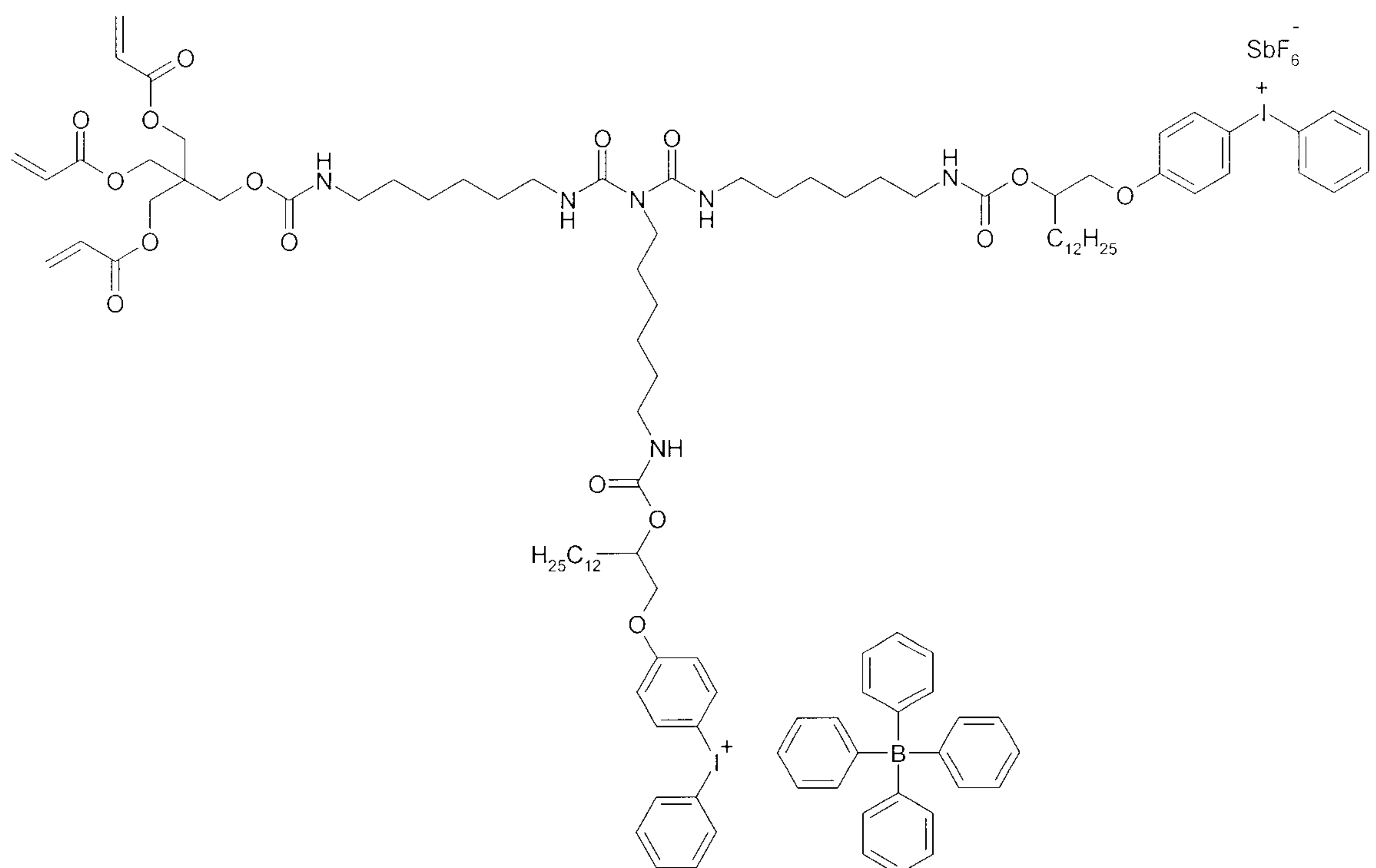
[0078] Formula 23 is the possible structure of a specific embodiment of an iodonium salt of the present invention:



[0079] Formula 24 is the possible structure of a specific embodiment of an iodonium salt of the present invention:



[0080] Formula 25 is the possible structure of a specific embodiment of an iodonium salt of the present invention:



DETAILED DESCRIPTION OF SPECIFIC EMBODIMENTS

[0081] The present invention is illustrated in further details by the following non-limiting examples.

[0082] In these examples, these syntheses were performed in a 4 necks glass reactor equipped with a water condenser, a mechanical stirrer, a dropping funnel and

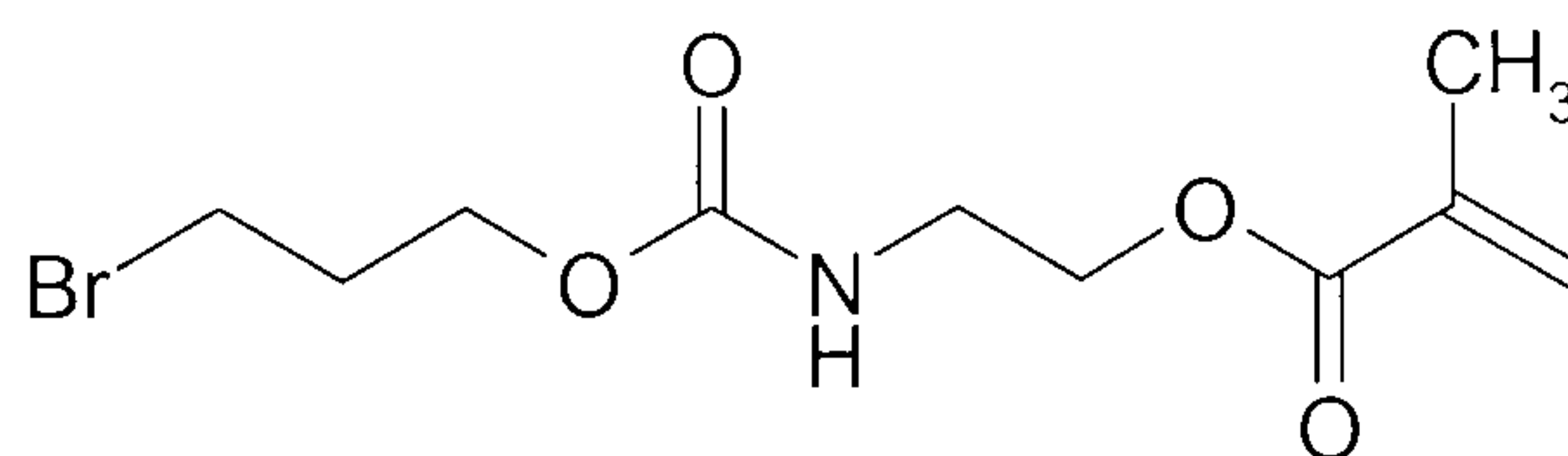
a nitrogen or air gas inlet. The molecular structures of the obtained materials were determined by proton NMR and FTIR spectroscopy. The average molecular weight of the copolymers obtained was determined by size exclusion chromatography (SEC), using N,N-dimethylformamide (DMF) solutions and calibrated with polystyrene standards. The UV-Visible near-infrared spectra of the synthesized polymers were measured in methanol solutions or on the solid films using a UV-VIS spectrophotometer (PerkinElmer, Model Lambda 35™).

[0083] Also, the coated plates were imaged using Creo Trendsetter 3244™ equipped with 830 nm lasers. The imaged plate was mounted on AB Dick™ duplicator press using black ink (available from Pacific Inks, Vietnam) and fountain solution containing 3.0 parts of MYLAN-FS100™ in 97.0 parts of water (available from MyLan Chemicals Inc., Vietnam).

Synthesis of the reactive near-infrared sensitizing polyvinyl alcohol acetal copolymers (dyes):

EXAMPLE 1

[0084] The thermally reactive near-infrared sensitizing polyvinyl alcohol acetal copolymer PVA-01 was synthesized by adding, by portions, 90 grams of polyvinyl alcohol (Celvol™ 103, a 98% hydrolyzed polyvinyl acetate having an average molecular weight of about 18,000) to a reaction flask containing 500 grams of dimethylsulfoxide (DMSO) at 60°C, under nitrogen atmosphere and with constant stirring. After complete dissolution, 3 ml of concentrated sulfuric acid, which acts as a catalyst for this reaction, were added to the flask. After thirty minutes, 12.2 grams of 4-hydroxybenzaldehyde (100 mmole, available from Sigma-Aldrich, Canada) were slowly added to the flask and the mixture was stirred at 60°C for 4 hours. Then, 1 gram of sodium hydride (60 % in mineral oil, available from Sigma-Aldrich, Canada) was slowly added into the reaction. After hydrogen gas was no longer produced from the reaction, 3.0 grams of 3-bromopropyl-methacryloyl-ethyl carbamate (see structure below, available from American Dye Source Inc., Canada) was added into the reaction mixture.



3-bromopropyl-methacryloyl-ethyl carbamate.

[0085] The reaction was continued for 30 minutes, then 20 grams of 2-[2-[2-chloro-3-[[1,3-dihydro-1,1-dimethyl-3-(4-sulfonylbutyl)-2H-benzo[e]indol-2-ylidene]-ethylidene]-1-cyclohexen-1-yl]ethenyl]-1,1-dimethyl-3-(4-sulfonylbutyl)-1H-benzo[e]indolium hydroxy inner salt, sodium salt (13 mmole, available from American Dye Source, Inc.) was slowly added to the flask. The resulting mixture was stirred at 60°C for another 5 hours. The reaction product was precipitated in acetone, filtered and washed copiously with acetone. It was then dried in air until constant weight.

[0086] The UV-Vis-NIR spectrum of the obtained PVA-01 thermally reactive near-infrared absorbing polyvinyl alcohol acetal copolymer was recorded in methanol and exhibited a strong absorption band at 803 nm. The ideal structure of the PVA-01 near-infrared absorbing polyvinyl alcohol acetal copolymer is shown in Figure 1, wherein a = 6.65%, b = 1.00 %, c = 2.35%, d = 88.00% and e = 2.00%.

EXAMPLE 2

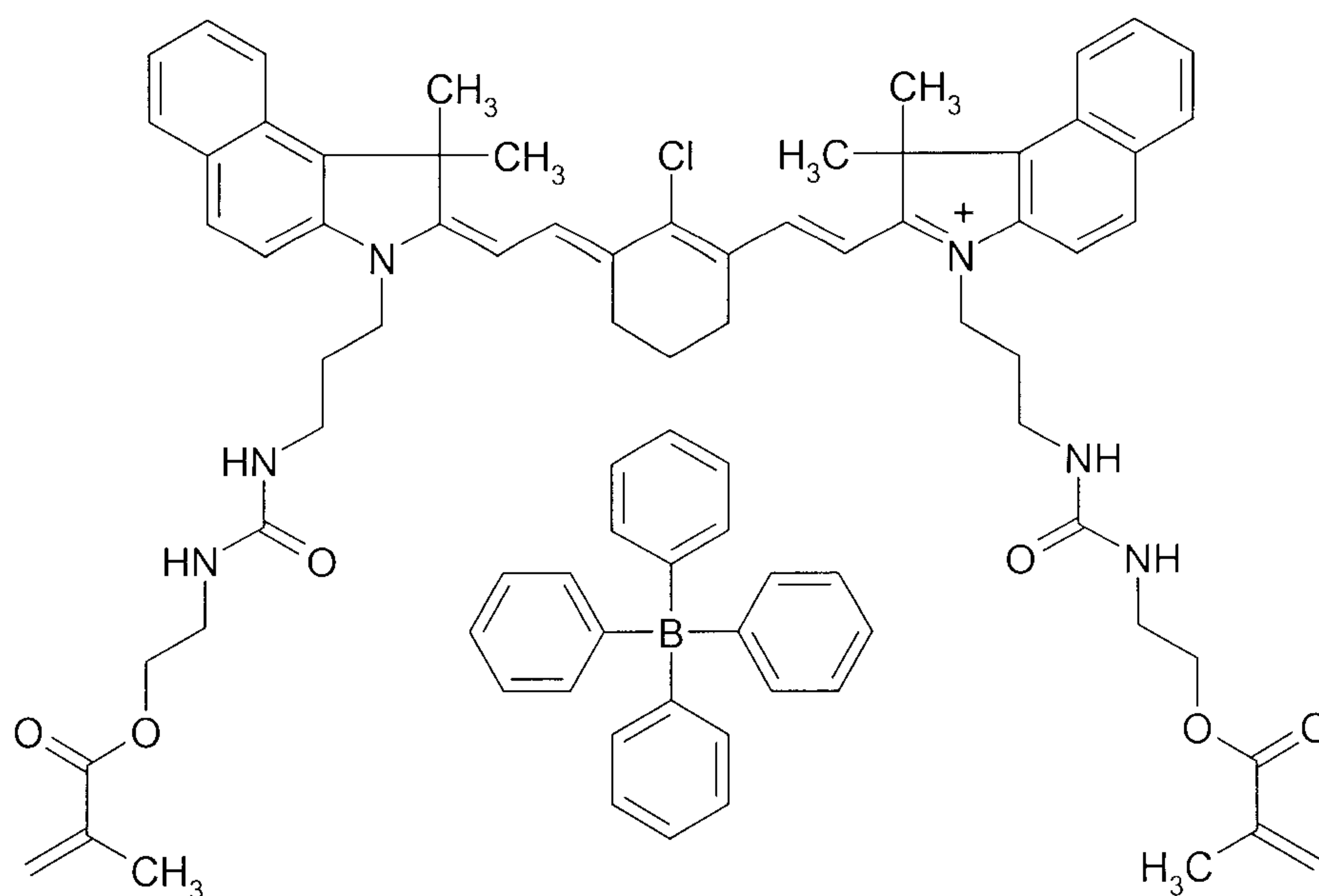
[0087] The thermally reactive near-infrared absorbing polyvinyl alcohol acetal copolymer PVA-01 was synthesized by adding, by portions, 90 grams of polyvinyl alcohol (Celvol™ 103, a 98% hydrolyzed polyvinyl acetate having an average molecular weight of about 18,000) to a reaction flask containing 500 grams of dimethylsulfoxide (DMSO) at 60°C, under nitrogen atmosphere and with constant stirring. After complete dissolution, 3 ml of concentrated sulfuric acid, which acts as a catalyst for this reaction, were added to the flask. After thirty minutes, 12.2 grams of 4-hydroxybenzaldehyde (100 mmole, available from Sigma-Aldrich, Canada) were slowly added to the flask and the mixture was stirred at 60°C for 4 hours. Then, 1 gram of sodium hydride (60 % in mineral oil, available from Sigma-Aldrich, Canada) was slowly added into the reaction. After hydrogen gas was no longer produced from the reaction, 3.0 grams of 3-bromopropyl-methacryloyl-ethyl carbamate was added into the reaction mixture. The reaction was continued for 30 minutes, then 20 grams of 2-[2-[2-chloro-3-[2-(1,3-dihydro-1,3,3-trimethyl-2H-indol-2-ylidene)-ethylidene]-1-cyclohexen-1-yl]ethenyl]-1,3,3-trimethyl-1H-indolium chloride (available from American Dye Source, Inc.) was slowly added to the flask. The resulting mixture was stirred at 60°C for another 3 hours. Then, 5 grams of sodium tetraphenylborate was added into the reaction flask and it continued to stir for additional 2 hours. The reaction product

was precipitated in de-ionized water, filtered and washed copiously with water. It was then dried in air until constant weight.

[0088] The UV-Vis-NIR spectrum of the obtained PVA-02 thermally reactive near-infrared absorbing polyvinyl alcohol acetal copolymer was recorded on a thin film and exhibited a strong absorption band at 800 nm. The ideal structure of the PVA-02 near-infrared absorbing polyvinyl alcohol acetal copolymer is shown in Formula 2, wherein a = 5.15%, b = 1.00%, c = 3.85%, d = 88.00% and e = 2.00%.

EXAMPLE 3

[0089] The thermally reactive near-infrared absorbing polyvinyl alcohol acetal copolymer, PVA-01, was synthesized by adding, by portions, 90 grams of polyvinyl alcohol (Celvol™ 103, a 98% hydrolyzed polyvinyl acetate having an average molecular weight of about 18,000) to a reaction flask containing 500 grams of dimethylsulfoxide (DMSO) at 60°C, under nitrogen atmosphere and with constant stirring. After complete dissolution, 3 ml of concentrated sulfuric acid, which acts as a catalyst for this reaction, were added to the flask. After thirty minutes, 6.1 grams of 4-hydroxybenzaldehyde (available from Sigma-Aldrich, Canada) were slowly added to the flask and the mixture was stirred at 60°C for 4 hours. Then, 0.5 grams of sodium hydride (60 % in mineral oil, After hydrogen gas was no longer produced from the reaction, 10 grams near infrared absorption containing reactive functional groups having the structure shown below (available from American Dye Source, Inc.) was slowly added to the flask.

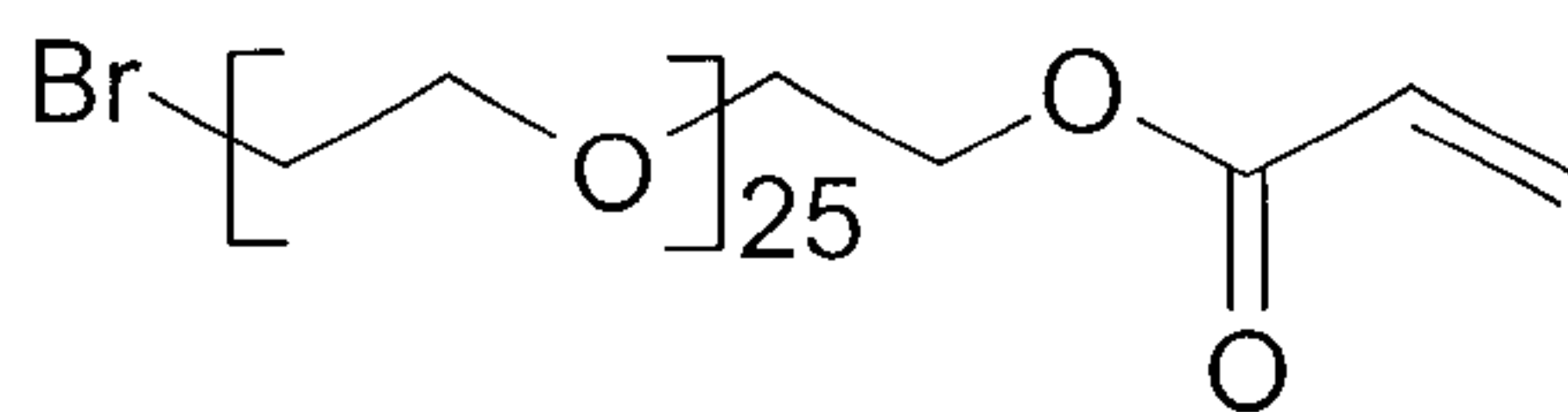


[0090] The resulting mixture was stirred at 50°C for another 5 hours. The reaction product was precipitated in 10 liters of de-ionized water, filtered and washed copiously with water. It was then dried in air until constant weight.

[0091] The UV-Vis-NIR spectrum of the obtained PVA-03 thermally reactive near-infrared absorbing polyvinyl alcohol acetal copolymer was recorded on a thin film and exhibited a strong absorption band at 830 nm. The ideal structure of the near infrared absorbing polyvinyl alcohol acetal copolymer PVA-03 is shown in Formula 3, wherein a = 3.42 %, c=1.58 %, d= 93.00% and e=2.00%.

EXAMPLE 4

[0092] The thermally reactive near-infrared absorbing polyvinyl alcohol acetal copolymer PVA-01 was synthesized by adding, by portions, 90 grams of polyvinyl alcohol (Celvol™ 103, a 98% hydrolyzed polyvinyl acetate having an average molecular weight of about 18,000) to a reaction flask containing 500 grams of dimethylsulfoxide (DMSO) at 60°C, under nitrogen atmosphere and with constant stirring. After complete dissolution, 3 ml of concentrated sulfuric acid, which acts as a catalyst for this reaction, were added to the flask. After thirty minutes, 12.2 grams of 4-hydroxybenzaldehyde (available from Sigma-Aldrich, Canada) were slowly added to the flask and the mixture was stirred at 60°C for 4 hours. Then, 1 gram of sodium hydride (60 % in mineral oil, available from Sigma-Aldrich, Canada) was slowly added into the reaction. When hydrogen gas was no longer produced from the reaction, 11.0 grams of 10 grams of bromo-terminated poly(ethylene glycol) acrylate (see below structure, available from American Dye Source Inc.) was added into the reaction mixture.



Bromo-terminated poly(ethylene glycol) acrylate

[0093] The reaction was continued for 30 minutes, then 20 grams of 2-[2-[2-chloro-3-[2-(1,3-dihydro-1,3,3-trimethyl-2H-indol-2-ylidene)-ethylidene]-1-cyclohexen-1-yl]ethenyl]-1,3,3-trimethyl-1H-indolium 4-methylbenzene sulfonate (available from American Dye Source, Inc.) was slowly added to the flask. The resulting mixture was

stirred at 60°C for another 3 hours. Then, 5 grams of sodium tetraphenylborate was added into the reaction flask and it continued to stir for additional 2 hours. The reaction product was precipitated in de-ionized water, filtered and washed copiously with water. It was then dried in air until constant weight.

[0094] The UV-Vis-NIR spectrum of the obtained PVA-04 thermally reactive near-infrared absorbing polyvinyl alcohol acetal copolymer was recorded on a thin film and exhibited a strong absorption band at 800 nm. The ideal structure of the PVA-04 near-infrared absorbing polyvinyl alcohol acetal copolymer is shown in Formula 4, wherein a = 5.15%, b = 1.00%, c = 3.85%, d = 88.00% and e = 2.00%.

Synthesis of Reactive Iodonium Salts:

[0095] For the ease of manufacturing and cost effectiveness, the iodonium salts containing reactive functional groups may be synthesized and used as a mixture of various salts. Further, this mixture may be used directly without further purification.

EXAMPLE 5

[0096] A mixture of reactive iodonium tetraphenylborate having possible structures as in Formulas 5, 6, 7, 8, 9 and 10 was obtained by heating 320 grams of 1,3-dioxolane solution containing 573 grams of Desmodur™ N100 (available from Bayer Canada), 60 grams of 2-hydroxyethylacrylate (available from Sigma-Aldrich, Canada), 245 grams of poly(ethylene glycol) acrylate (Mn ~ 375, available from Sigma-Aldrich, Canada), 500 grams of pentaerythritol triacrylate (SR-444, available from Sartomer, USA), 1 gram of hydroquinone (available from Sigma-Aldrich, Canada) and 1 gram of dibutyl tin dilaurate (available from Sigma-Aldrich, Canada) to 60°C under an oxygen atmosphere and constant stirring for 10 hours. A sample of reaction mixture was withdrawn from the reaction flask and its FTIR spectrum, recorded on KBr pellet, showed a --N=C=O peak at 2274 cm^{-1} . Then, 150 grams of [4-(2-hydroxy-1-tetradecyloxy)phenyl] phenyliodonium tetraphenylborate (available from American Dye Source Inc., Canada) was slowly added into the reaction mixture, which was stirred at 60°C for an additional 6 hours. The FTIR spectrum then indicated that the --N=C=O peak at 2274 cm^{-1} had disappeared, which was indicative of the completion of the reaction. The clear viscous product obtained was ready for use.

EXAMPLE 6

[0097] A mixture of reactive iodonium tetraphenylborate having possible structures as in Formulas 6, 7 and 8) was obtained by heating 320 grams of anhydrous methyl ethyl ketone solution containing 573 grams of Desmodur™ N100 (available from Lanxess, Canada), 138 grams of 2-hydroxyethylacrylate (available from Sigma-Aldrich, Canada), and 500 grams of pentaerythritol triacrylate (SR-444, available from Sartomer, USA), 1 gram of hydroquinone (available from Sigma-Aldrich, Canada) and 1 gram of dibutyl tin dilaurate (available from Sigma-Aldrich, Canada) to 60°C under an oxygen atmosphere and constant stirring for 10 hours. A sample of reaction mixture was withdraw from the reaction flask and its FTIR spectrum, recorded on KBr pellet, showed a --N=C=O peak at 2274 cm^{-1} . Then, 150 grams of [4-(2-hydroxy-1-tetradecyloxy)phenyl] phenyliodonium tetraphenylborate (available from American Dye Source Inc., Canada) was slowly added into the reaction mixture, which was stirred at 60°C for an additional 6 hours. The FTIR spectrum then indicated that the --N=C=O peak at 2274 cm^{-1} had disappeared, which was indicative of the completion of the reaction. The clear viscous product obtained was ready for use.

EXAMPLE 7

[0098] A mixture of reactive iodonium tetraphenylborate having possible structures as in Formulas 8, 9 and 10 was obtained by heating 320 grams of methyl ethyl ketone solution containing 573 grams of Desmodur™ N100 (available from Lanxess, Canada), 430 grams of poly(ethylene glycol) acrylate ($M_n \sim 375$, available from Sigma-Aldrich, Canada), 500 grams of pentaerythritol triacrylate (SR-444, available from Sartomer, USA) and 1 gram of hydroquinone (available from Sigma-Aldrich, Canada) and 1 gram of dibutyl tin dilaurate (available from Sigma-Aldrich, Canada) to 60°C under oxygen atmosphere and constant stirring for 10 hours. A sample of reaction mixture was withdraw from the reaction flask and its FTIR spectrum, recorded on KBr pellet, showed a --N=C=O peak at 2274 cm^{-1} . Then, 150 grams of [4-(2-hydroxy-1-tetradecyloxy)phenyl] phenyliodonium tetraphenylborate (available from American Dye Source Inc., Canada) was slowly added into the reaction mixture, which was stirred at 60°C for an additional 6 hours. The FTIR spectrum then indicated that the --N=C=O peak at 2274 cm^{-1} had disappeared, which

was indicative of the completion of the reaction. The clear viscous product obtained was ready for use.

EXAMPLE 8

[0099] A mixture of reactive iodonium tetraphenylborate having possible structures as in Formulas 6, 7, 11, 12 and 13 was obtained by heating 320 grams of 1,3-dioxolane solution containing 573 grams of Desmodur™ N100 (available from Bayer Canada), 50 grams of 2-hydroxyethylmethacrylate (available from Sigma-Aldrich, Canada), 275 grams of pentaerythritol triacrylate (SR-444, available from Sartomer, USA), 780 grams of dipentaerythritol pentaacrylate (SR-399 available from Sartomer, USA), 1 gram of hydroquinone (available from Sigma-Aldrich, Canada) and 1 gram of dibutyl tin dilaurate (available from Sigma-Aldrich, Canada) to 60°C under an oxygen atmosphere and constant stirring for 10 hours. A sample of reaction mixture was withdraw from the reaction flask and its FTIR spectrum, recorded on KBr pellet, showed a --N=C=O peak at 2274 cm^{-1} . Then, 150 grams of [4-(2-hydroxy-1-tetradecyloxy)phenyl] phenyliodonium tetraphenylborate (available from American Dye Source Inc., Canada) was slowly added into the reaction mixture, which was stirred at 60°C for an additional 6 hours. The FTIR spectrum indicated that the --N=C=O peak at 2274 cm^{-1} had disappeared, which was indicative of the completion of the reaction. The clear viscous product obtained was ready for use.

EXAMPLE 9

[00100] A mixture of reactive iodonium tetraphenylborate having possible structures as in Formulas 7, 9, 10, 11 and 12 was obtained by heating 137 grams of 1,3-dioxolane solution containing 245 grams of Desmodur™ N100 (available from Bayer Canada), 310 grams of poly(ethylene glycol) acrylate ($M_n \sim 375$, available from Sigma-Aldrich, Canada), 244 grams of pentaerythritol triacrylate (SR-444, available from Sartomer, USA), 100 grams of dipentaerythritol pentaacrylate (SR-399 available from Sartomer, USA), 1 gram of hydroquinone (available from Sigma-Aldrich, Canada) and 1 gram of dibutyl tin dilaurate (available from Sigma-Aldrich, Canada) to 60°C under an oxygen atmosphere and constant stirring for 10 hours. A sample of reaction mixture was withdraw from the reaction flask and its FTIR spectrum, recorded on KBr pellet, showed a --N=C=O peak at 2274 cm^{-1} . Then, 75 grams of [4-(2-hydroxy-1-tetradecyloxy)phenyl] phenyliodonium tetraphenylborate (available from American Dye Source Inc., Canada) was slowly added into the reaction mixture, which was stirred at

60°C for an additional 6 hours. The FTIR spectrum then indicated that the --N=C=O peak at 2274 cm^{-1} had disappeared, which was indicative of the completion of the reaction. The clear viscous product obtained was ready for use.

EXAMPLE 10

[00101] Reactive iodonium salt having the structure as shown in Formula 14 was synthesized by slowly adding 31.5 grams of 2-isocyanato-ethylmethacrylate into 300 ml solution of 1,3-dioxolane dissolving with 80 grams of [2-[9,9-(3-hydroxypropyl)fluorenyl] 4-methylphenyliodonium triphenyl-n-butylborate and 0.1 grams of dibutyl tin dilaurate at 60°C under constant stirring and an oxygen atmosphere. The reaction was monitored by FTIR, which indicated that the reaction was completed within 5 hours. The product was precipitated in de-ionized water, filtered and washed copiously with de-ionized water. It was then washed with ether and dried in air until constant weight.

[00102] The iodonium salts of Formulas 20-25 were also synthesized.

Synthesis of Thermally Reactive Polymer Binders:

EXAMPLE 11

[00103] The thermally reactive polymer binder, RPB-01 was synthesized by adding, by portions, 25 grams of hydroxypropyl cellulose (Klucel[®] E, available from Hercules, USA) to a reaction flask containing 500 grams of 1,3-dioxolane at 60°C, under air atmosphere and with constant stirring. After complete dissolution, 3 drops of dibutyl tin dilaurate, which acts as a catalyst for this reaction, were added to the flask. Then, 5.0 grams of 2-isocyanatoethylmethacrylate (available from American Dye Source, Canada) were slowly added to the reaction flask and the mixture was stirred at 60°C for 7 hours. FTIR spectrum of the polymer on KBr pellet indicated that the reaction was completed with the disappearance of the --N=C=O peak at 2274 cm^{-1} . The ideal structure of RPB-01 is shown in Formula 15. n-Propanol was added into the reaction to provide 5.0 % solid content solution.

EXAMPLE 12

[00104] The reactive polymer binder, RPB-02 was synthesized in way similar to that of Example 11 with the exception that 10 grams of 2-isocyanatoethylmethacrylate was used in the reaction. The ideal structure of RPB-02 is similar to that of RPB-01

with more reactive functional groups present in the polymer. n-Propanol was added into the reaction to provide 5.0 % solid content solution.

EXAMPLE 13

[00105] The reactive polymer binder RPB-03 was synthesized by adding, by portions, 90 grams of polyvinyl alcohol (Celvol™ 103, a 98% hydrolyzed polyvinyl acetate having an average molecular weight of about 18,000) to a reaction flask containing 500 grams of dimethylsulfoxide (DMSO) at 60°C, under nitrogen atmosphere and with constant stirring. After complete dissolution, 3 ml of concentrated sulfuric acid, which acts as a catalyst for this reaction, were added to the flask. After thirty minutes, 12.2 grams of 4-hydroxybenzaldehyde (100 mmole, available from Sigma-Aldrich, Canada) were slowly added to the flask and the mixture was stirred at 60°C for 4 hours. Then, 0.5 gram of sodium hydride (60 % in mineral oil, available from Sigma-Aldrich, Canada) was slowly added into the reaction. After hydrogen gas was no longer produced from the reaction, 3.0 grams of 3-bromopropyl-methacryloyl-ethyl carbamate was added into the reaction mixture. The reaction was continued for 5 hours at 60°C. The product was precipitated in de-ionized water, filtered and washed copiously with de-ionized water. It was then dried in air until constant weight. The ideal structure of RPB-03 is shown in Formula 16, wherein a= 9.00%, b=1.00%, d=88.00% and e=2.00%.

EXAMPLE 14

[00106] The reactive polymer binder RPB-04 was synthesized by adding, by portions, 90 grams of polyvinyl alcohol (Celvol™ 103, a 98% hydrolyzed polyvinyl acetate having an average molecular weight of about 18,000) to a reaction flask containing 500 grams of dimethylsulfoxide (DMSO) at 60°C, under nitrogen atmosphere and with constant stirring. After complete dissolution, 3 ml of concentrated sulfuric acid, which acts as a catalyst for this reaction, were added to the flask. After thirty minutes, 6.5 grams of butyraldehyde and 2.35 grams of acryloyl-propyloxybenzaldehyde (available from American Dye Source Inc., Canada) were added into the reaction mixture. The reaction was continued for 5 hours at 60°C. The product was precipitated in de-ionized water, filtered and washed copiously with de-ionized water. It was then dried in air until constant weight. The ideal structure of RPB-04 is shown in Formula 17, wherein a= 9.00%, b=1.00%, d=88.00% and e=2.00%.

EXAMPLE 15

[00107] The reactive polymer binder, RPB-05 was synthesized by heating a mixture of 200 grams of anhydrous 1,3-dioxolane, dissolving with 15.0 g poly(ethylene glycol) acrylate ($M_n \sim 2,010$, available from American Dye Source Inc., Canada), 15.0 g styrene, 50.0 g acrylonitrile and in a 1L 4-neck flask at 75°C under a nitrogen atmosphere and constant stirring. After heating for 30 minutes, 0.5 g of Vazo™ 64 was added to the reaction mixture. After 10 hours of polymerization at 75°C, another 0.5 g of Vazo™ 64 was added into the reaction mixture and the polymerization was continued for another 14 hours. Air was introduced into the reaction mixture and it stirring at 75°C continued for an additional 2 hours to terminate the polymerization. The reaction temperature was lowered to 5°C and 4 grams of triethylamine were added into the reaction mixture. Then, a solution containing 10 grams of 1,3-dioxolane and 2 grams of acryloyl chloride was slowly introduced into the reaction. The reaction was stirred at room temperature for 5 hours. The product was precipitated in water and dried until constant weight. The molecular weight of RPB-03 was determined to be around 28,000 with a polymer dispersity of 1.4. The ideal structure of RPB-05 is shown in Formula 18, wherein $a=86.16\%$, $b=13.16\%$ and $c=0.68\%$.

[00108] An emulsion of RPB-05 was prepared by slowly adding 50 grams of de-ionized water into 200 grams n-propanol solution, in which 80 grams of RPB-03 were dissolved, using a high shear mixer set at 7,500 rpm.

EXAMPLE 16

[00109] The reactive polymer binder, RPB-06 was synthesized by heating a mixture of 200 grams of n-propanol and 50 grams of de-ionized water, which in which 15.0 g poly(ethylene glycol) acrylate ($M_n \sim 2,000$, available from American Dye Source Inc., Canada) were dissolved, 5.0 grams of N-methoxymethylmethacrylamide (available from American Dye Source Inc., Canada), 15.0 g styrene and 50.0 g acrylonitrile, in a 1L 4-neck flask at 75°C under a nitrogen atmosphere and constant stirring. After heating for 30 minutes, 0.5 g of Vazo™ 64 was added into the reaction mixture. The solution became hazy within 30 minutes of polymerization. After polymerization for 10 hours at 75°C, another 0.5 g of Vazo™ 64 was added into the reaction mixture and the polymerization was continued for another 14 hours. Air was introduced into the reaction mixture and stirring at 75°C was continued for an additional 2 hours to terminate the polymerization. The molecular weight of RPB-06

was determined to be around 29,000 with polymer dispersity of 1.7. The ideal structure of RPB-06 is shown in Formula 19, wherein a=82.88 %, b=12.66 %, c= 3.81 % and d=0.65 %.

On-Press Developable Negative-Working Lithographic Printing Plates

EXAMPLE 17

[00110] A coating solution with the following composition was coated on a brush-grained, phosphoric acid anodized aluminum substrate using wire-wound rod and dried at 80°C with hot air. The obtained coating weight was around 1.0 g/m².

Composition	From example	% by Solid Weight
PVA-01	1	2.00
Iodonium Salt Mixture	9	5.00
RPB-01	10	0.50
RPB-05	14	2.15
3-Mercapto triazol		0.25
Blue Color Former (*)		0.10
n-Propanol		90.0
Water		10.0
BYK 336		0.10
(*) Blue Color Former is Blue-63 (available from Yamamoto Chemicals Inc., Japan)		

[00111] The plate was imaged between 100 and 250 mJ/cm² and mounted on the AB Dick press. High quality printing image was obtained on paper after 10 impressions. The plate can be used to print more than 20,000 high-resolution copies.

EXAMPLE 18

[00112] A coating solution with the following composition was coated on a brush-grained, phosphoric acid anodized aluminum substrate using wire-wound rod and dried at 80°C with hot air. The obtained coating weight was around 1.0 g/m².

Composition	From example	% by Solid Weight
PVA-02	2	2.00
Iodonium Salt Mixture	9	5.00
RPB-01	10	0.50
RPB-05	14	2.15
3-Mercapto triazol		0.25
Blue Color Former (*)		0.10
n-Propanol		90.0
Water		10.0
BYK 336		0.10
(*) Blue Color Former is Blue-63 (available from Yamamoto Chemicals Inc., Japan)		

[00113] The plate was imaged between 100 and 250 mJ/cm² and mounted on the AB Dick press. High quality printing image was obtained on paper after 10 impressions. The plate can be used to print more than 20,000 high-resolution copies.

EXAMPLE 19

[00114] A coating solution with the following composition was coated on a brush-grained, phosphoric acid anodized aluminum substrate using wire-wound rod and dried at 80°C with hot air. The obtained coating weight was around 1.0 g/m².

Composition	From example	% by Solid Weight
PVA-01	1	2.00
Iodonium Salt Mixture	9	5.00
RPB-01	10	0.50
RPB-06	15	2.15

3-Mercapto triazol		0.25
Blue Color Former (*)		0.10
n-Propanol		90.0
Water		10.0
BYK 336		0.10
(*) Blue Color Former is Blue-63 (available from Yamamoto Chemicals Inc., Japan)		

[00115] The plate was imaged between 100 and 250 mJ/cm² and mounted on the AB Dick press. High quality printing image was obtained on paper after 10 impressions. The plate can be used to print more than 20,000 high-resolution copies.

EXAMPLE 20

[00116] A coating solution with the following composition was coated on a brush-grained, phosphoric acid anodized aluminum substrate using wire-wound rod and dried at 80°C with hot air. The obtained coating weight was around 1.0 g/m².

Composition	From example	% by Solid Weight
PVA-01	1	2.00
Iodonium Salt Mixture	9	5.00
RPB-01	10	1.00
RPB-03	15	1.65
3-Mercapto triazol		0.25
Blue Color Former (*)		0.10
n-Propanol		90.0
Water		10.0
BYK 336		0.10
(*) Blue Color Former is Blue-63 (available from Yamamoto Chemicals Inc., Japan)		

[0001] The plate was imaged between 100 and 250 mJ/cm² and mounted on the AB Dick press. High quality printing image was obtained on paper after 10 impressions. The plate can be used to print more than 20,000 high-resolution copies.

EXAMPLE 21

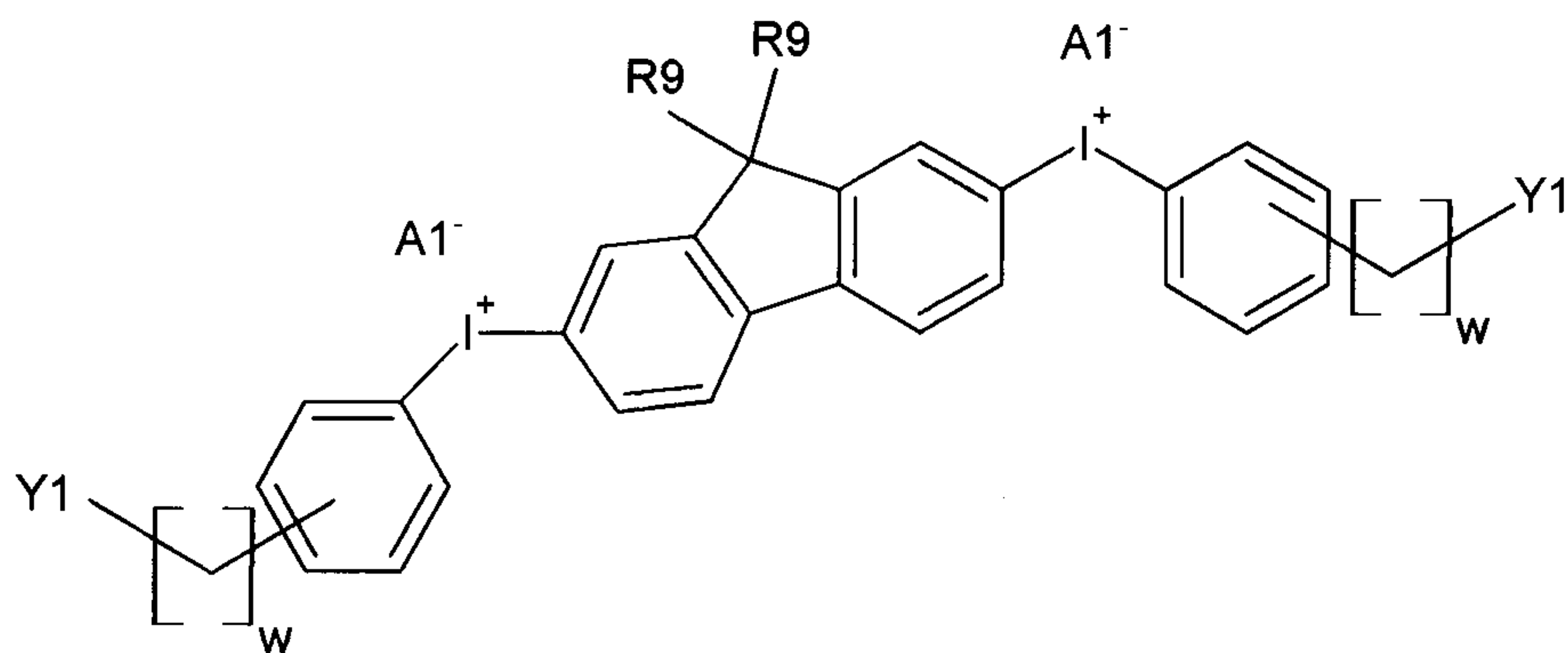
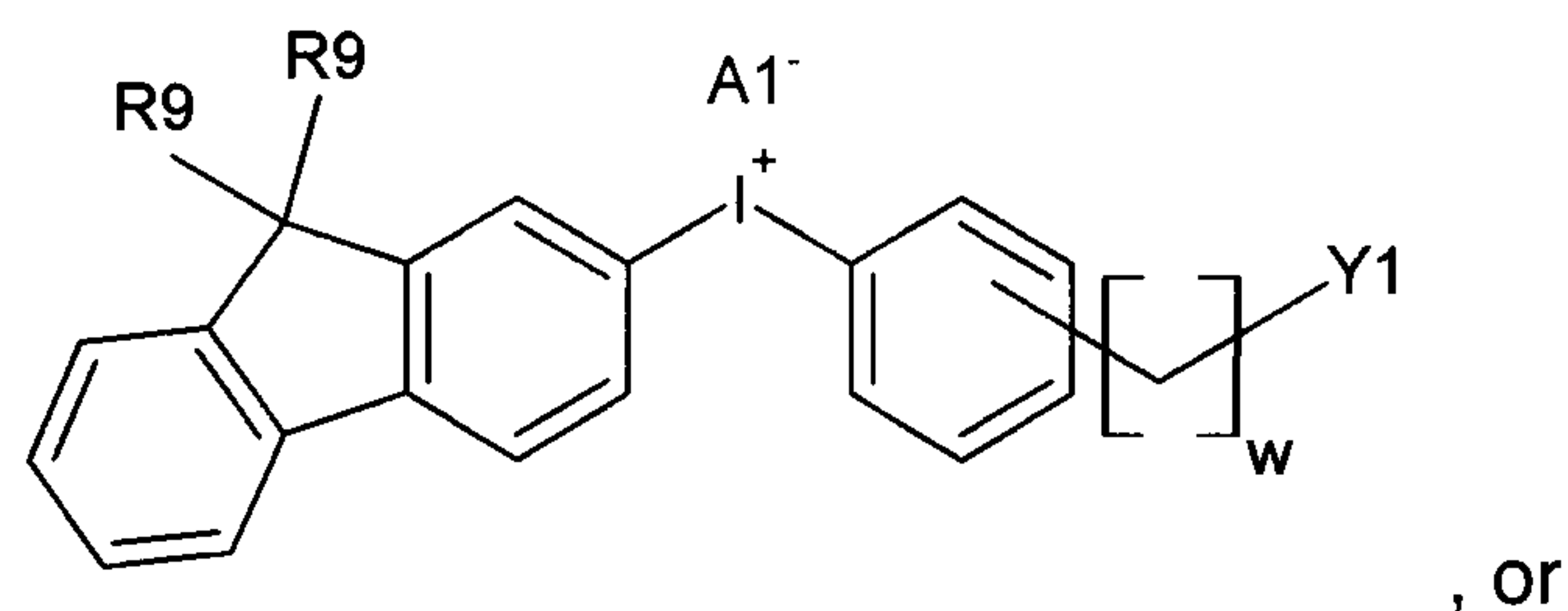
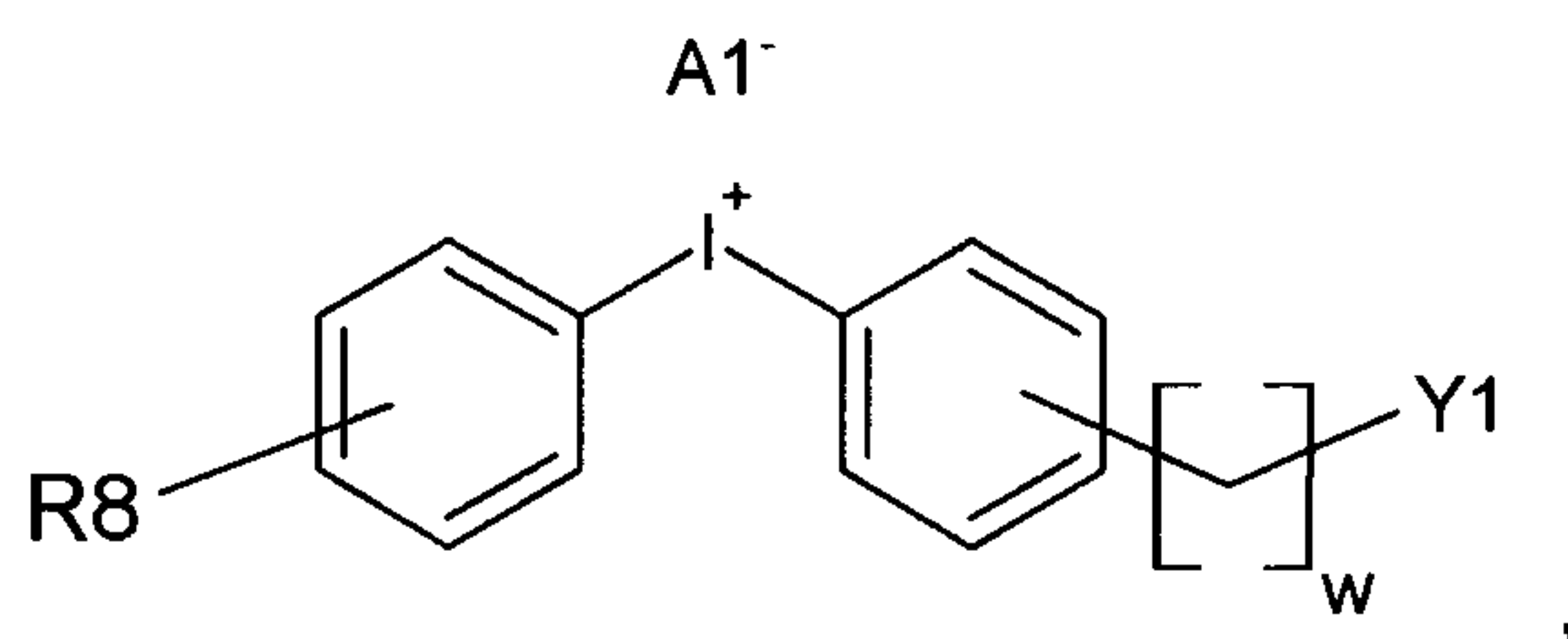
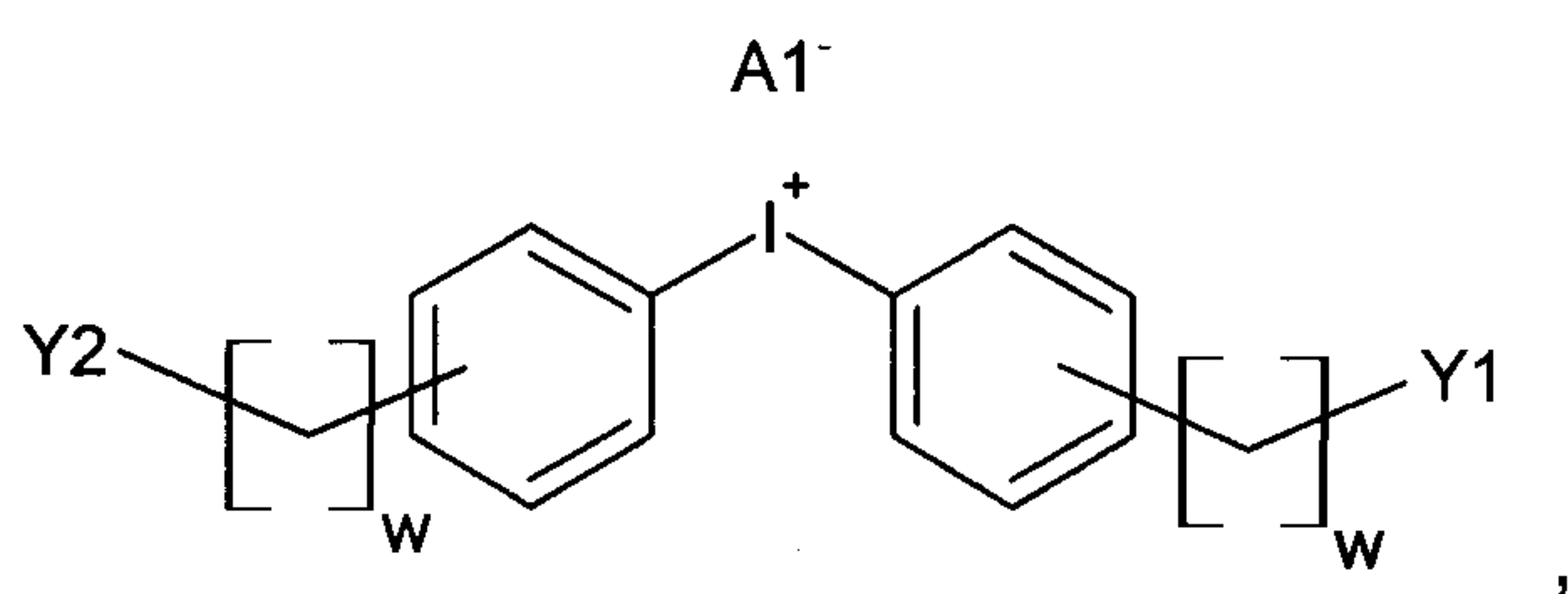
[0002] A coating solution with the following composition was coated on a brush-grained, phosphoric acid anodized aluminum substrate using wire-wound rod and dried at 80°C with hot air. The obtained coating weight was around 1.0 g/m².

Composition	From example	% by Solid Weight
PVA-01	1	2.00
Iodonium Salt Mixture	9	5.00
RPB-01	10	1.00
RPB-04	15	1.65
3-Mercapto triazol		0.25
Blue Color Former (*)		0.10
n-Propanol		90.0
Water		10.0
BYK 336		0.10
(*) Blue Color Former is Blue-63 (available from Yamamoto Chemicals Inc., Japan)		

[0003] The plate was imaged between 100 and 250 mJ/cm² and mounted on the AB Dick press. High quality printing image was obtained on paper after 10 impressions. The plate can be used to print more than 20,000 high-resolution copies.

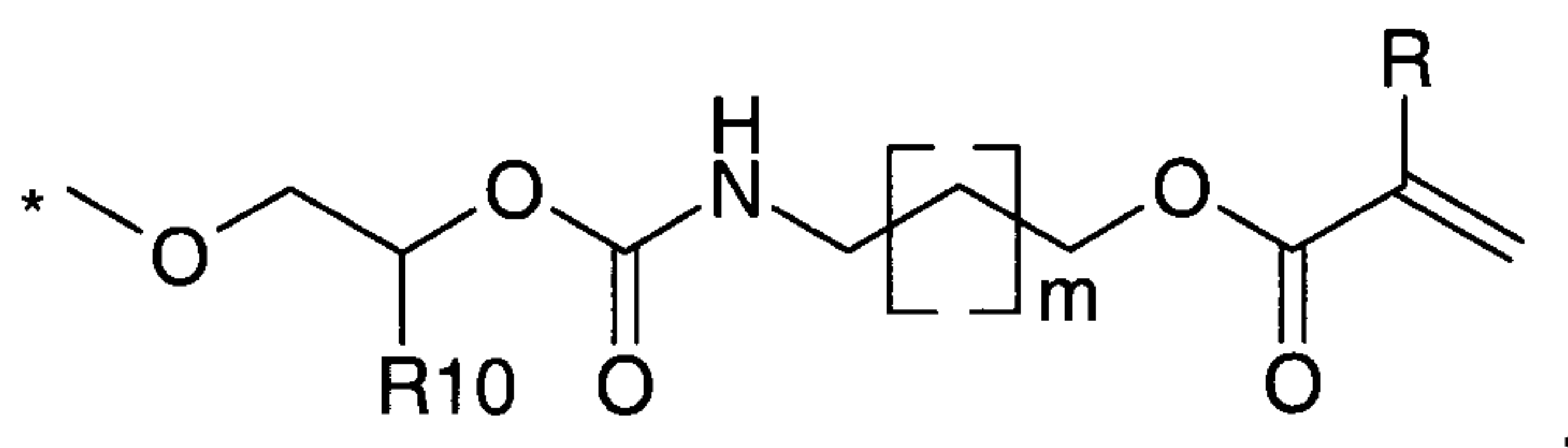
WHAT IS CLAIMED IS:

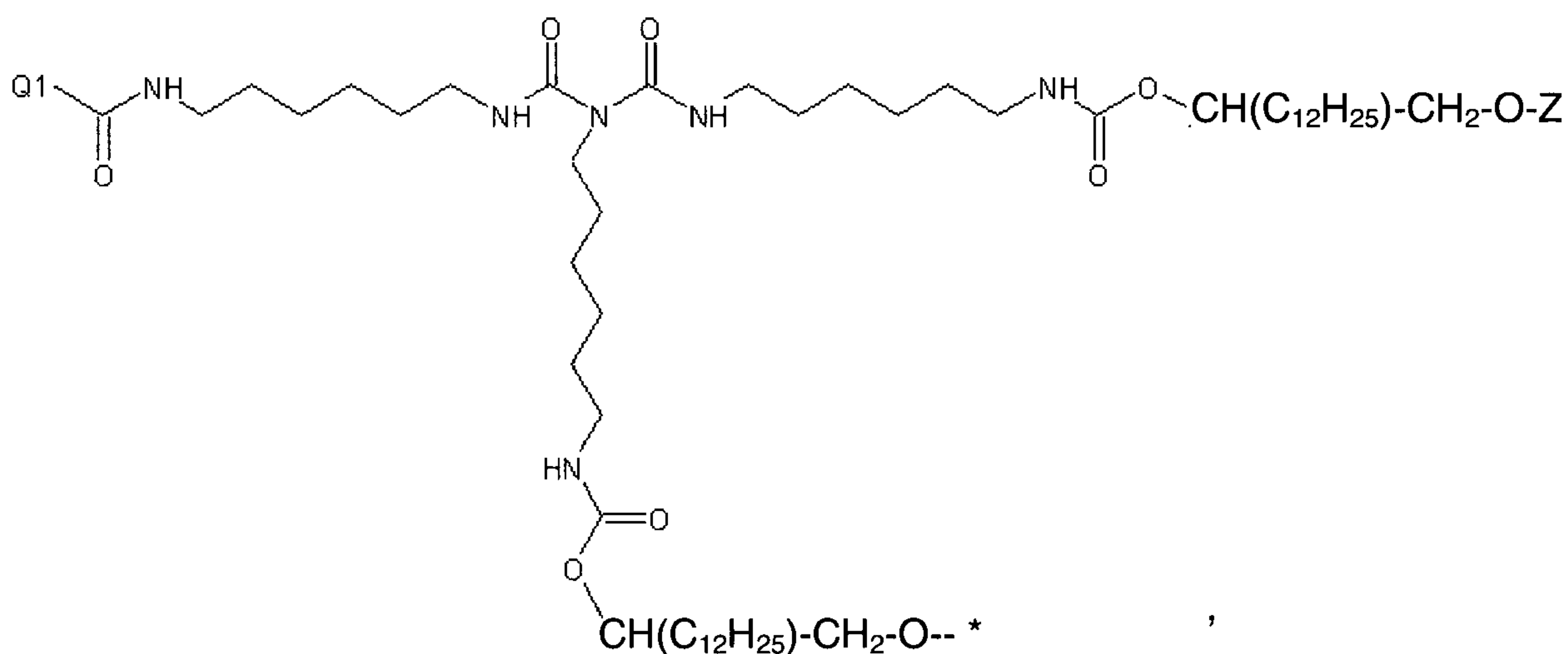
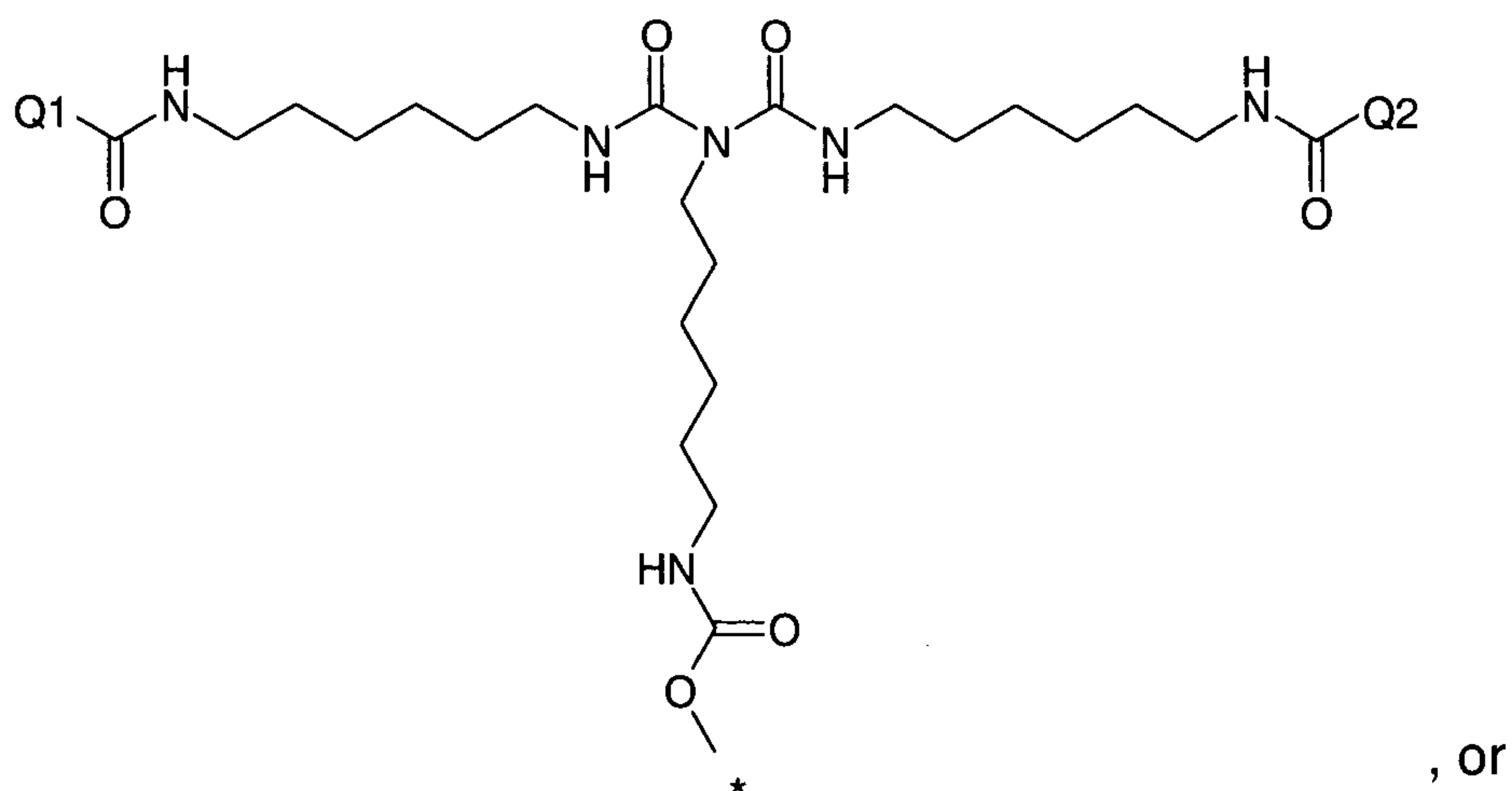
1. A polymerizable iodonium salt comprising a positively charged iodine atom to which two aryl rings are attached, and a negatively charged counter ion, wherein at least one first functional group capable of undergoing cationic or radical polymerization is attached to one of the aryl rings of the iodonium salt via an urethane or an urea bond.
2. The iodonium salt of Claim 1, wherein said first functional group is acrylate, methacrylate, or vinyl ether.
3. The iodonium salt of Claim 1 or 2 having as a general formula:



wherein:

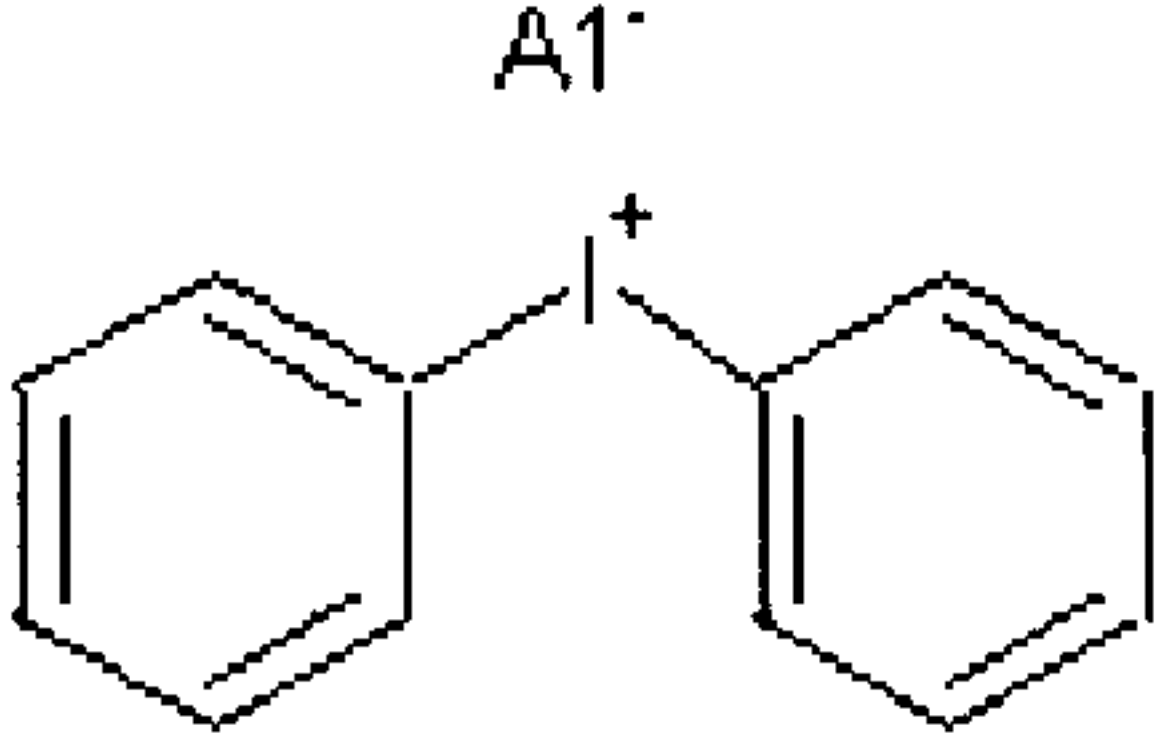
- A1 is a tosylate, triflate, hexafluoroantimonate, tetrafluoroborate, tetraphenylborate or triphenyl-n-alkylborate anionic counter ion;
 - w is an integer varying between 0 and 18;
 - R8 and R9 are independently hydrogen, linear C₁ – C₁₈ alkyl, branched C₁ – C₁₈ alkyl, alkyl oxy, poly(ethylene oxide) or poly(propylene oxide); and
 - Y1 and Y2 each independently represent a urethane-containing substituent having attached thereto said first functional group.
4. The iodonium salt of Claim 3, wherein R8 or at least one of R9 has attached thereto said first functional group.
 5. The iodonium salt of Claims 3 or 4, wherein at least one of Y1 or Y2 has been produced by reacting a mono-isocyanate, a di-isocyanate or a poly-isocyanate with an amine or an alcohol having attached thereto said first functional group.
 6. The iodonium salt of Claim 5, wherein said mono-isocyanate, di-isocyanate or poly-isocyanate is Desmodur™ N100, Desmodur™ N3300, Desmodur™ CB 75N, Desmodur™ I, Desmodur™ W, Desmodur™ M, Desmodur™ H or Desmodur™ TD80.
 7. The iodonium salt of Claim 5 or 6, wherein said alcohol is pentaerylthritol triacrylate, dipentaerylthritol pentaacrylate, 2-hydroxyethylacrylate, 2-hydroxyethylmethacrylate, 4-hydroxybutylacrylate, 4-hydroxybutylmethacrylate, 6-hydroxyhexylacrylate, 6-hydroxyhexylmethacrylate, poly(ethylene glycol) acrylate, poly(ethylene glycol) methacrylate, poly(propylene glycol) acrylate or poly(propylene glycol) methacrylate.
 8. The iodonium salt of Claim 3 or 4, wherein at least one of Y1 or Y2 is:



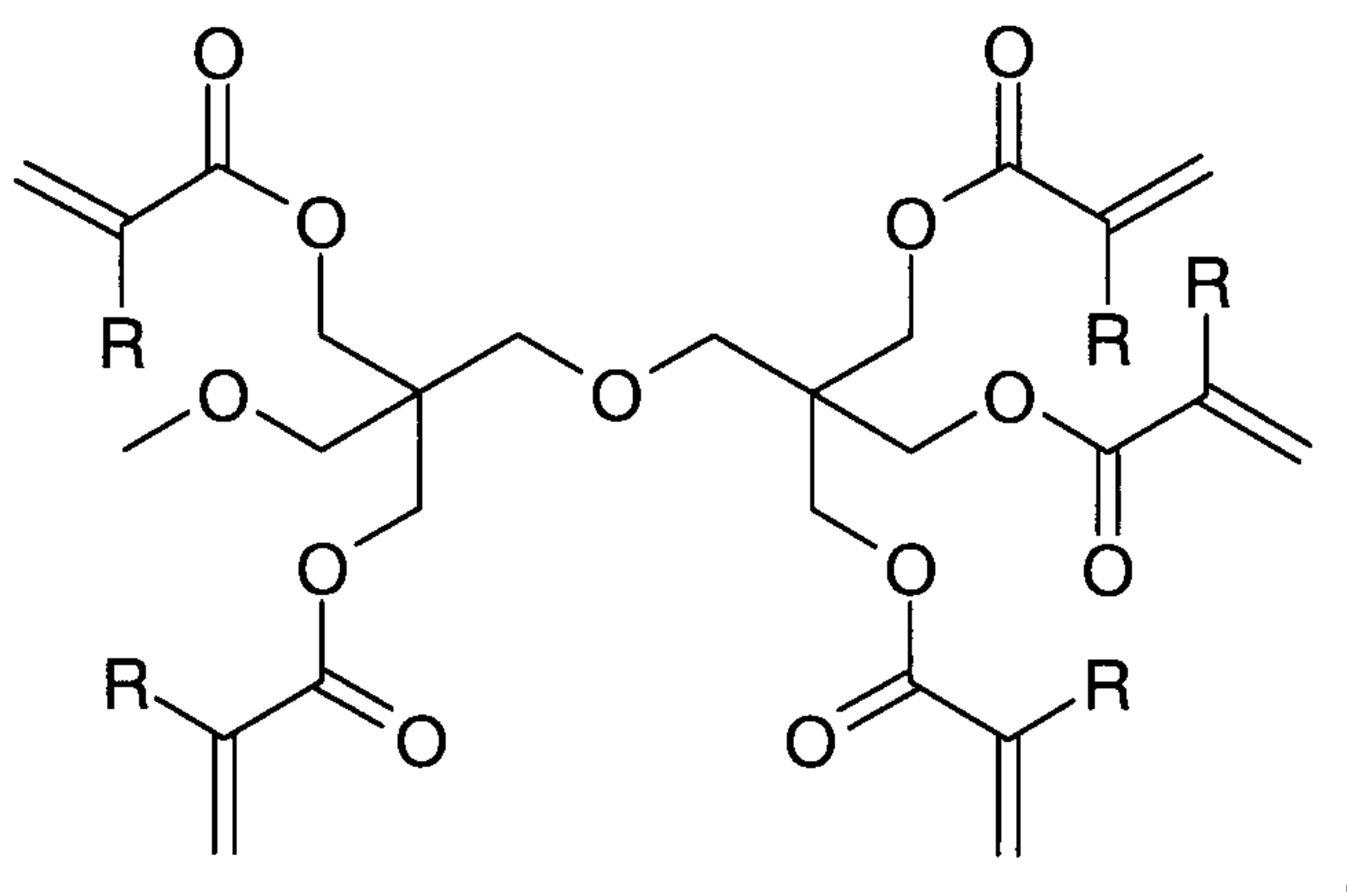
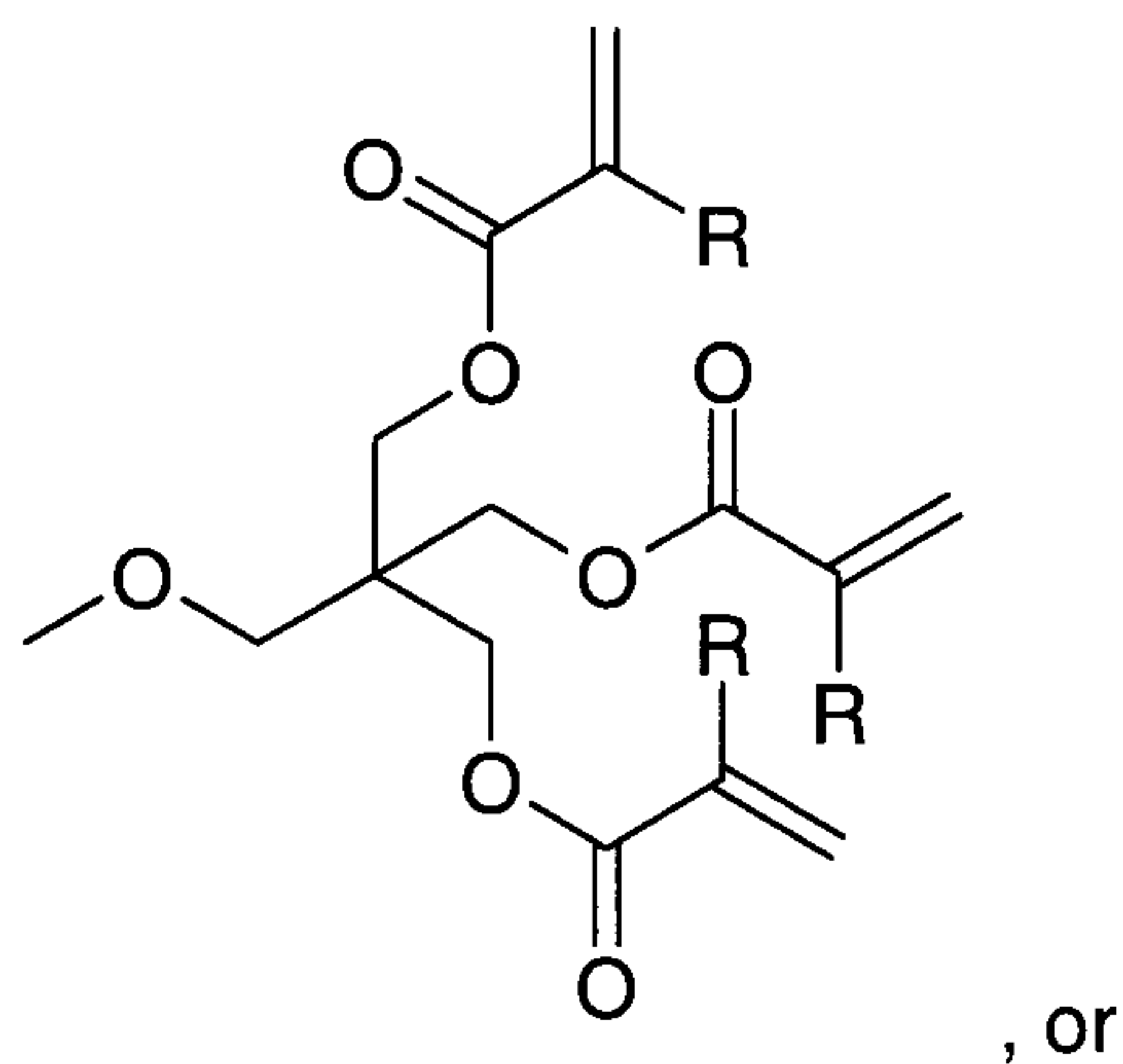
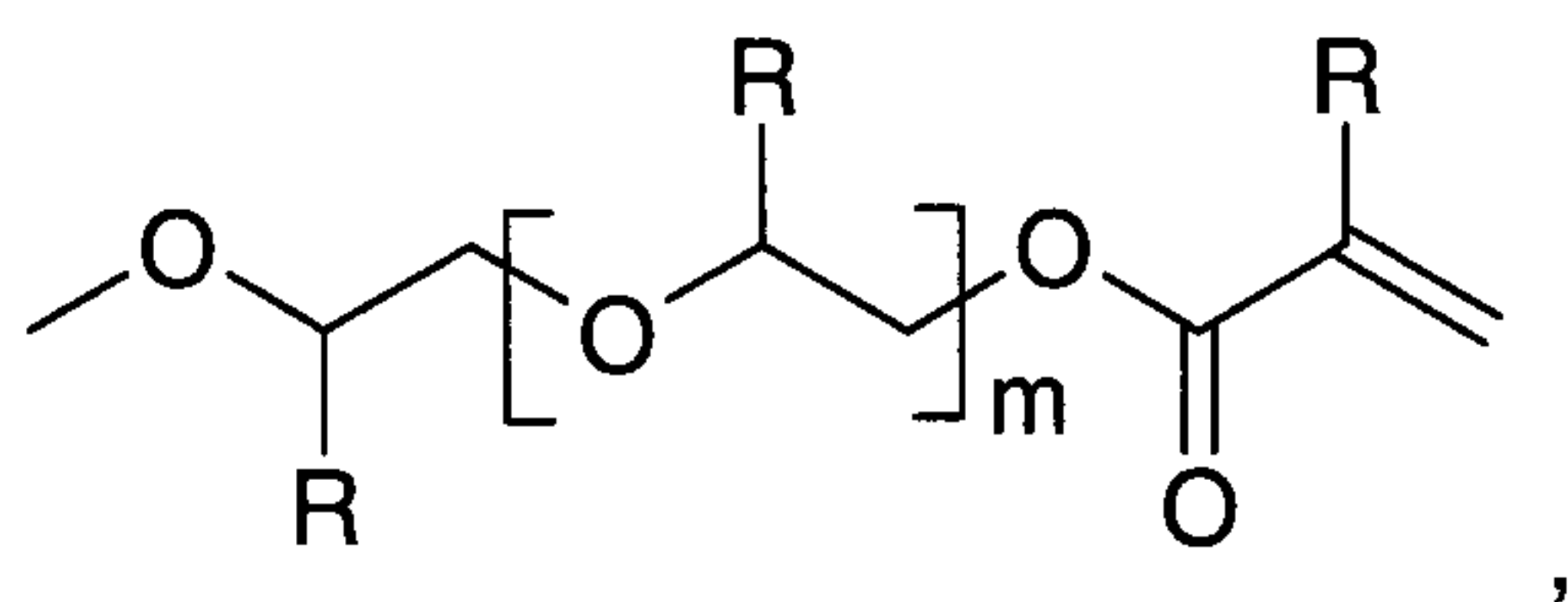
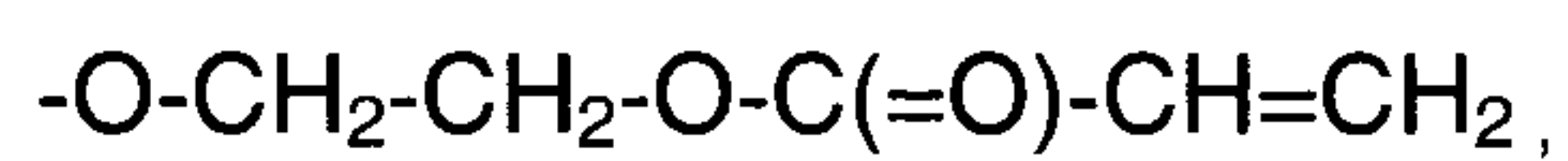


wherein:

- R is hydrogen or methyl,
- m is an integer varying between 1 and 18,
- R10 is hydrogen, linear or branched C₁₋₁₈ alkyl chain;
- Q1 and Q2 each independently represent an end compound having attached thereto said first functional group; and

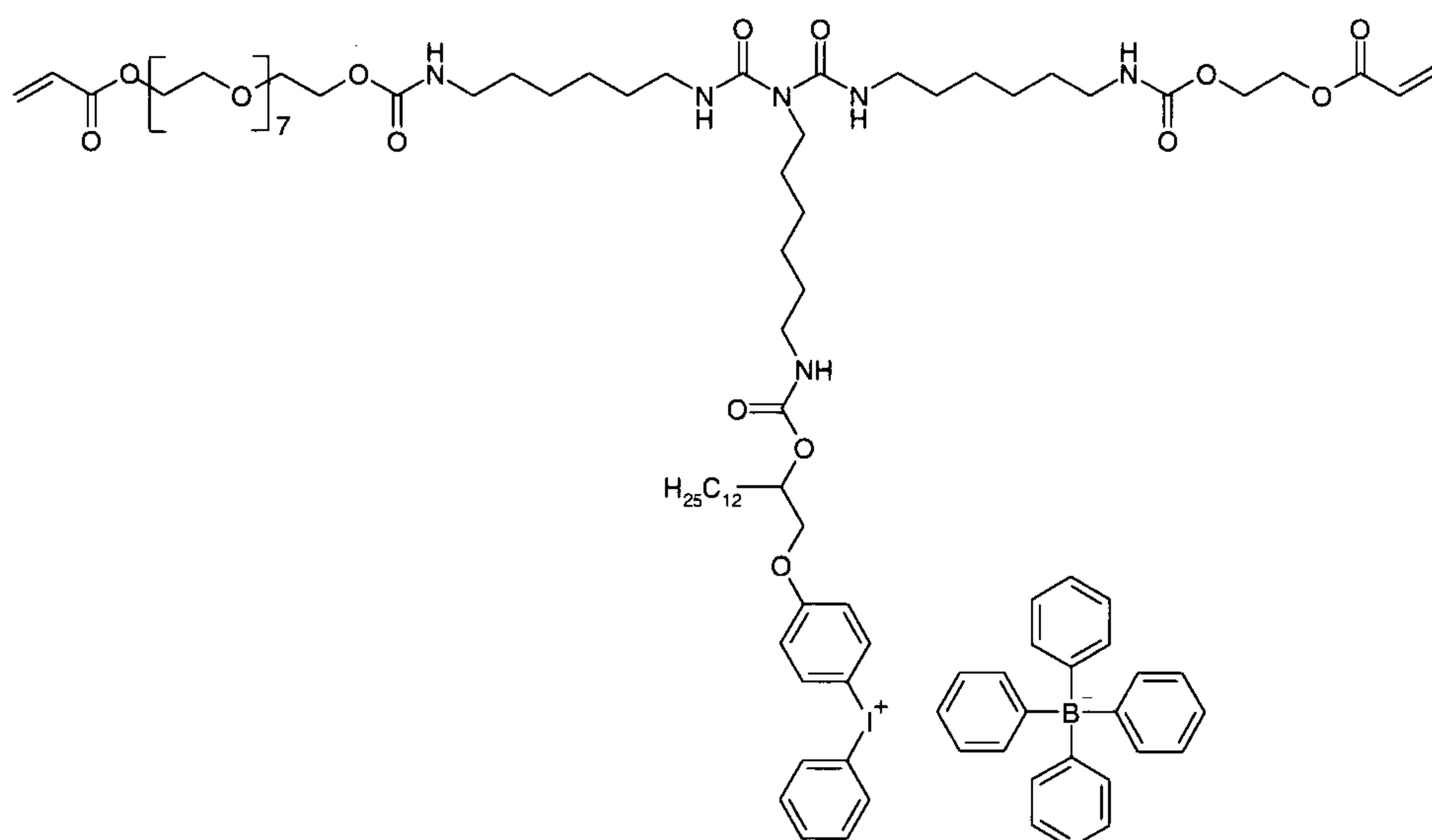
- Z represents a substituent comprising , wherein A1 is as defined in claim 3.

9. The iodonium salt of Claim 8, wherein at least one of Q1 or Q2 is :

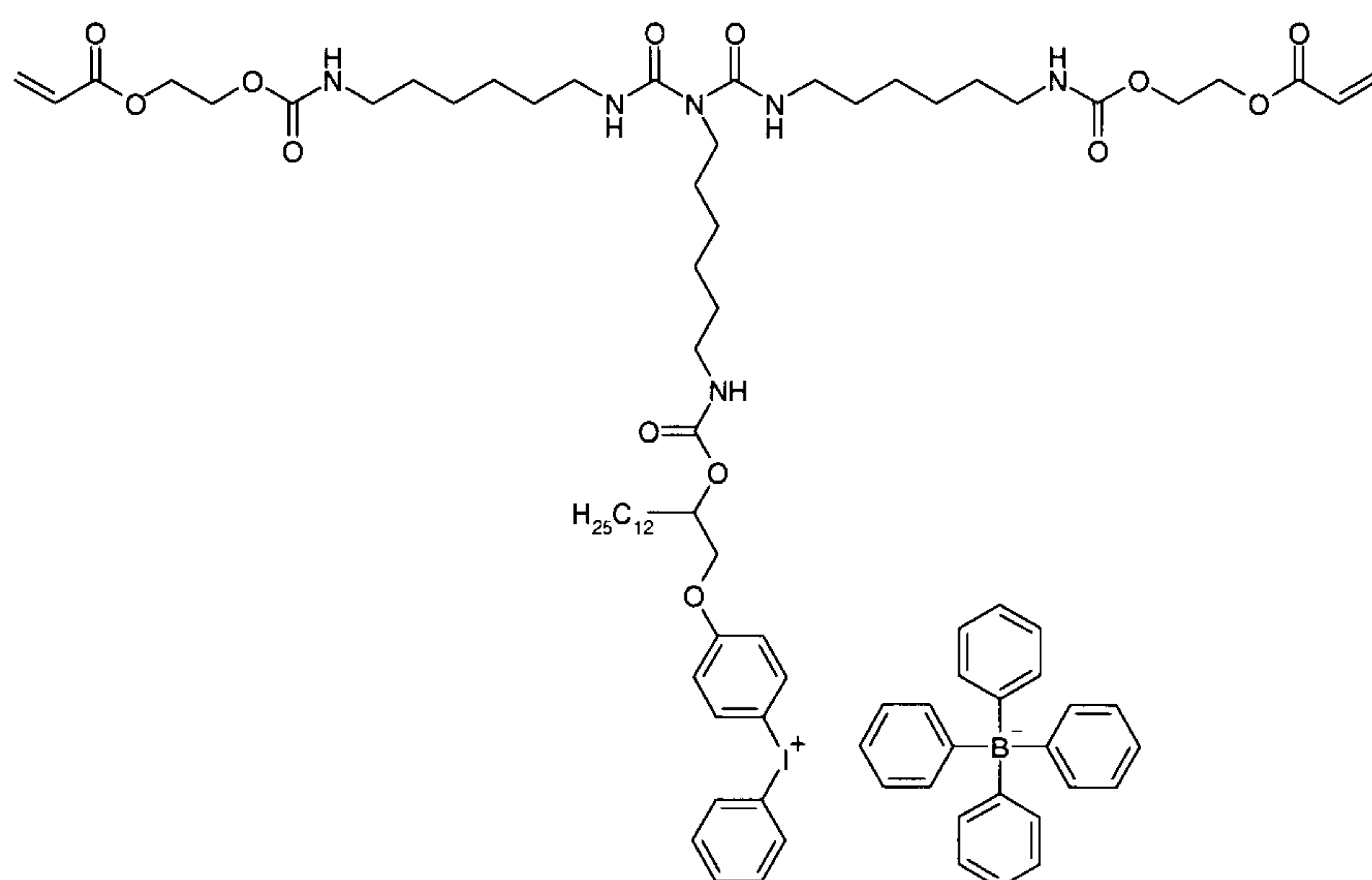


wherein R is hydrogen or methyl and m is an integer varying between 0 and 18.

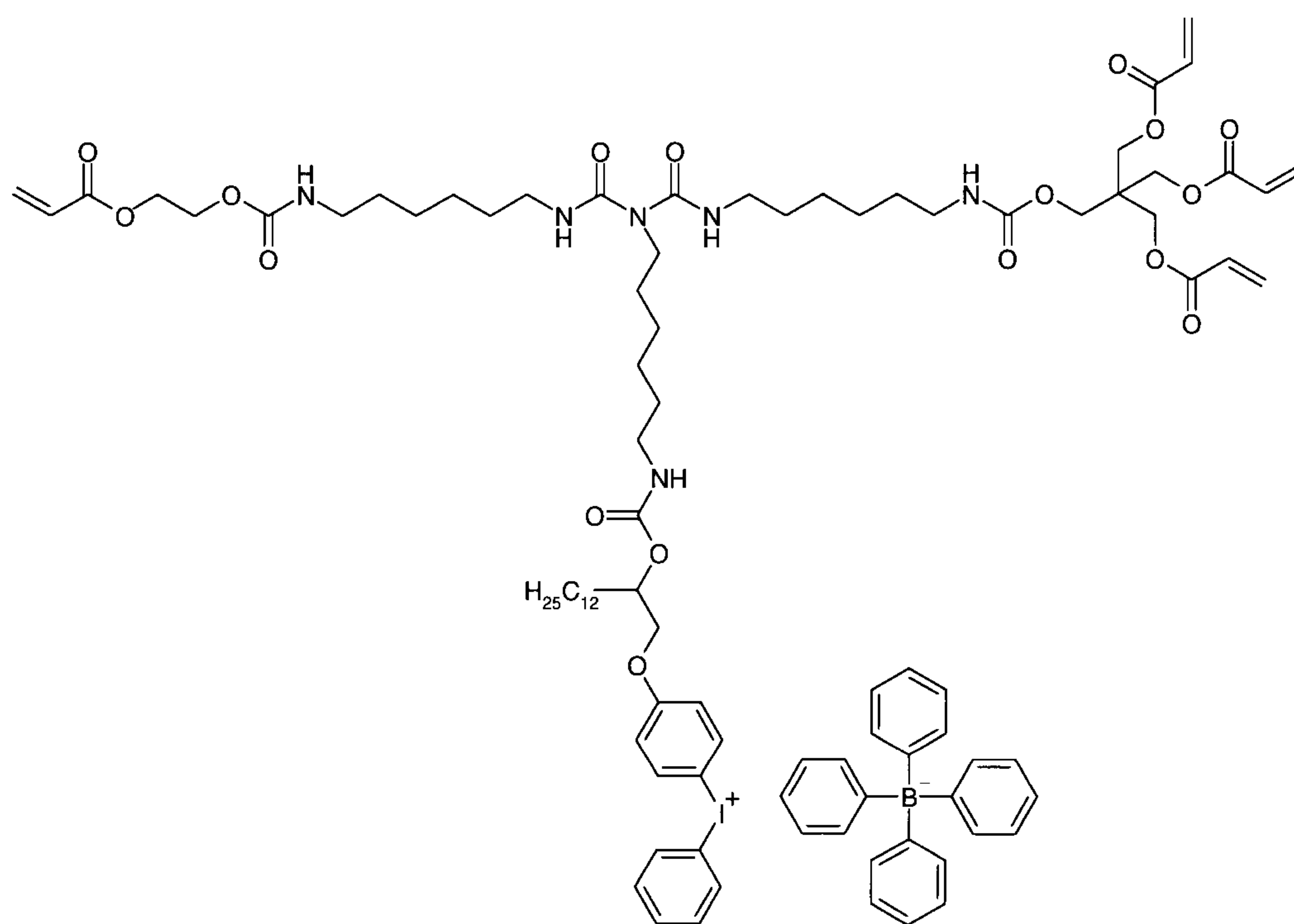
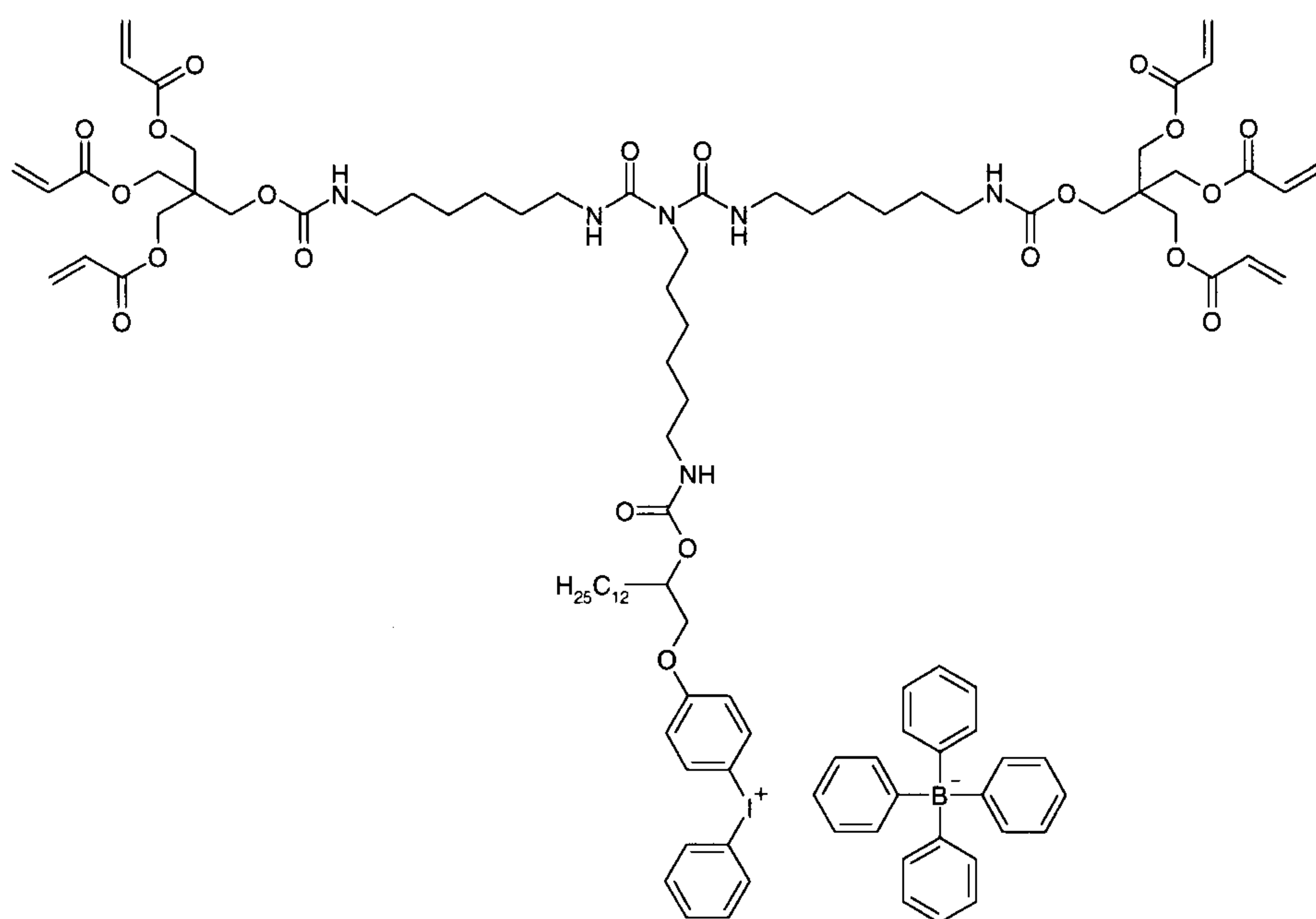
10. The iodonium salt of Claim 1 being:

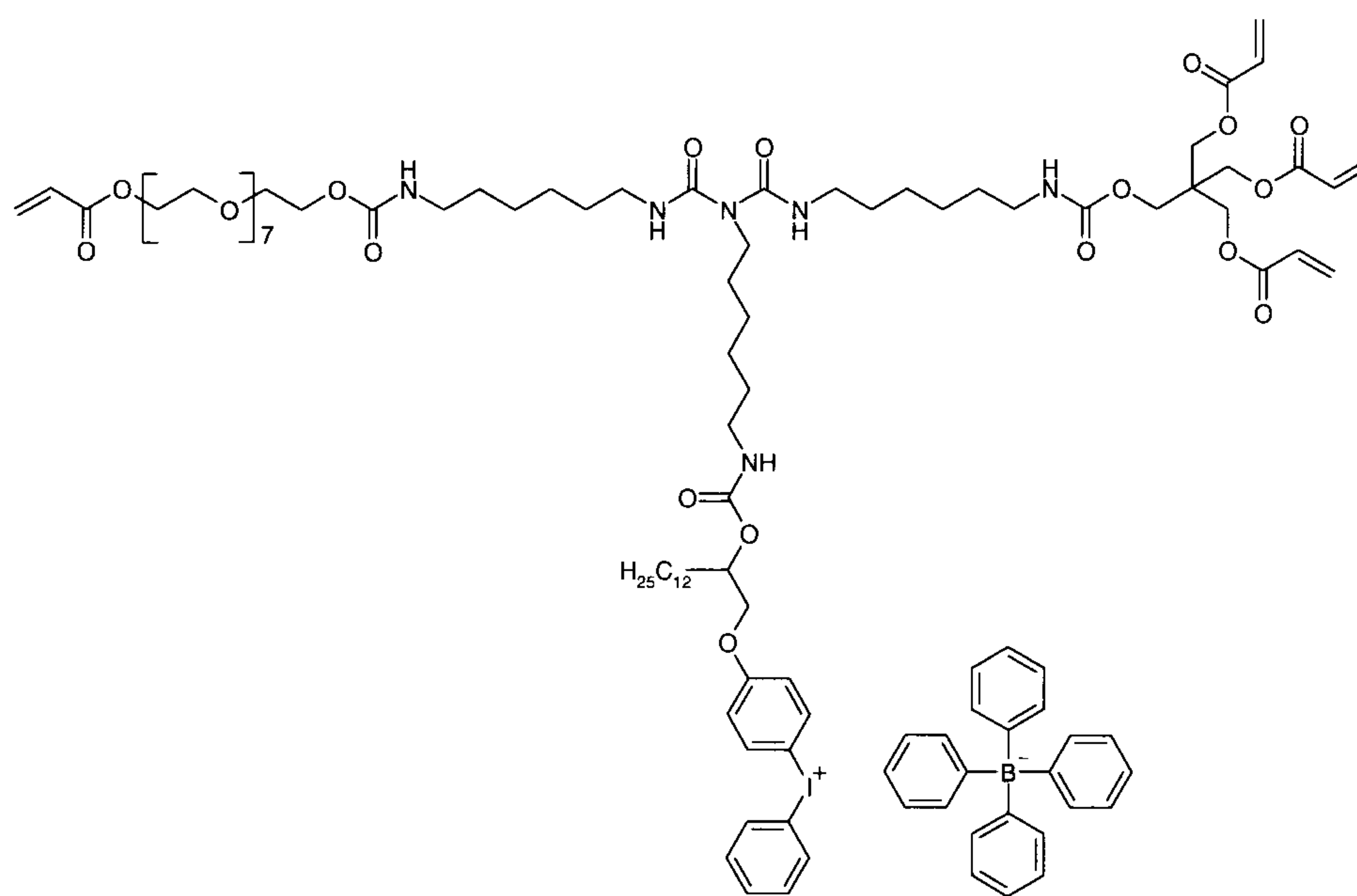
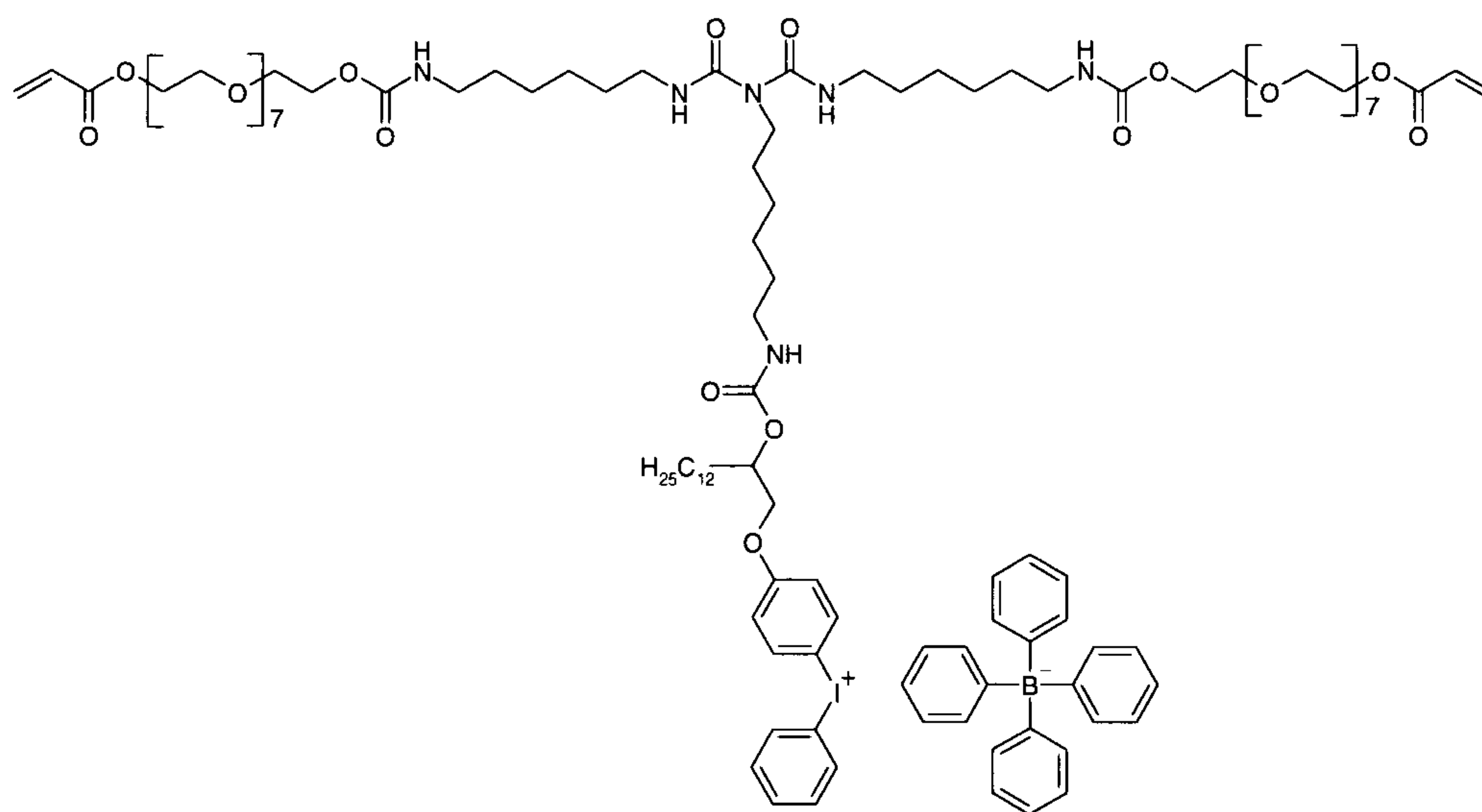


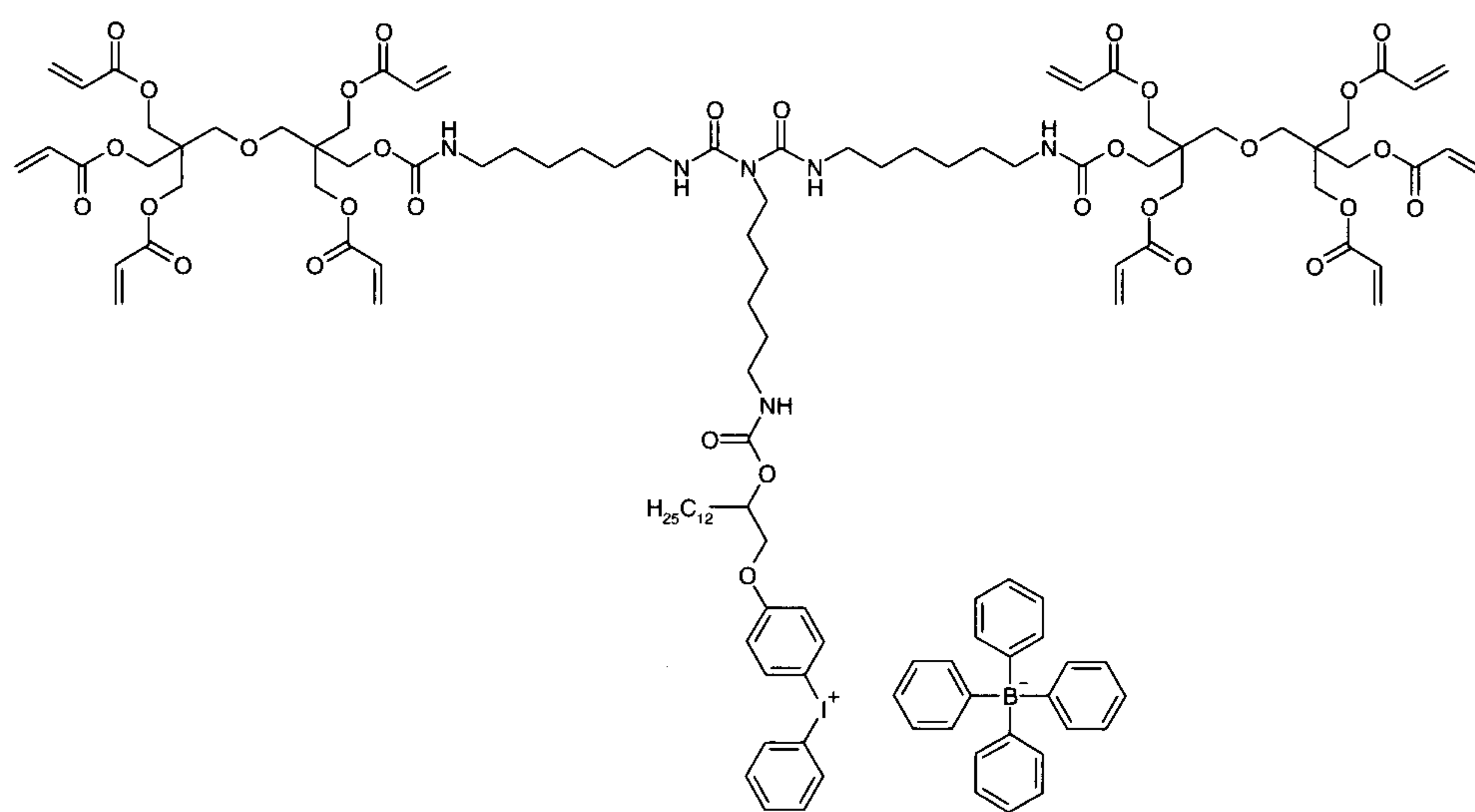
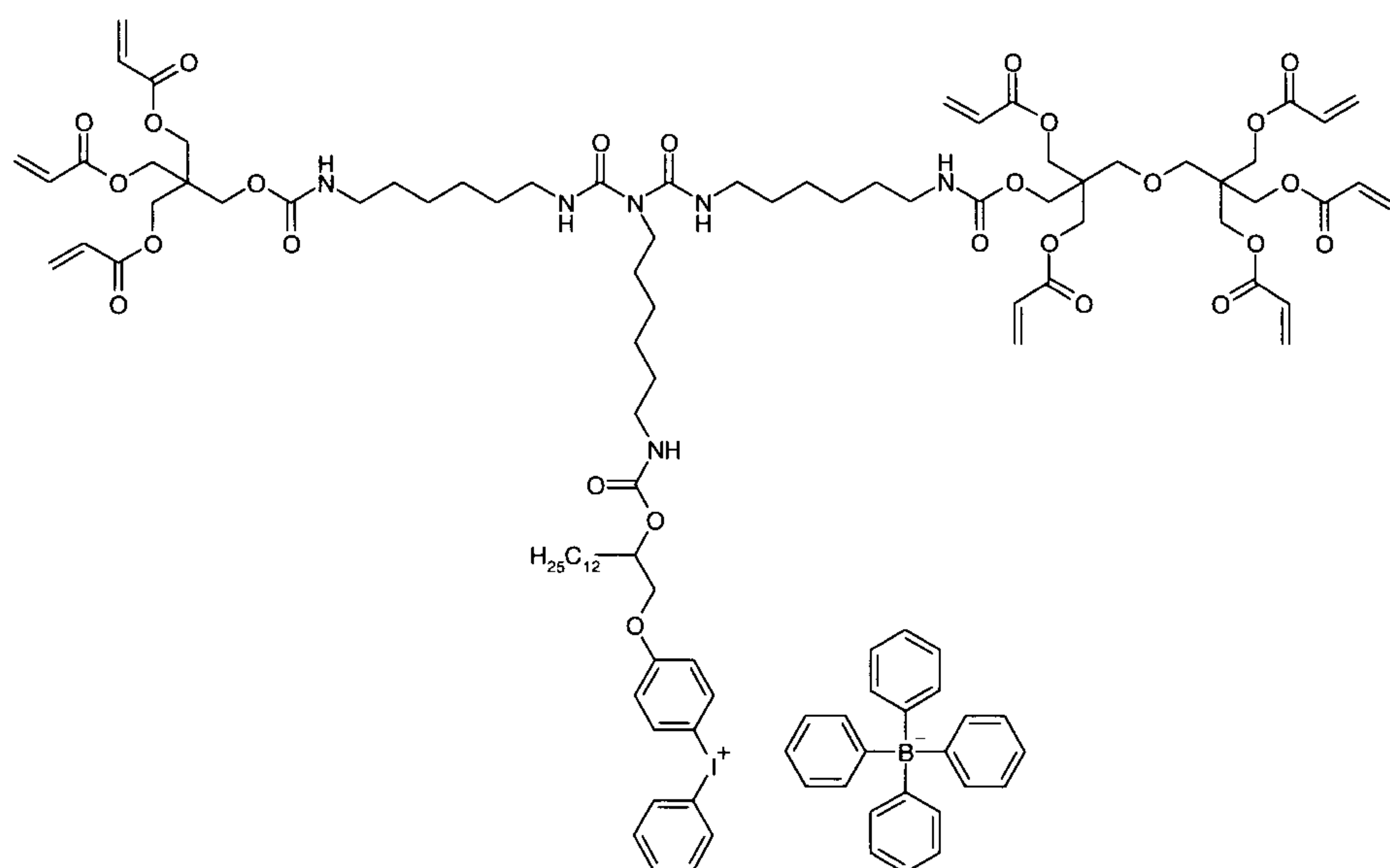
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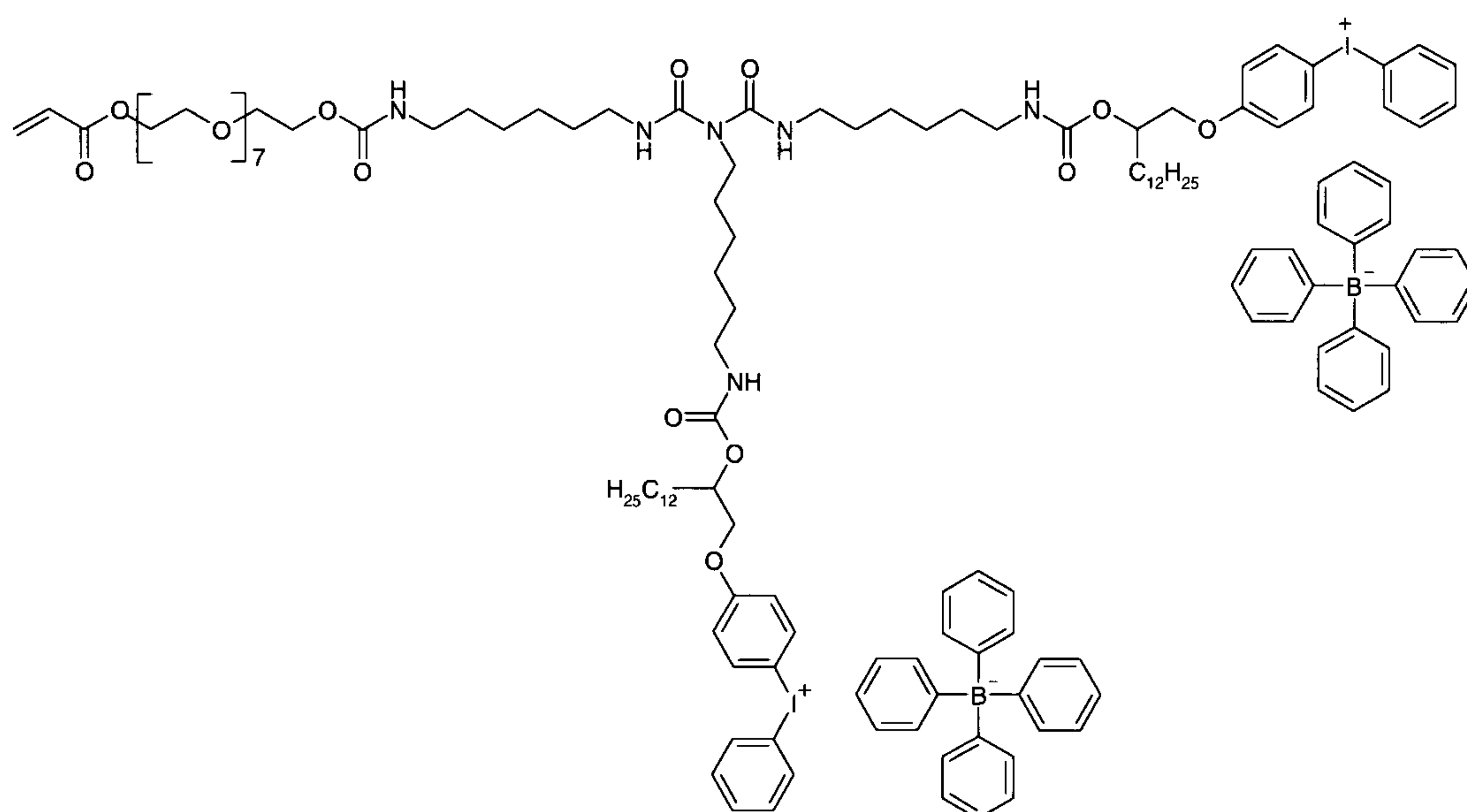
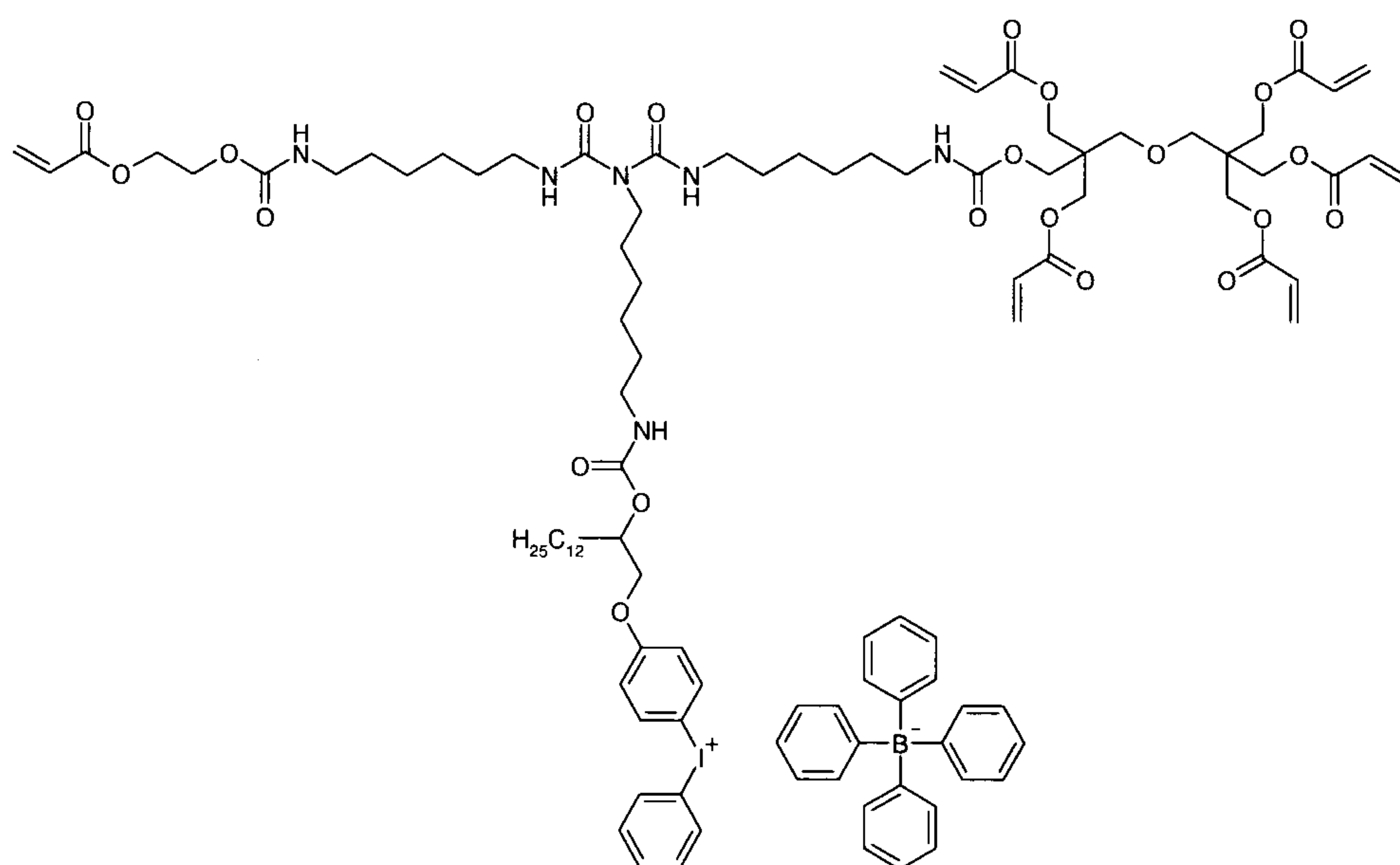


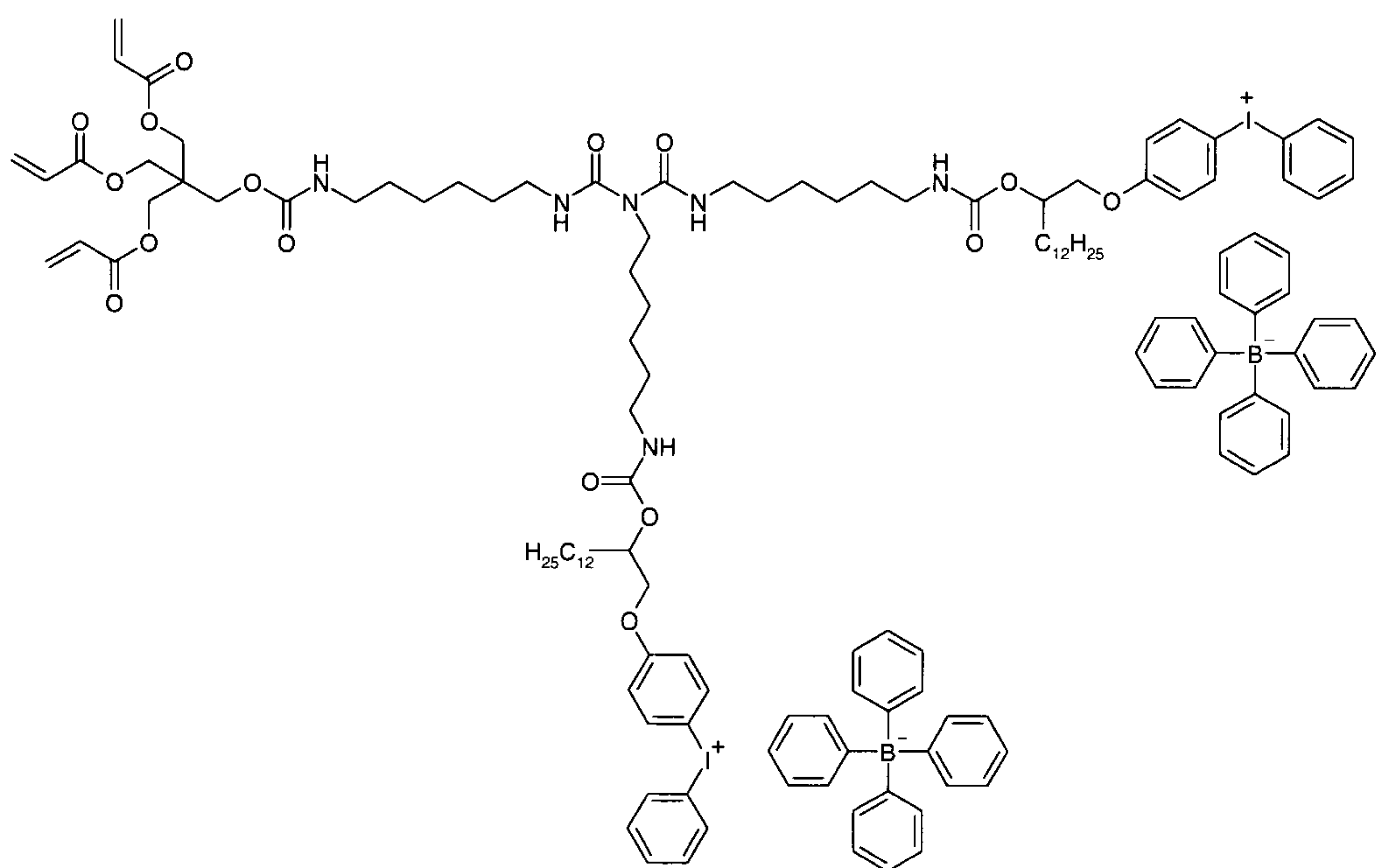
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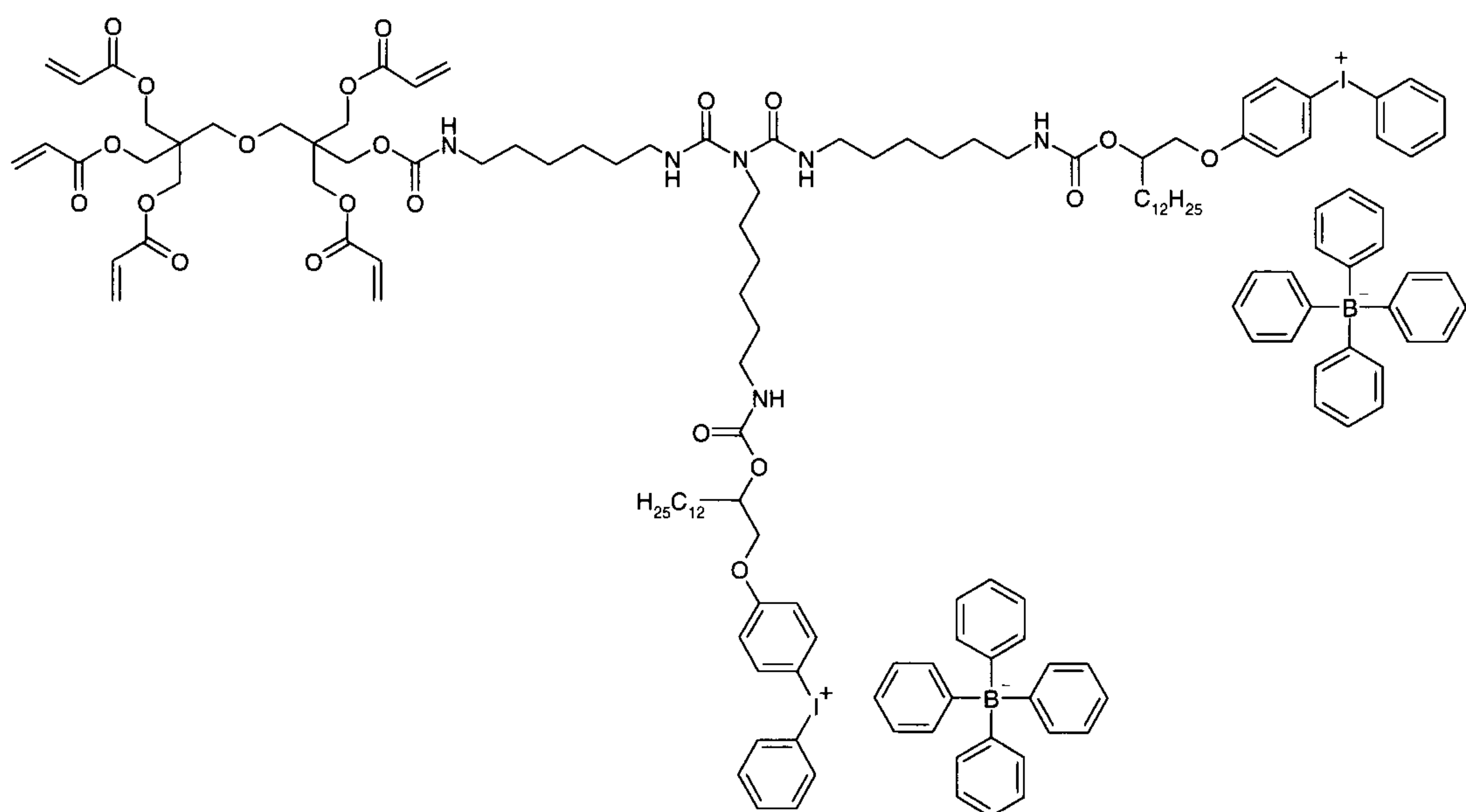




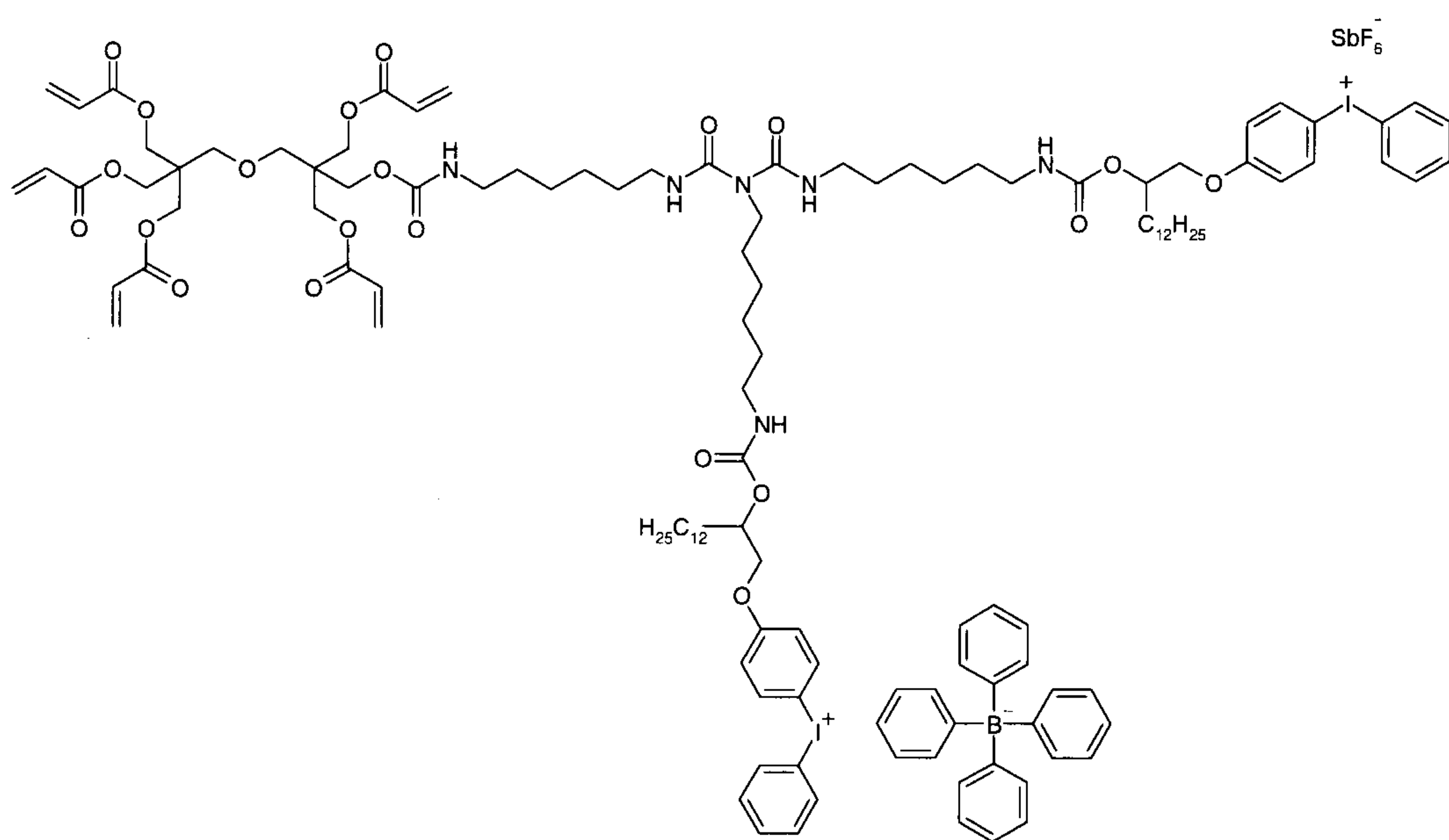




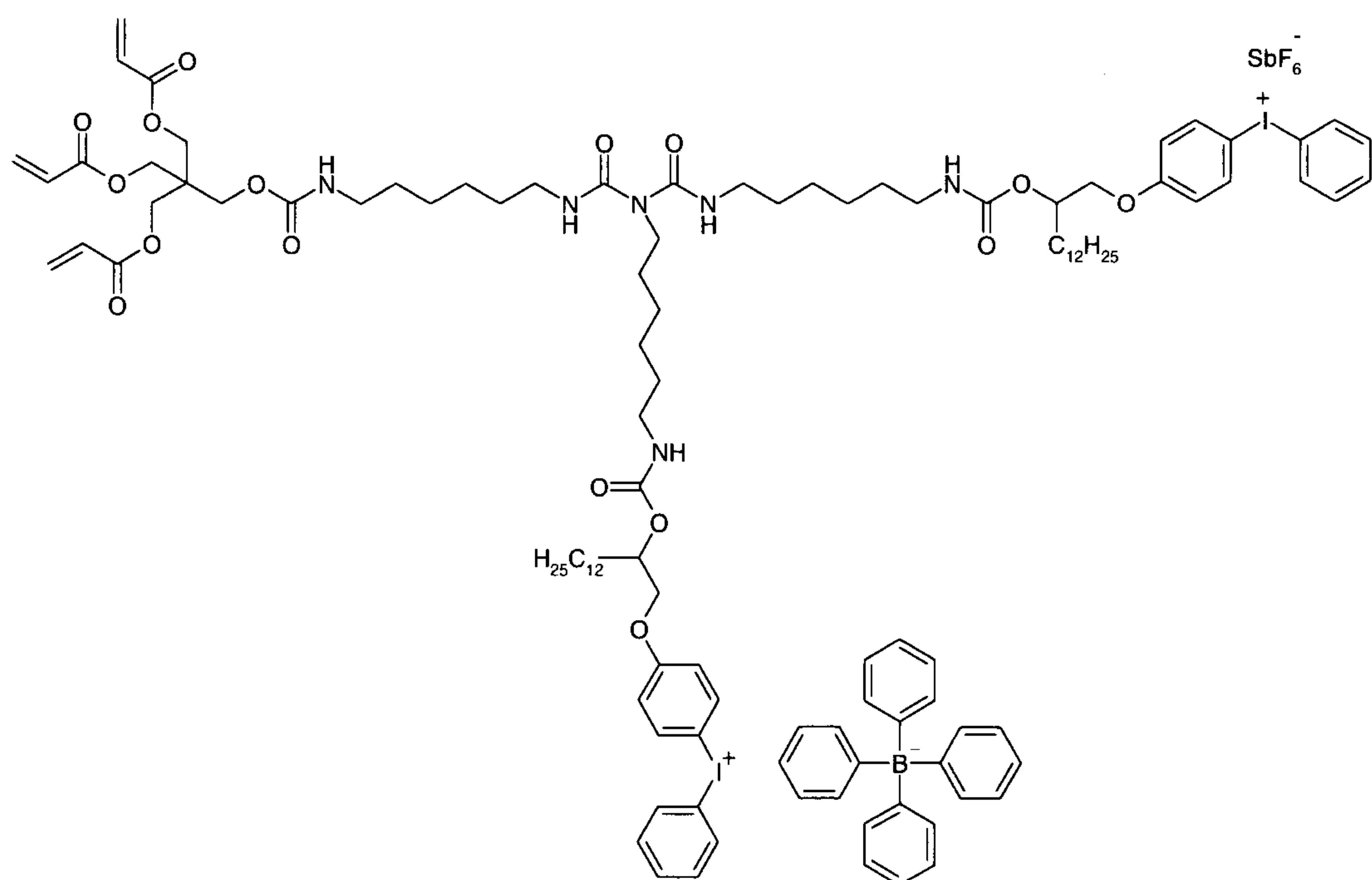




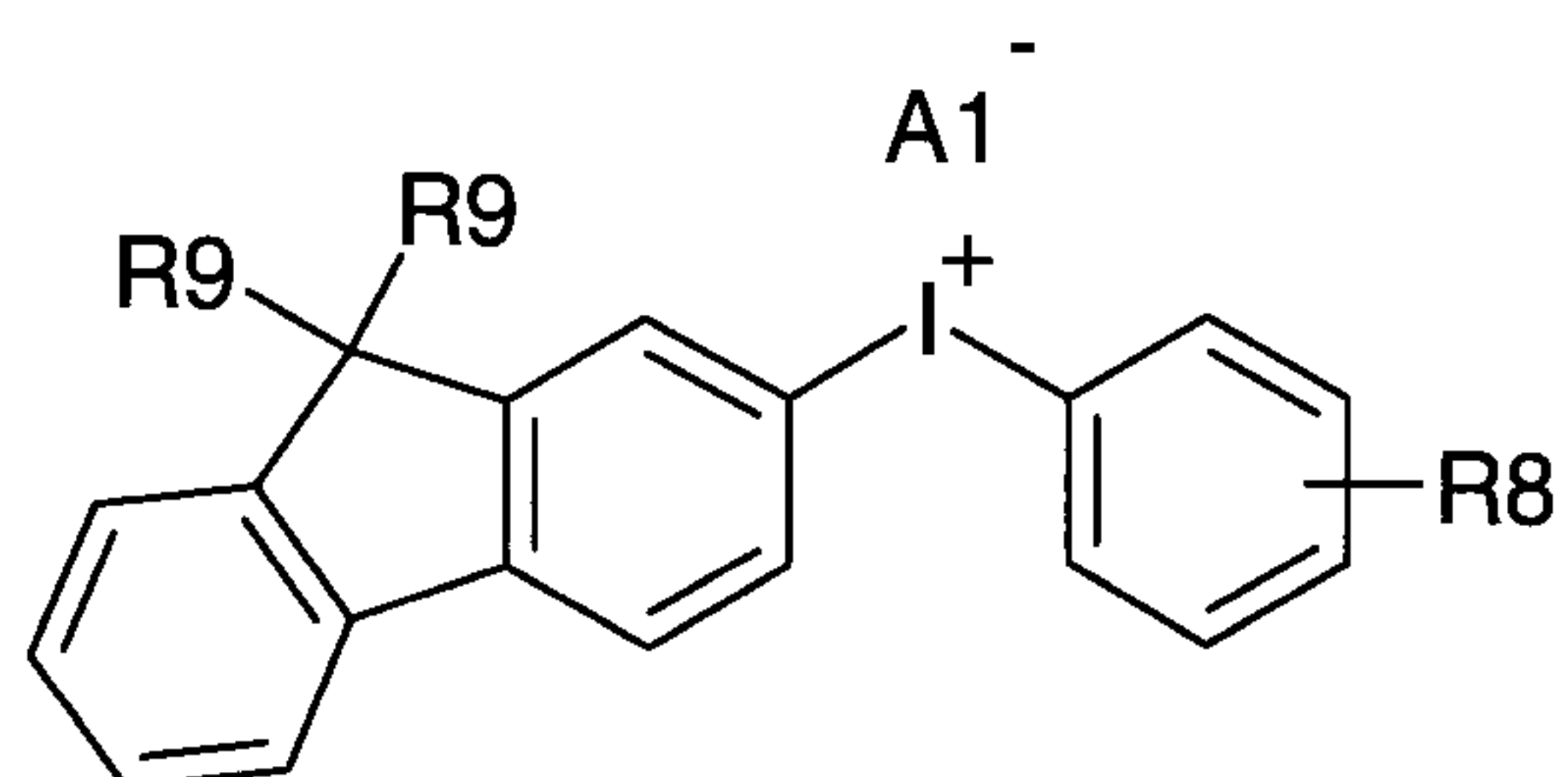
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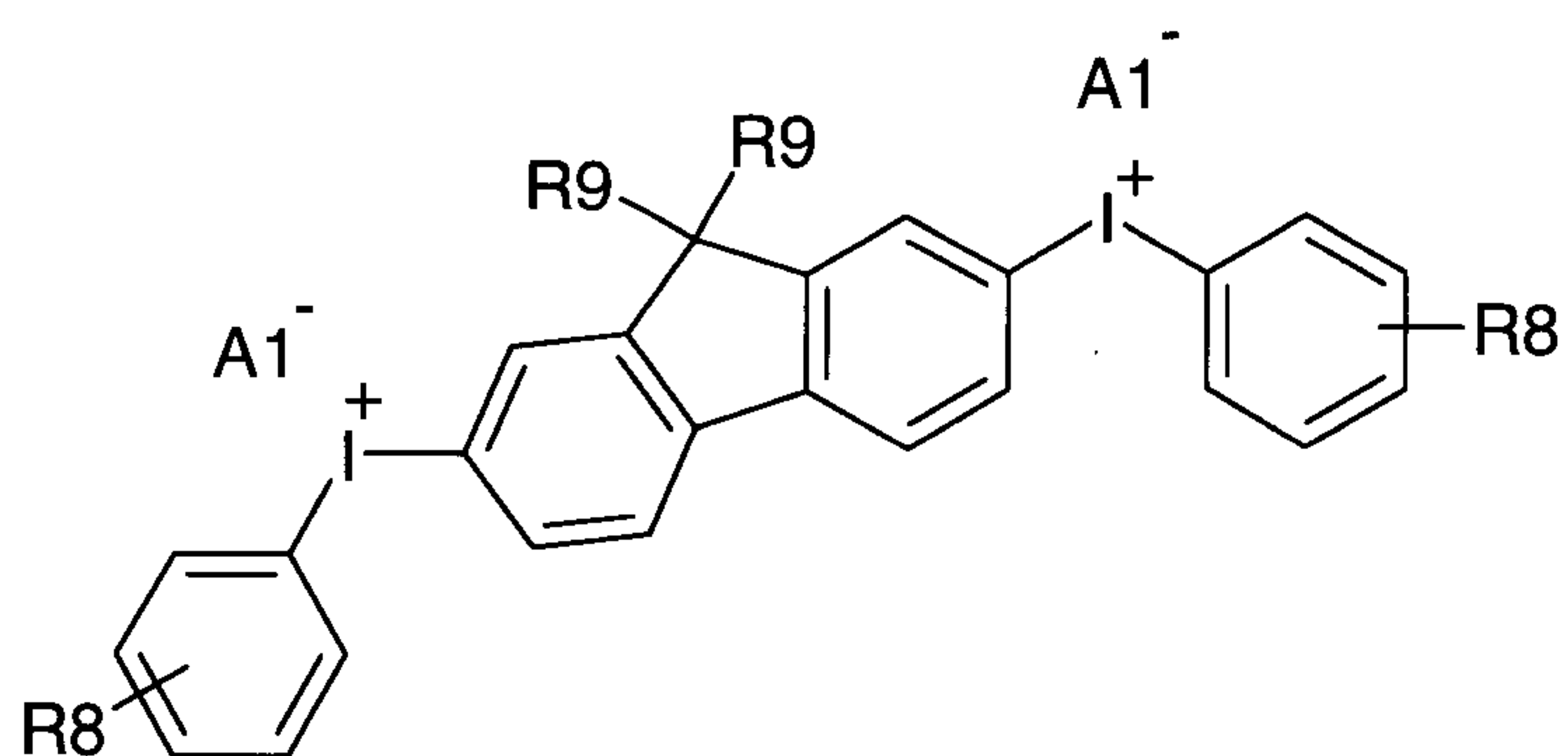
, or



11. The iodonium salt of Claim 1 or 2 having the general structure:



or

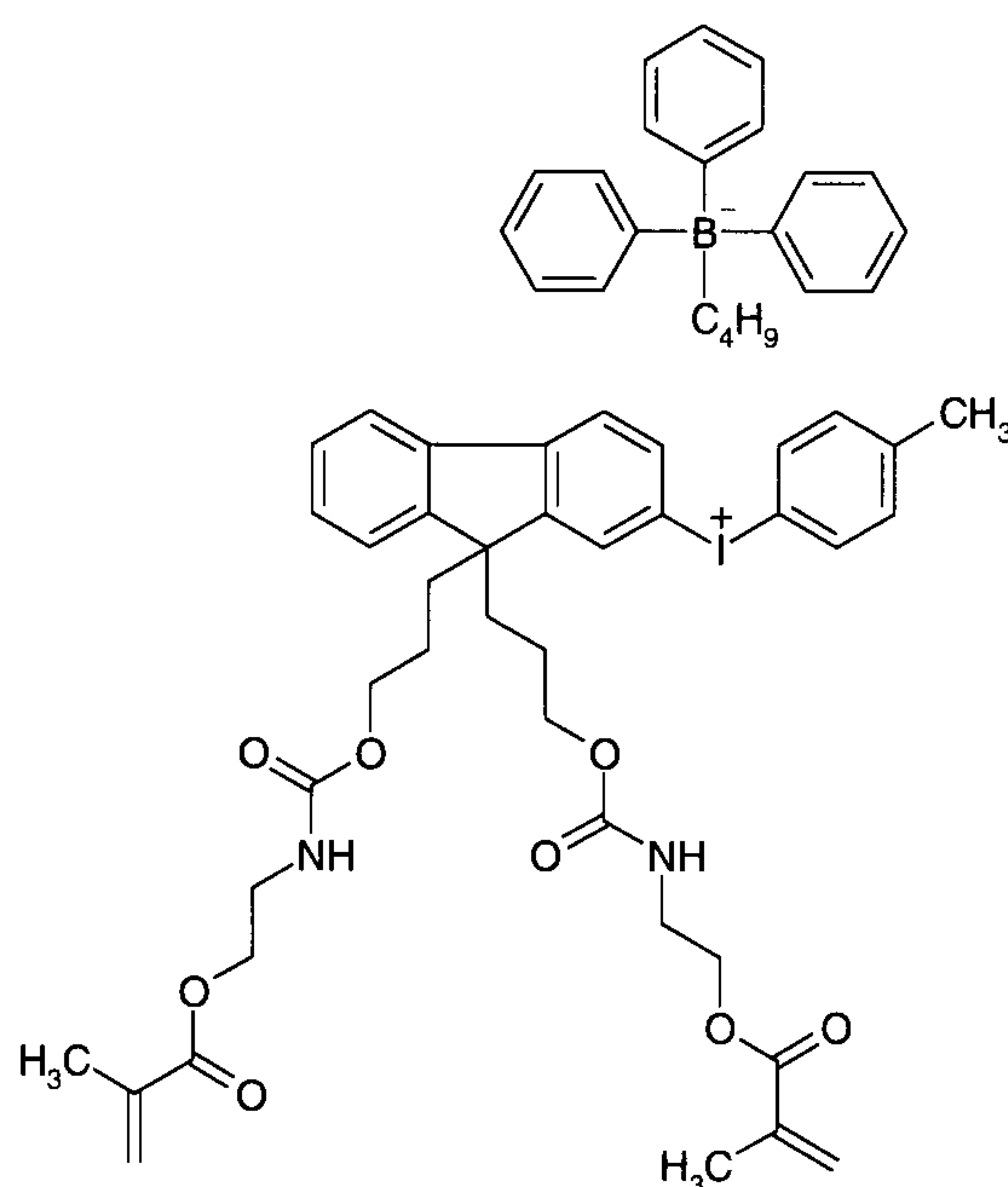


wherein:

- A1 represents a tosylate, triflate, hexafluoroantimonate, tetrafluoroborate, tetraphenylborate and triphenyl-n-alkylborate anionic counter ion; and
- R8 and R9 are independently hydrogen, linear C₁ – C₁₈ alkyl, branched C₁₋₁₈ alkyl, alkyl oxy, poly(ethylene oxide) or poly(propylene oxide),

and wherein at least one of R8 or R9 is not hydrogen and has attached thereto said first functional group.

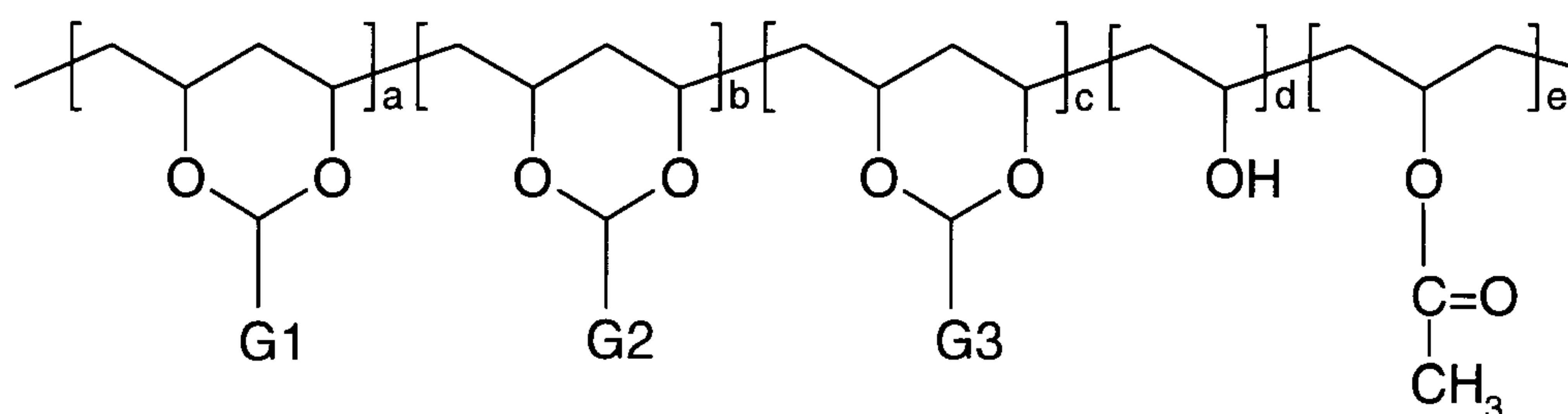
12. The iodonium salt of Claim 11 being:



13. A method of preparing the iodonium salts of any one of Claims 2 to 12 comprising attaching a pendant group to an iodonium salt, wherein said pendant group is obtained by reacting a mono-isocyanate, a di-isocyanate or a poly-isocyanate with an amine or an alcohol, wherein said amine or alcohol are terminated by an acrylate, a methacrylate or a vinyl-ether.
14. The method of claim 13, wherein the mono-isocyanate, di-isocyanate or poly-isocyanate is Desmodur™ N100, Desmodur™ N3300, Desmodur™ CB 75N, Desmodur™ I, Desmodur™ W, Desmodur™ M, Desmodur™ H or Desmodur™ TD 80.
15. The method of claim 13 or 14, wherein the alcohol is pentaerythritol triacrylate, 2-hydroxyethylacrylate, 2-hydroxyethylmethacrylate, 4-hydroxybutylacrylate, 4-

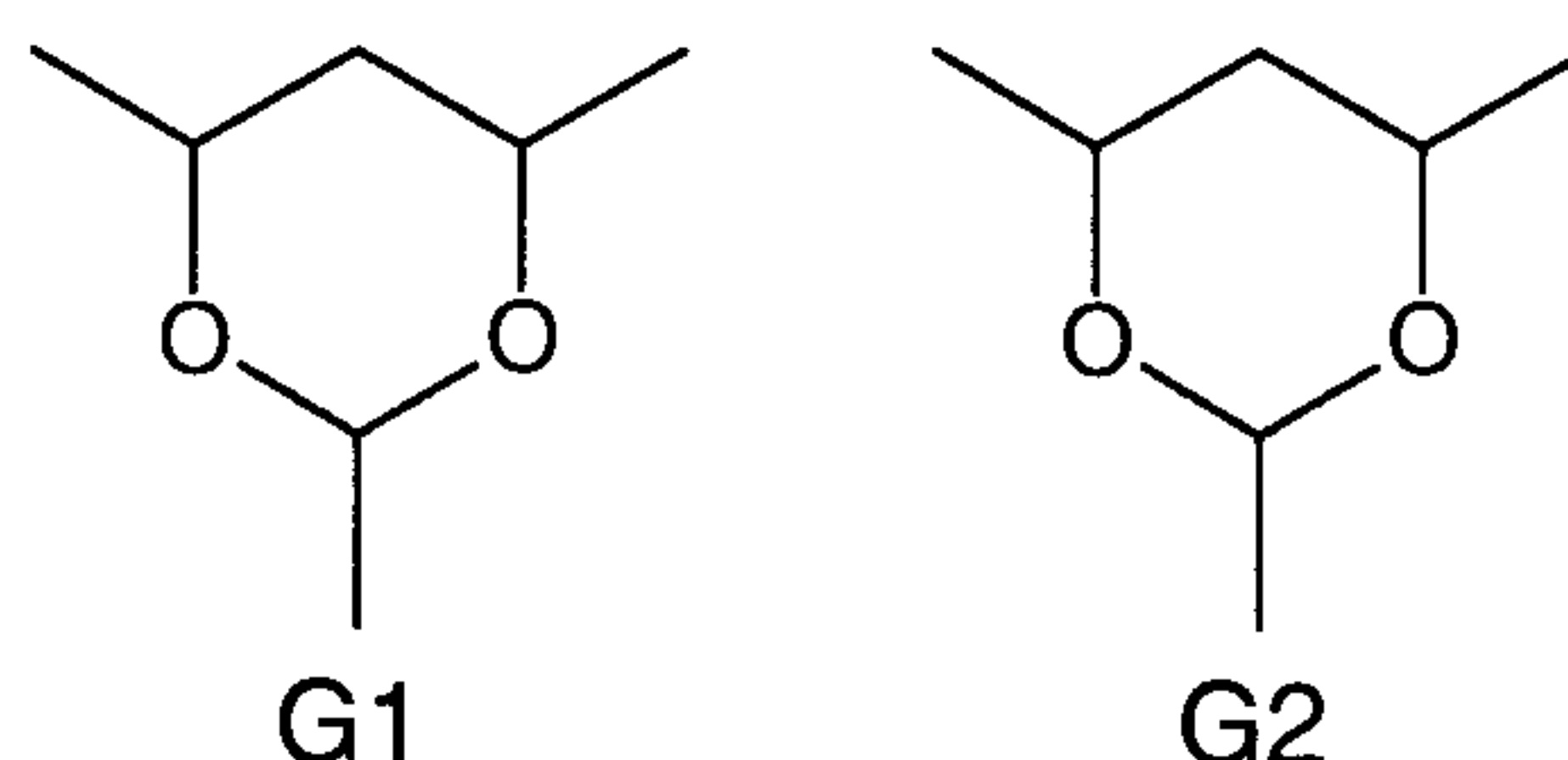
hydroxybutylmethacrylate, 6-hydroxyhexylacrylate, 6-hydroxyhexylmethacrylate, poly(ethylene glycol) acrylate, poly(ethylene glycol) methacrylate, poly(propylene glycol) acrylate or poly(propylene glycol) methacrylate.

16. Use of the iodonium salt of any one of Claims 1 to 12 or a mixture thereof in the preparation of a coating.
17. The use of Claim 16, wherein the coating is a negative working lithographic printing plate coating.
18. A lithographic printing plate coating solution comprising the iodonium salt of any one of Claims 1 to 12 or a mixture thereof.
19. The coating solution of Claim 18 comprising from about 5% to about 60 % by solid weight of said iodonium salt.
20. The coating solution of Claim 18 or 19 further comprising a near infrared absorbing dye.
21. The coating solution of Claim 20, wherein said near infrared absorbing dye is a molecular dye, a dimeric dye, a dendrimeric dye or a polymeric dye.
22. The coating solution of Claim 20 or 21, wherein said near infrared absorbing dye is a first polyvinyl alcohol acetal copolymer or a mixture thereof.
23. The coating solution of Claim 22 comprising from about 5% to about 50 % by solid weight of said first polyvinyl alcohol acetal copolymer.
24. The coating solution of Claim 22 or 23, wherein said first polyvinyl alcohol acetal copolymer has attached thereto at least one second functional group capable of undergoing cationic or radical polymerization.
25. The coating solution of any one of Claims 22 to 24, wherein the first polyvinyl alcohol acetal copolymer has the following structure:



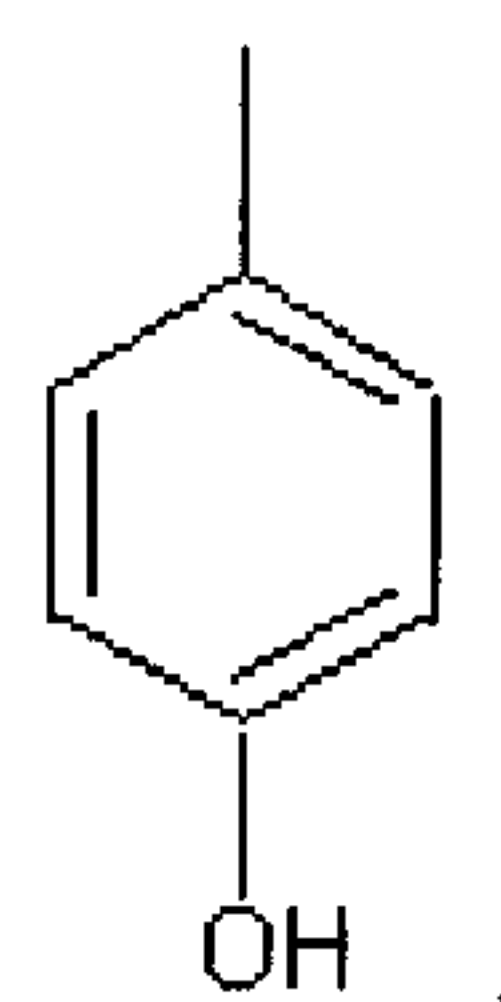
wherein:

- G1 represents a processing segment providing solubility in organic solvents;
- G2 represents a thermal reactive segment;
- G3 represents a radiation-absorbing segment exhibiting one or more strong absorption peaks between 700 and 1100 nm;
- a, b, c, d and e are molar ratios and may vary from 0.01 to 0.99;



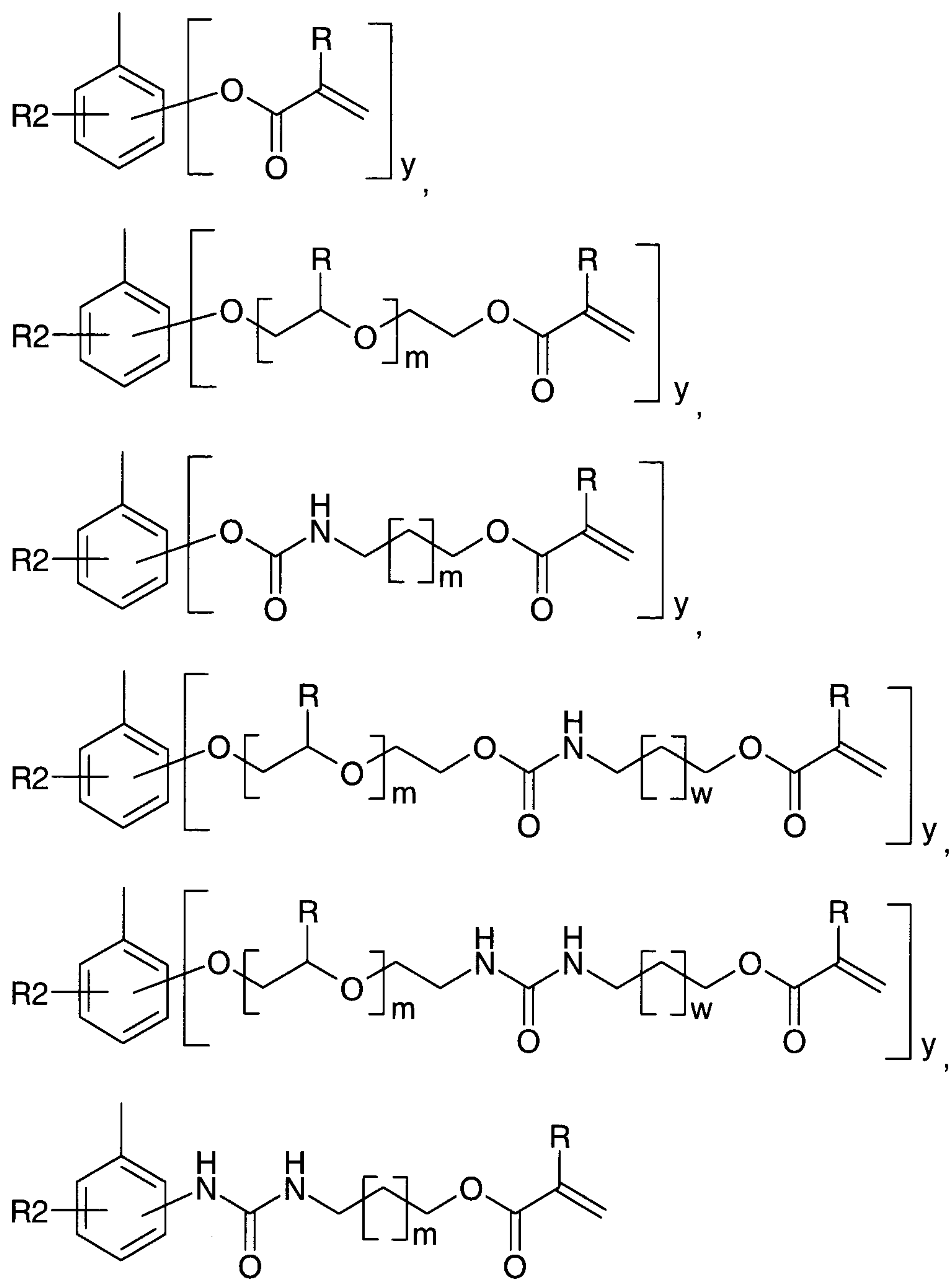
- any of and may independently be replaced by ; and
- said second functional group, when present, is attached to G2 or G3.

26. The coating solution of Claim 25, wherein G1 is linear alkyl, branched alkyl, linear aryl or branched aryl, wherein said linear alkyl, branched alkyl, linear aryl or branched aryl is substituted by a cyano, hydroxy, dialkylamino, trialkylammonium salts, ethylene oxide, propylene oxide methylbenzylsufonyl-carbamate, carboxylic acid or phosphoric acid functional group.



27. The coating solution of Claim 26, wherein G1 is .
28. The coating solution of any one of Claims 25 to 27, wherein G2 is linear alkyl, branched alkyl, linear aryl or branched aryl, wherein said linear alkyl, branched alkyl, linear aryl or branched aryl has attached thereto said second functional group.
29. The coating solution of Claim 28, wherein said second functional group is vinyl ether, alkoxy-methyl acrylamide, alkoxy methacrylamide, acrylate or methacrylate.

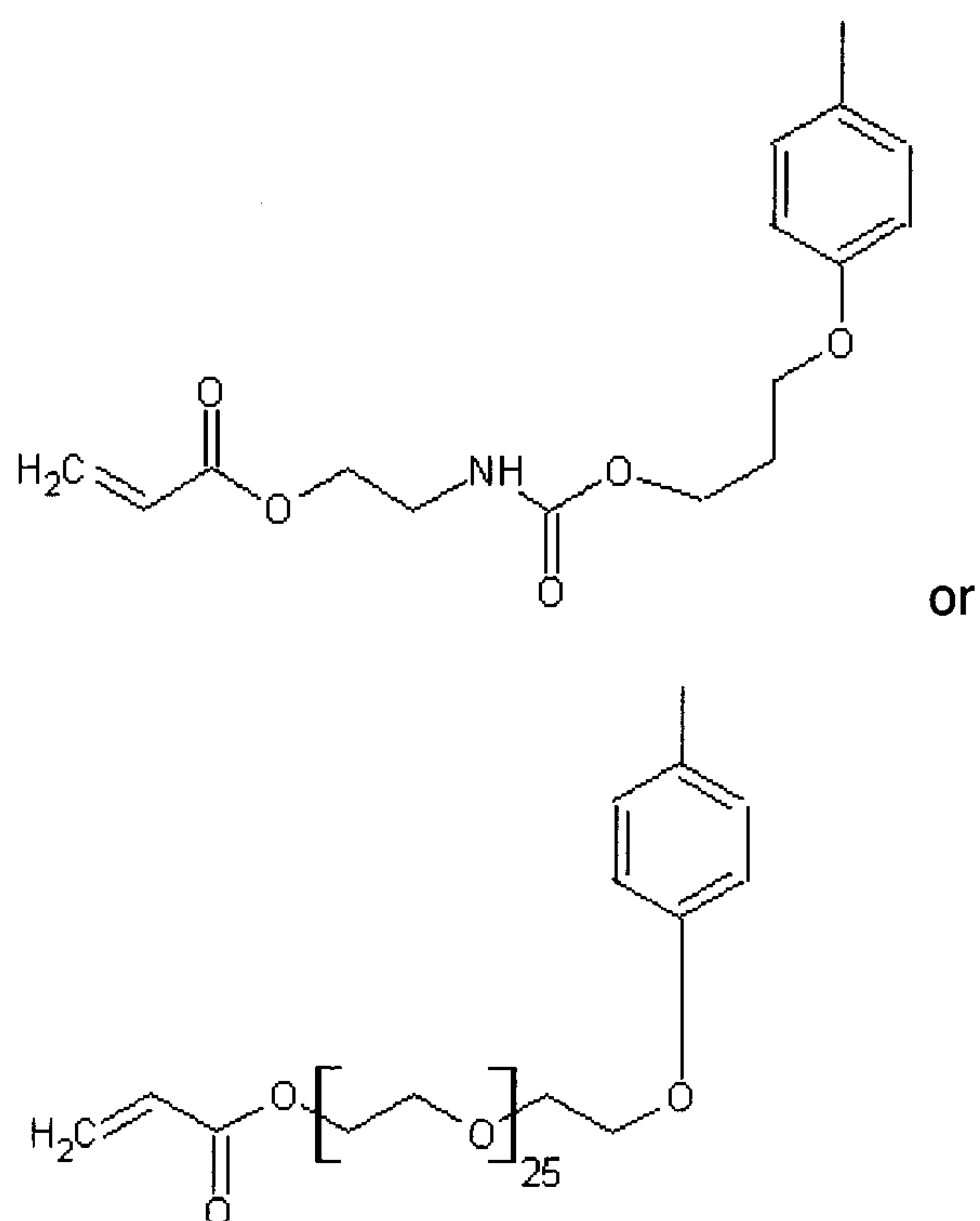
30. The coating solution of Claim 29, wherein G2 is:



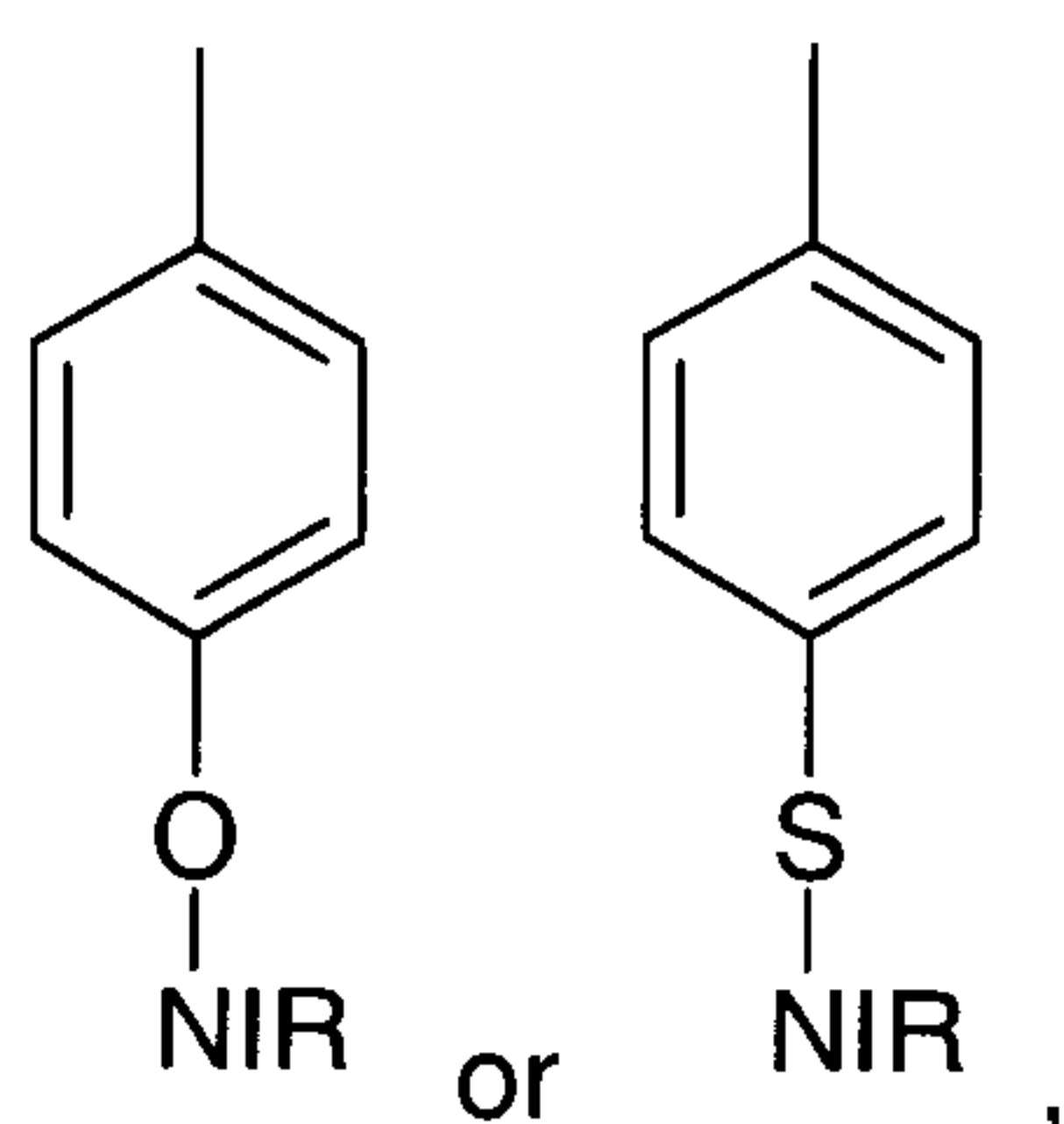
wherein:

- R is hydrogen or methyl;
- R2 is C₁₋₈ alkyl or alkoxy;
- m and w are integers varying between 0 and 50; and
- y is 1 or 2.

31. The coating solution of Claim 29, wherein G2 is:

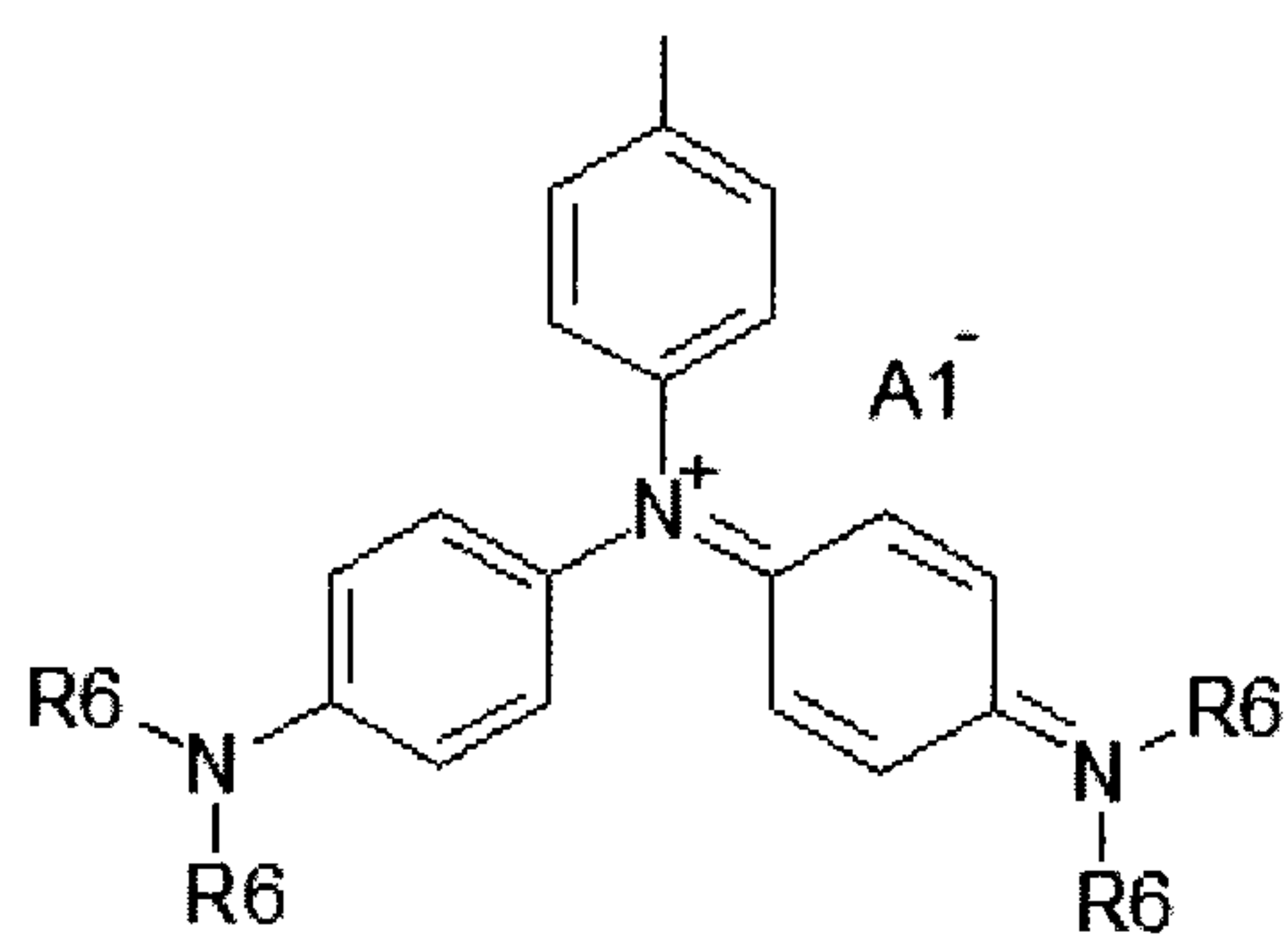
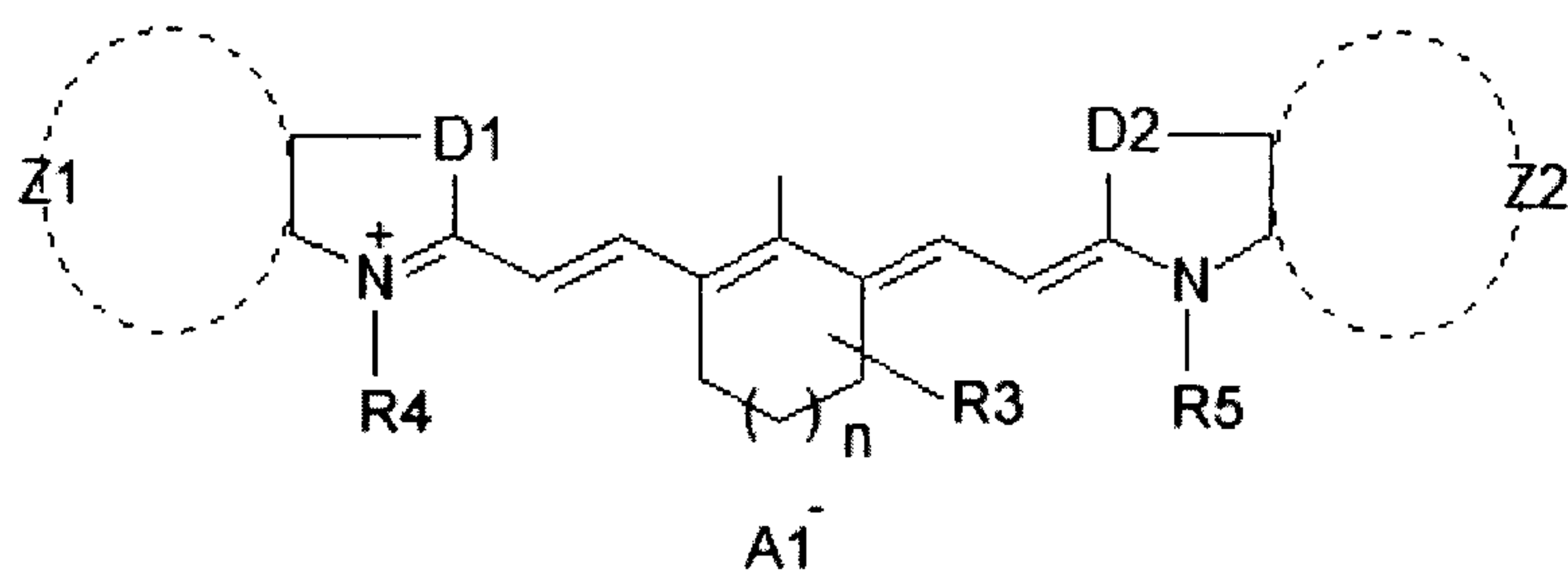
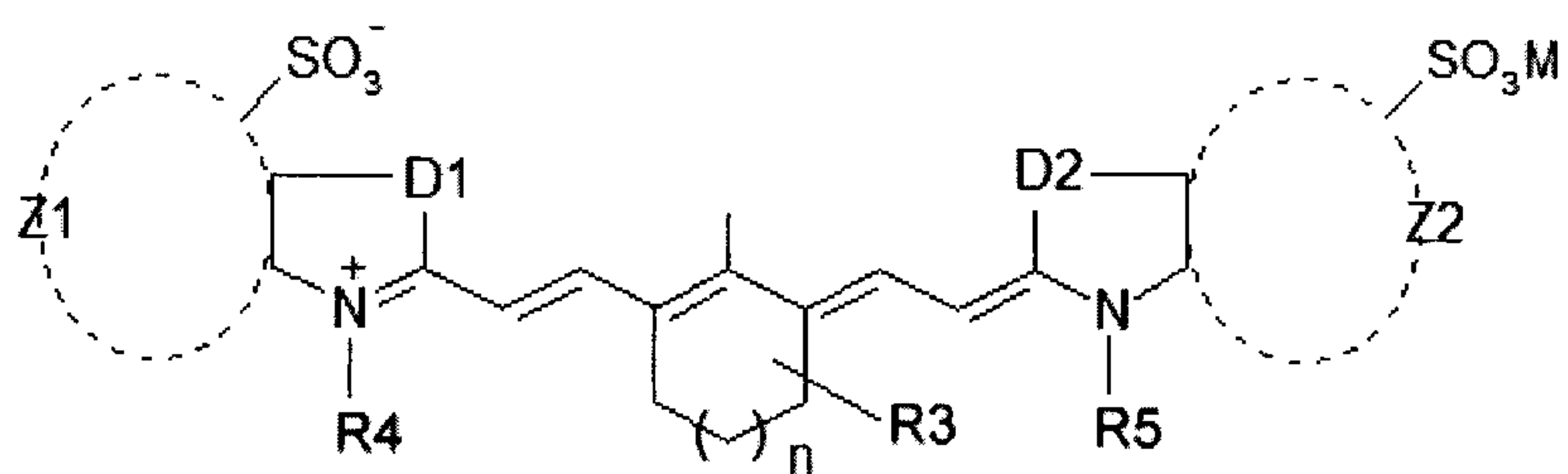
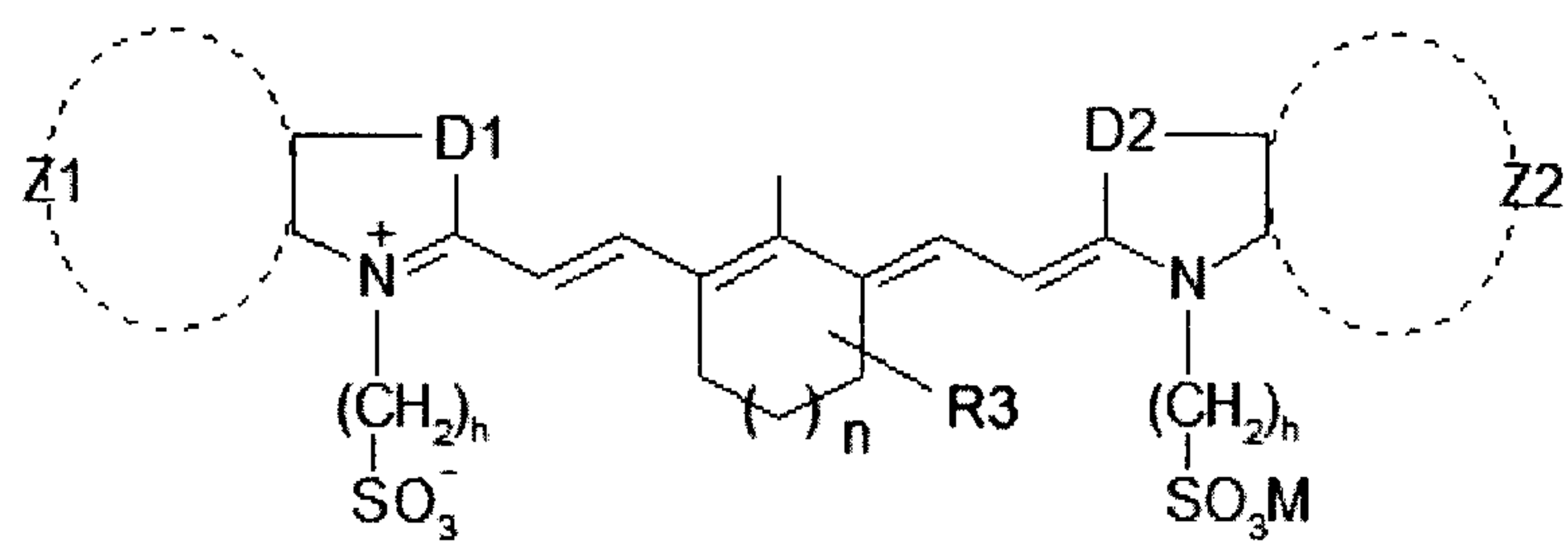


32. The coating solution of any one of Claims 25 to 31, wherein said first polyvinyl alcohol acetal copolymer comprises more than one G3 segments that may be identical to or different from each other.
33. The coating solution of any one of Claims 25 to 32, wherein G3 further exhibits one or more strong absorption peaks between 400 and 700 nm.
34. The coating solution of any one of Claims 25 to 33, wherein G3 is:

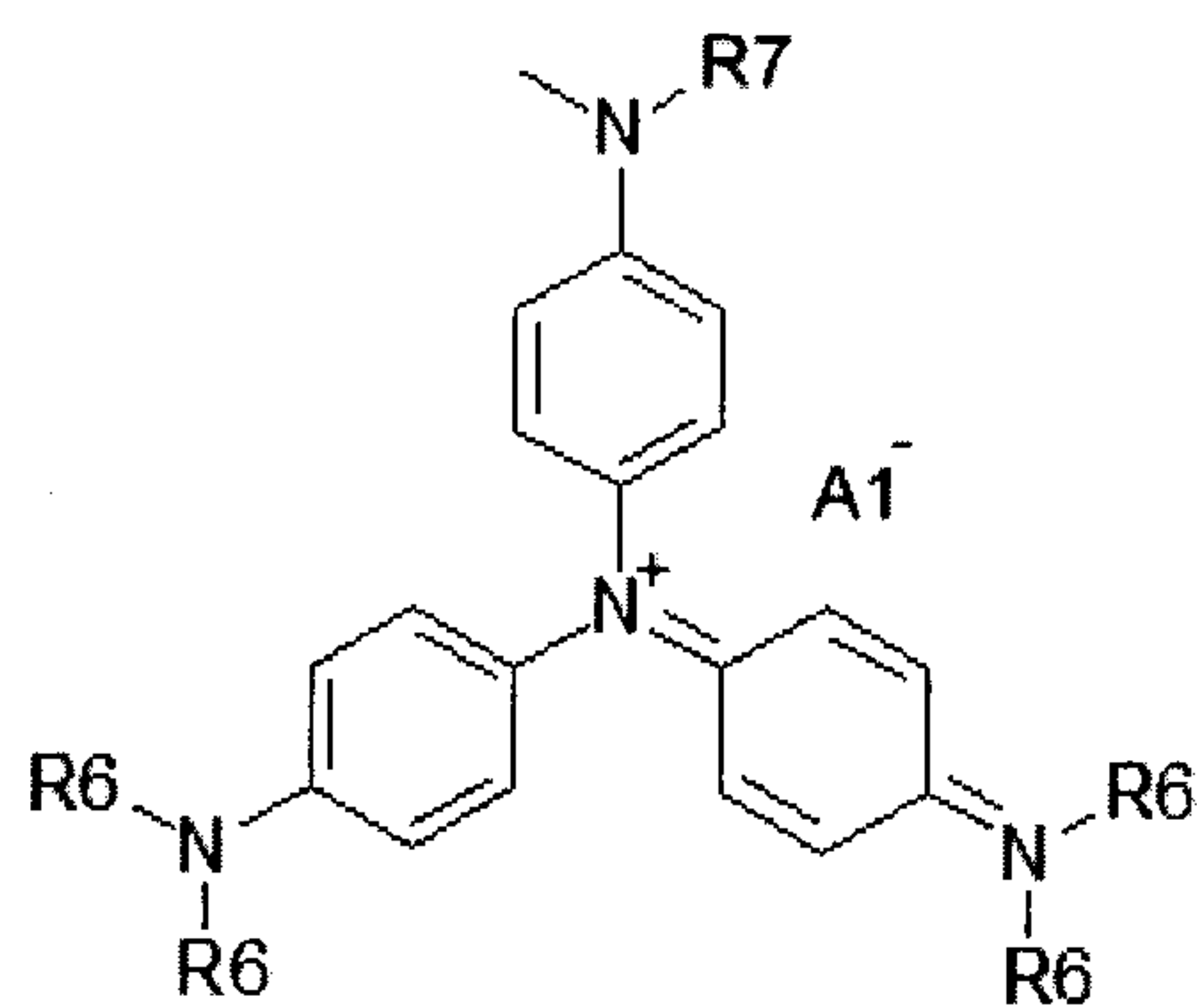


wherein NIR is a near-infrared absorbing chromophore exhibiting one or more strong absorption peaks between 700 and 1100 nm.

35. The coating solution of Claim 34, wherein said near-infrared absorbing chromophore is:

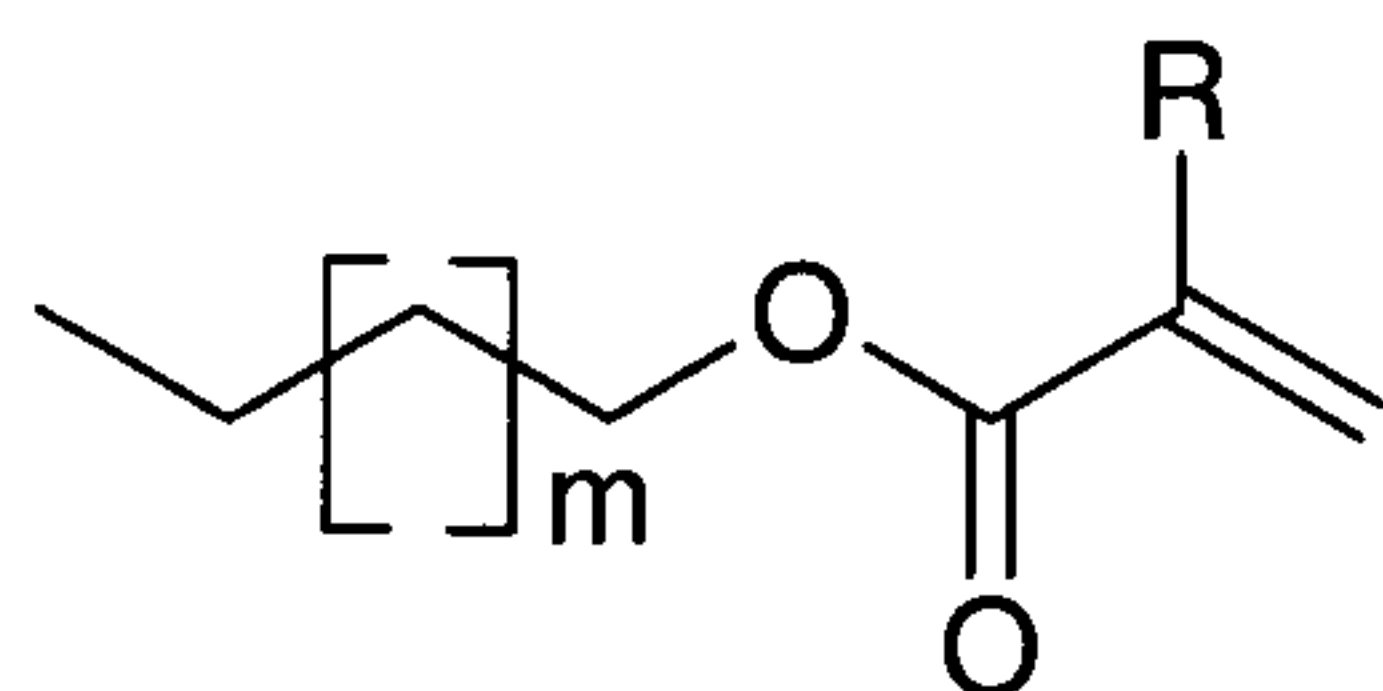


, or

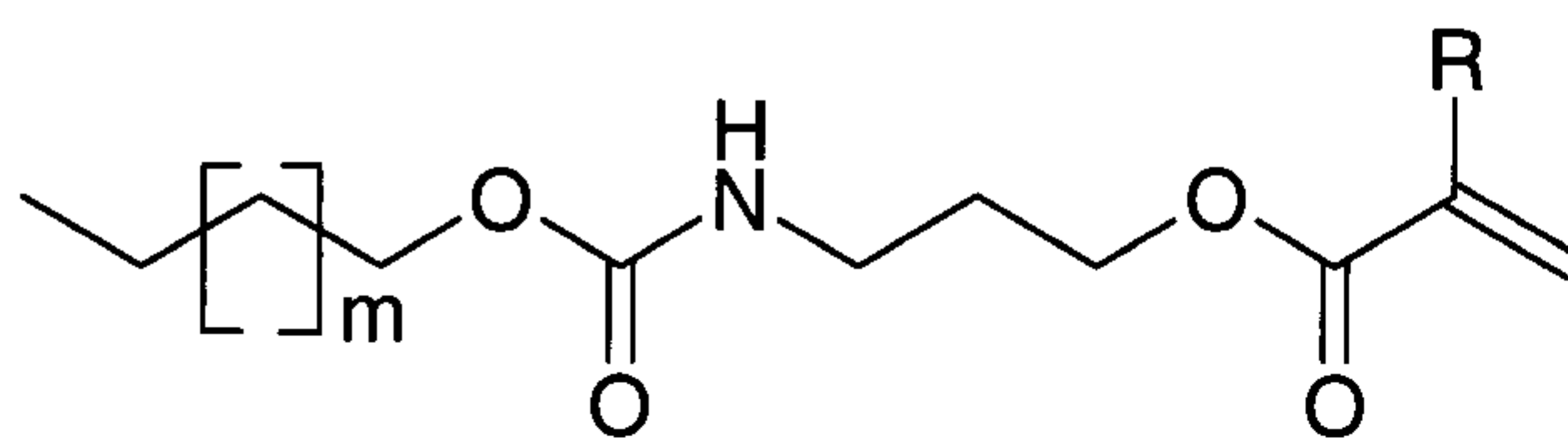


wherein:

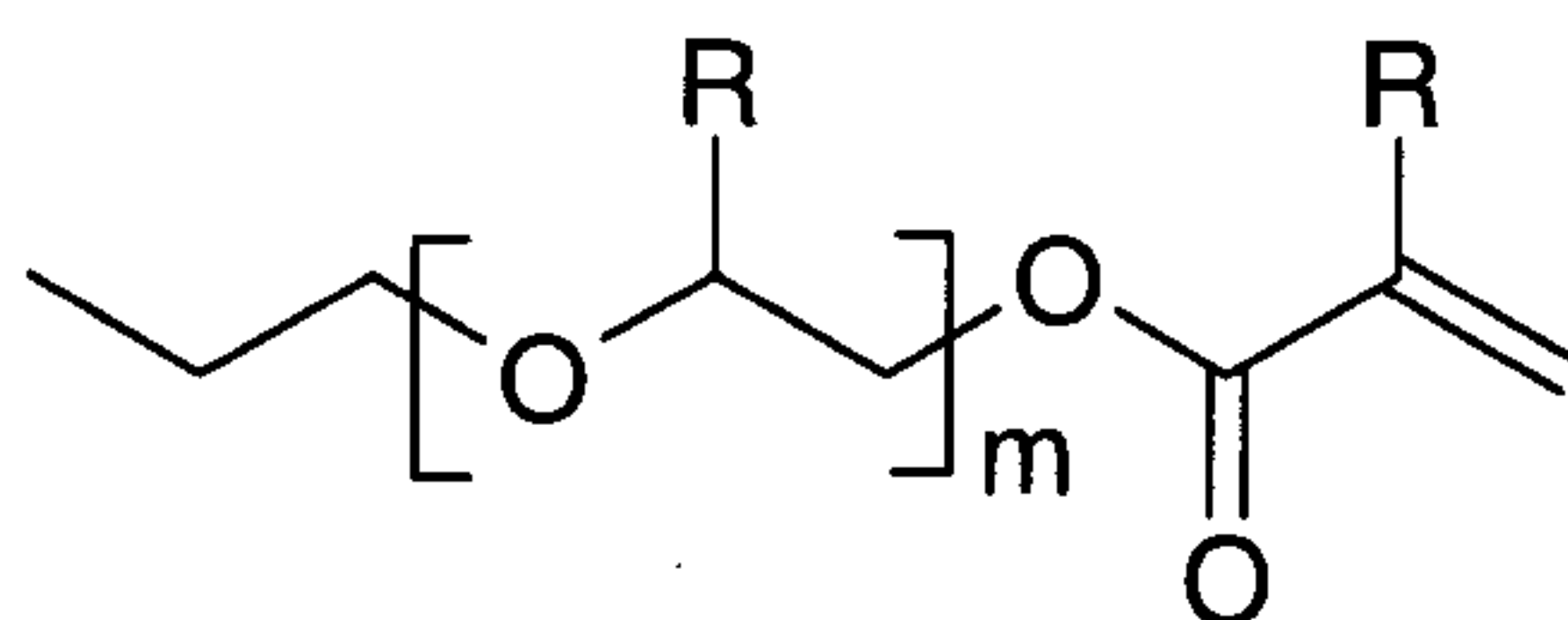
- D1 and D2 each independently represent -O-, -S-, -Se-, -CH = CH-, or -C(CH₃)₂;
- Z1 and Z2 each independently represent one or more fused substituted or unsubstituted aromatic ring;
- h is an integer varying between 2 and 8;
- n represents 0 or 1;
- M represents hydrogen or Na, K, or tetraalkylammonium salts cationic counter ion;
- A1 represents bromide, chloride, iodide, tosylate, triflate, trifluoromethane carbonate, dodecyl benzosulfonate or tetrafluoroborate, tetraphenylborate and triphenyl-n-butylborate anionic counter ion;
- R3 and R7 each independently represent hydrogen or alkyl;
- R4, R5 and R6 each independently represent alkyl, aryl alkyl, hydroxy alkyl, amino alkyl, carboxy alkyl, sulfo alkyl or a polymerizable substituent, said substituent comprising said second functional group and being of formula:



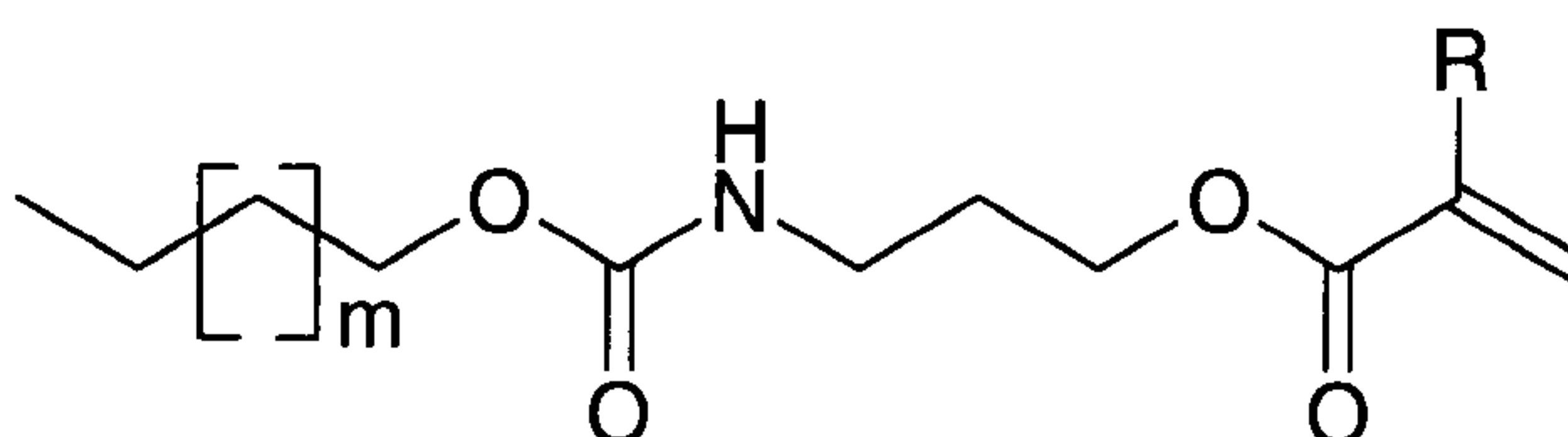
,



,



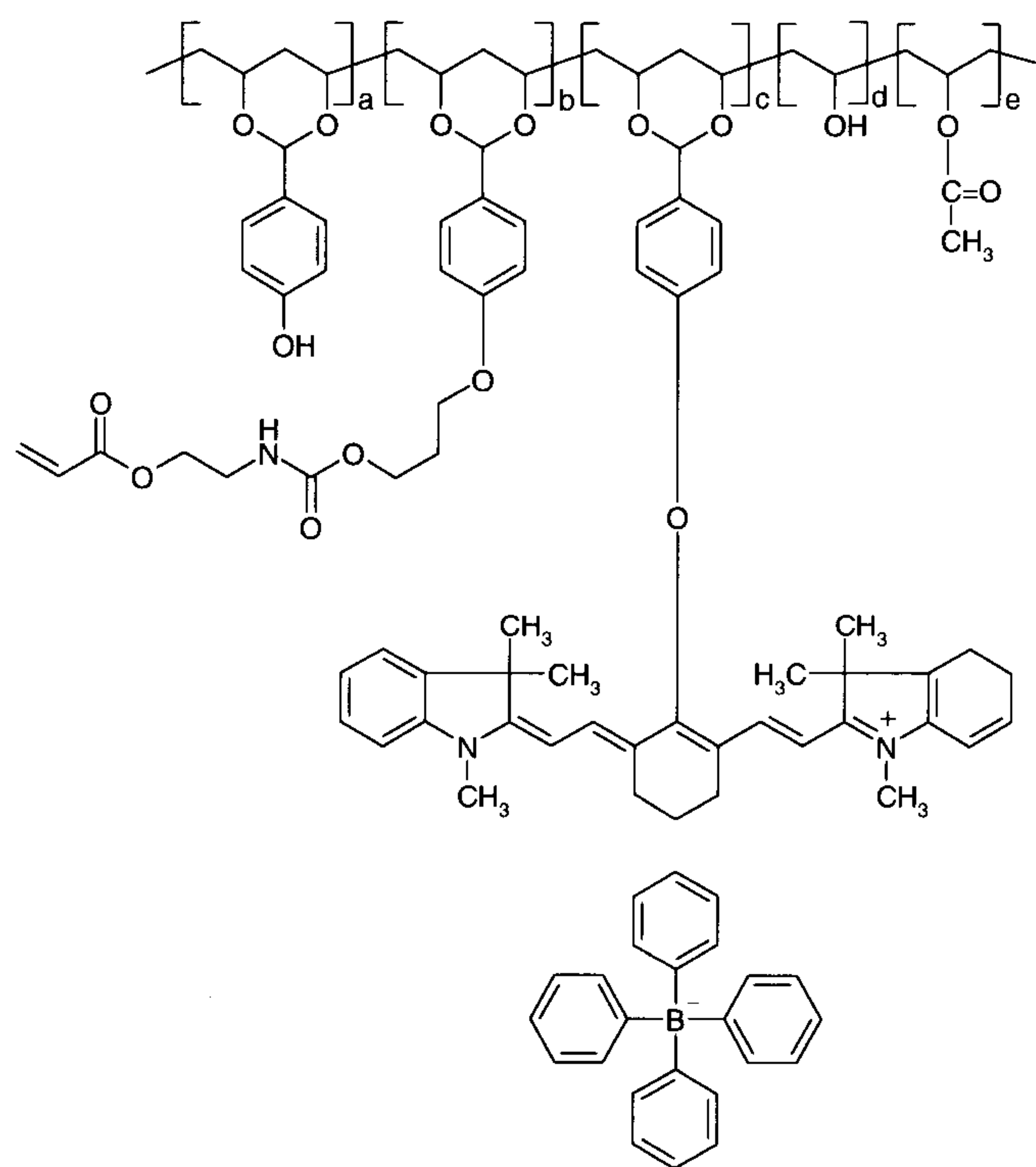
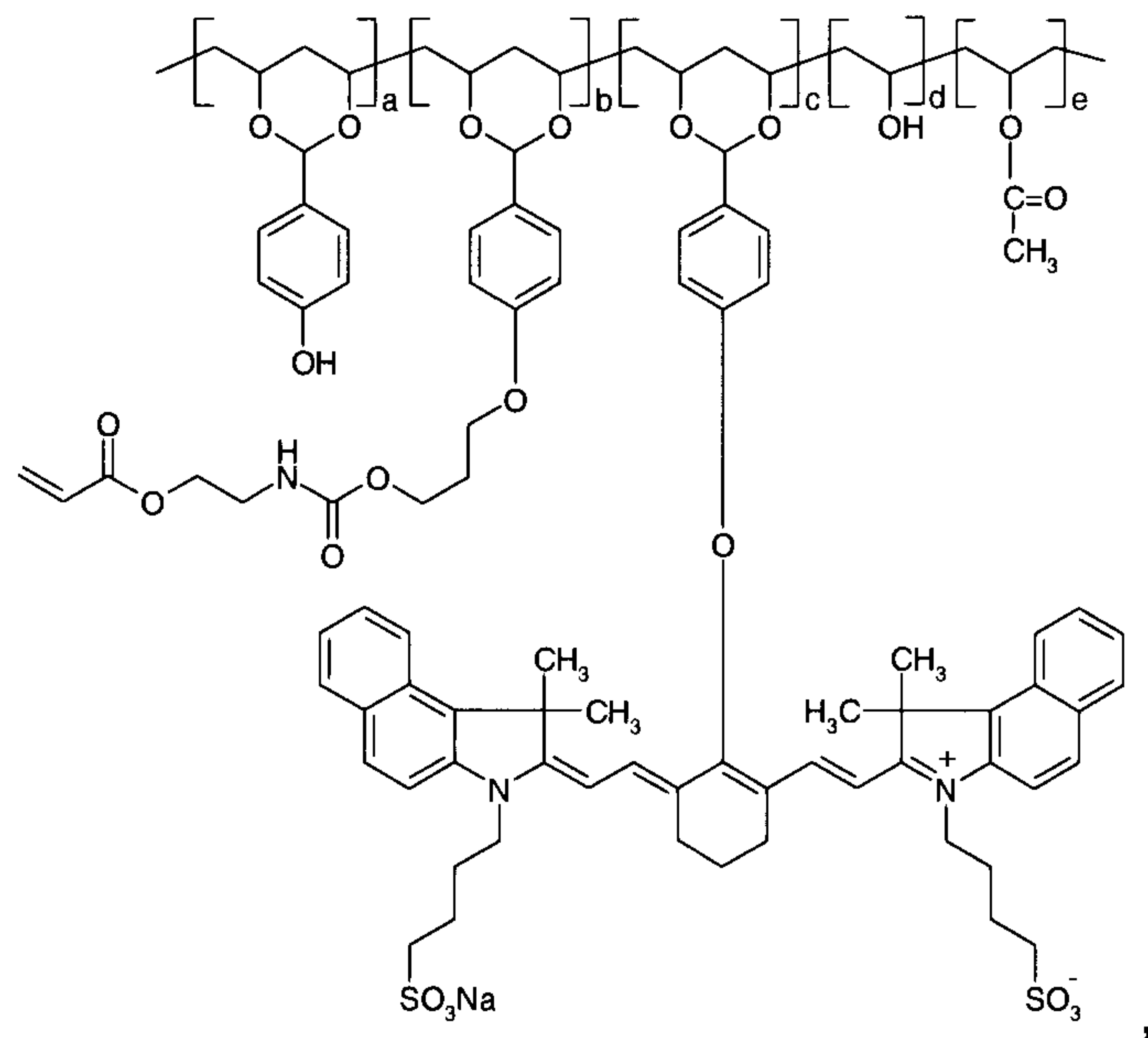
, or

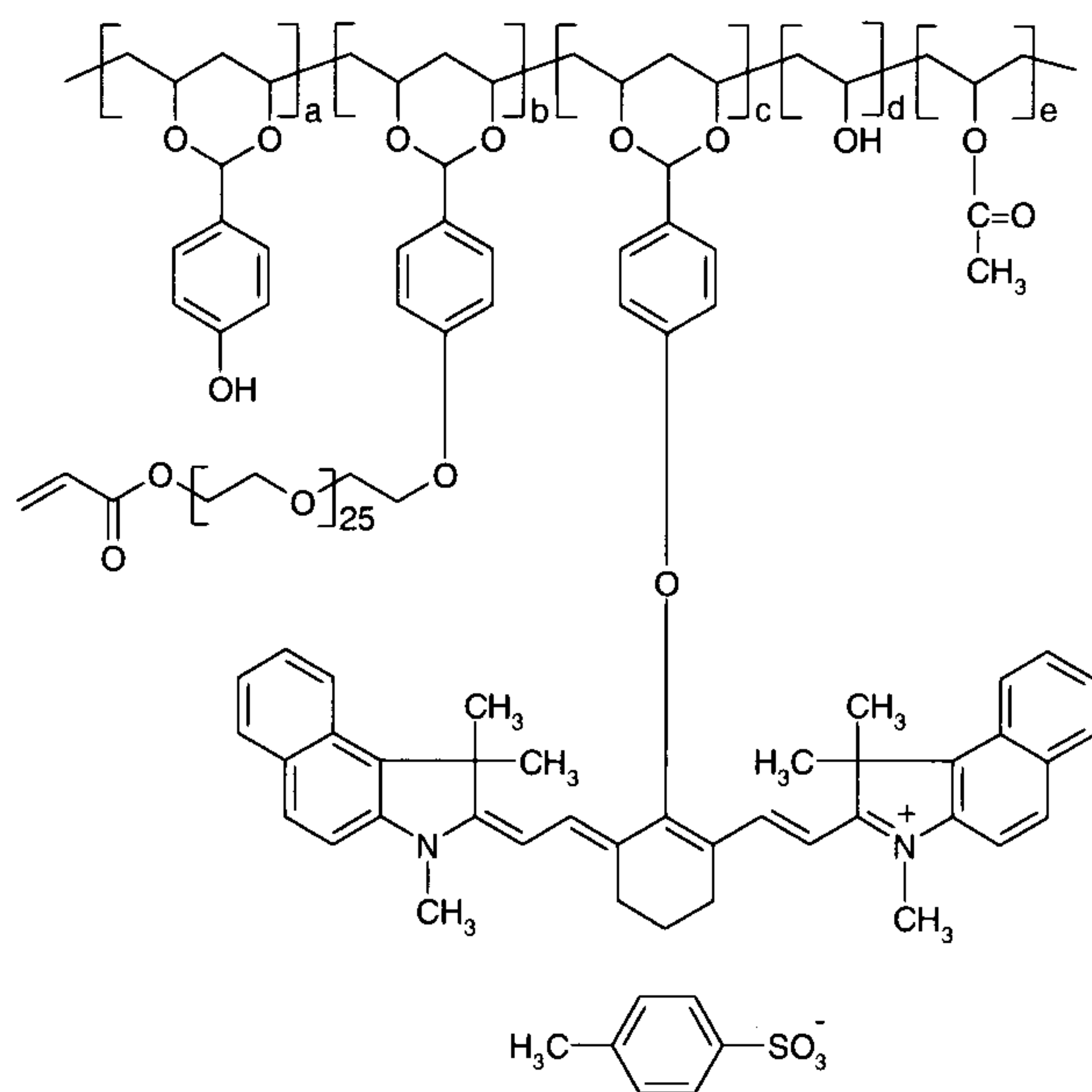
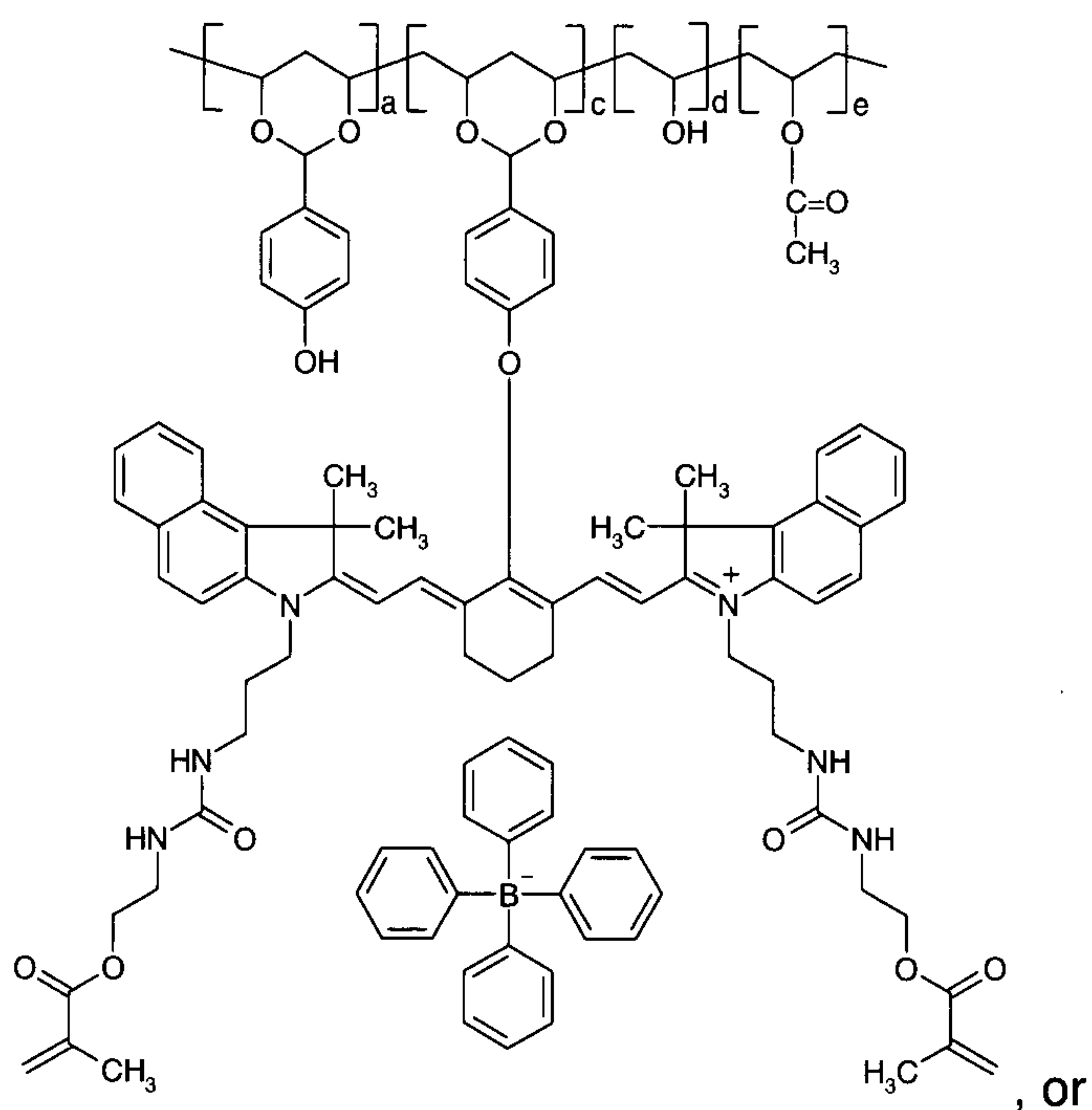


,

wherein m may vary between 0 and 50 and R is hydrogen or methyl.

36. The coating solution of Claim 35, wherein at least one of Z1 or Z2 is phenyl or naphthyl.
37. The coating solution of Claim 25, wherein said first polyvinyl alcohol acetal polymer is:



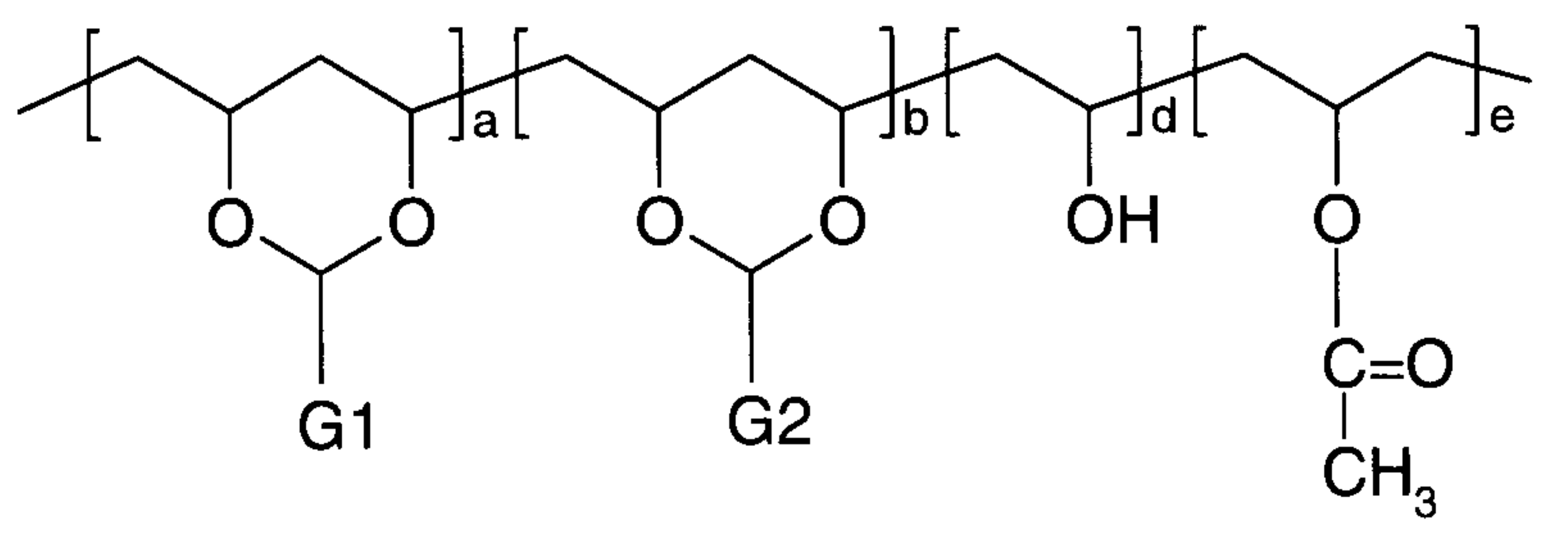


wherein a, b, c, d and e are molar ratios that can vary from 0.01 to 0.99.

38. The coating solution of any one of claims 18 to 37 further comprising a polymer binder.
39. The coating solution of Claim 38 comprising from about 1% to about 50 % by solid weight of said polymer binder.
40. The coating solution of Claim 38 or 39, wherein said polymer binder has attached thereto at least one third functional group capable of undergoing cationic or radical polymerization.
41. The coating solution of Claim 40, wherein said third functional group is acrylate,

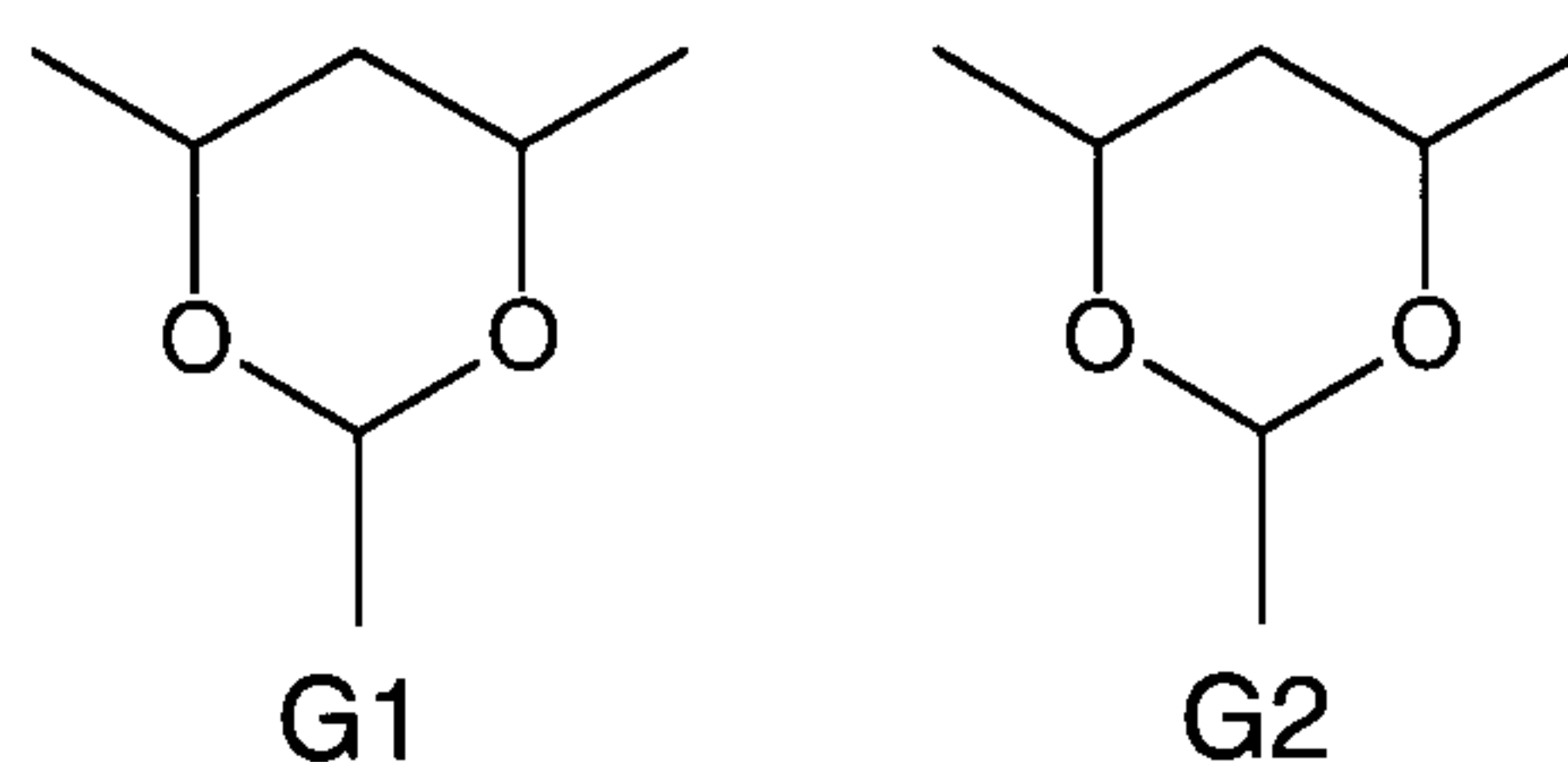
methacrylate, vinyl ether, hydroxyl, alkoxy-methyl acrylamide, alkoxy methacrylamide, N-methoxymethylacrylamide or N-methoxymethylmethacrylamide.

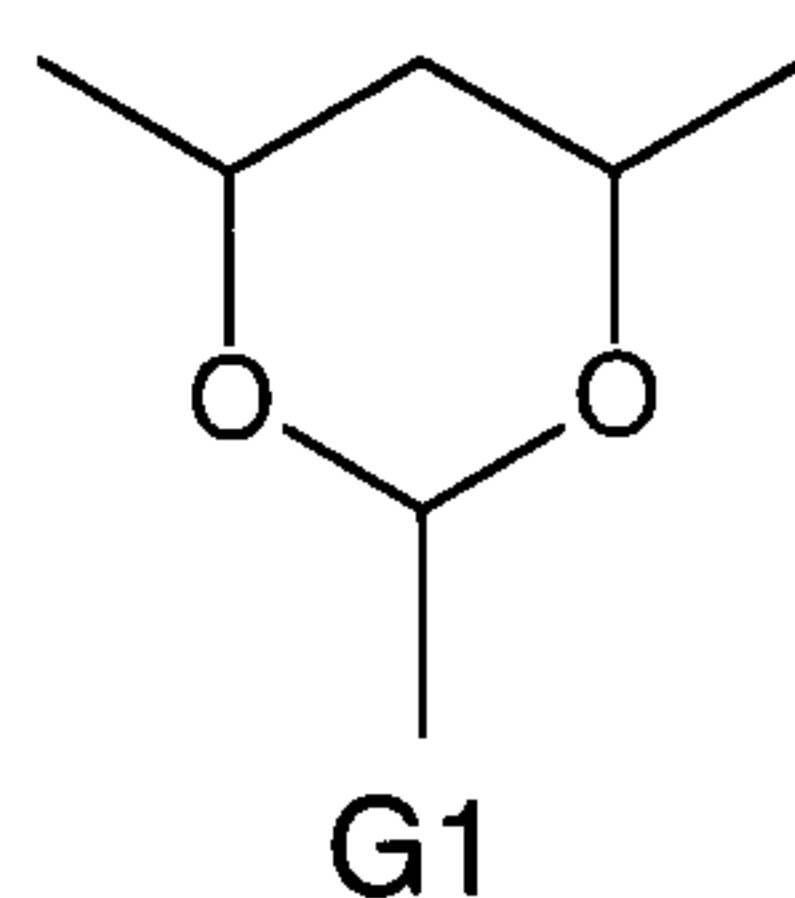
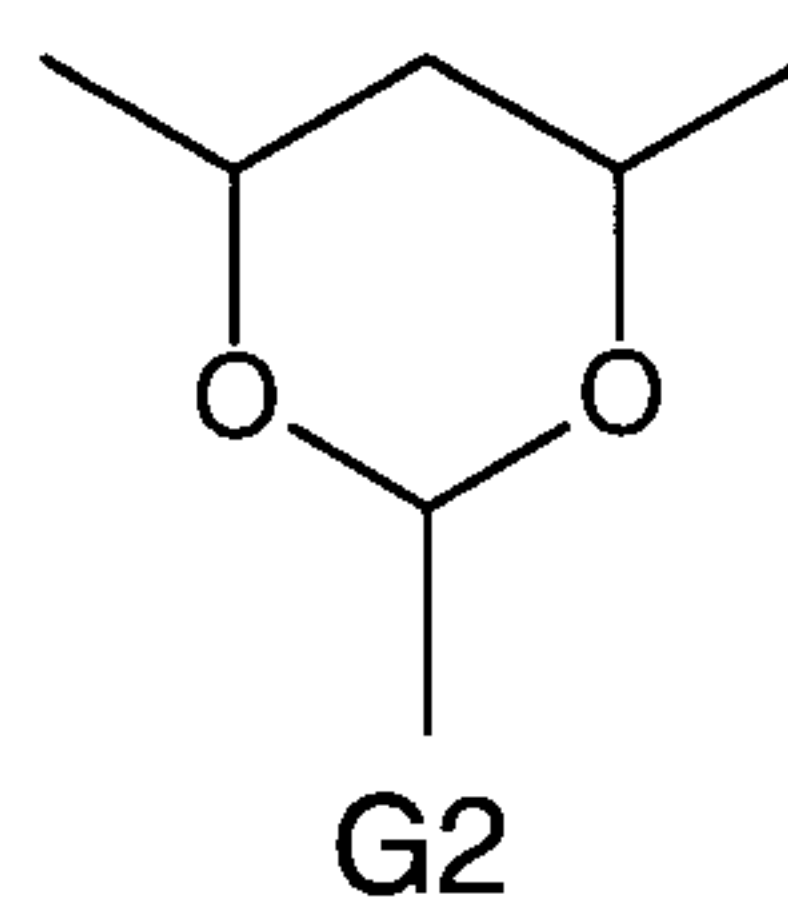
42. The coating solution of any one or Claims 38 to 41, wherein said polymer binder is a second polyvinyl alcohol acetal copolymer or a mixture thereof.
43. The coating solution of Claim 42, wherein said second polyvinyl alcohol acetal copolymer has the following structure:

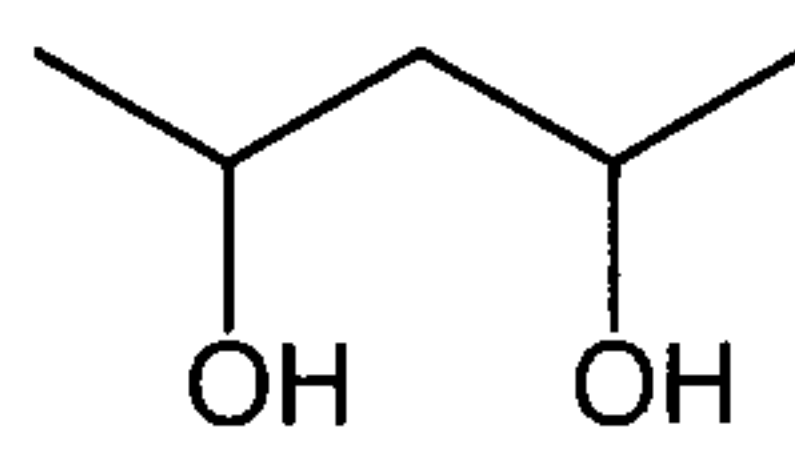


wherein

- G1 represents an processing segment providing solubility in organic solvents;
- G2 represents an thermal reactive segment;
- a, b, d and e are molar ratios and may vary from 0.01 to 0.99;

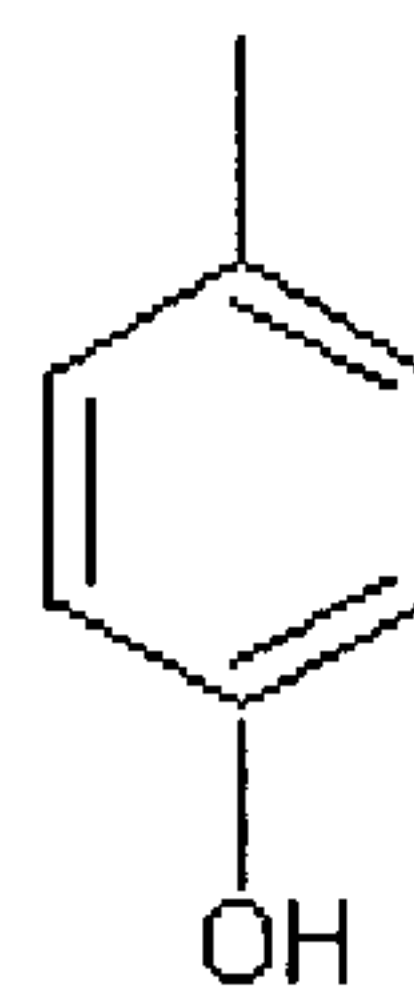


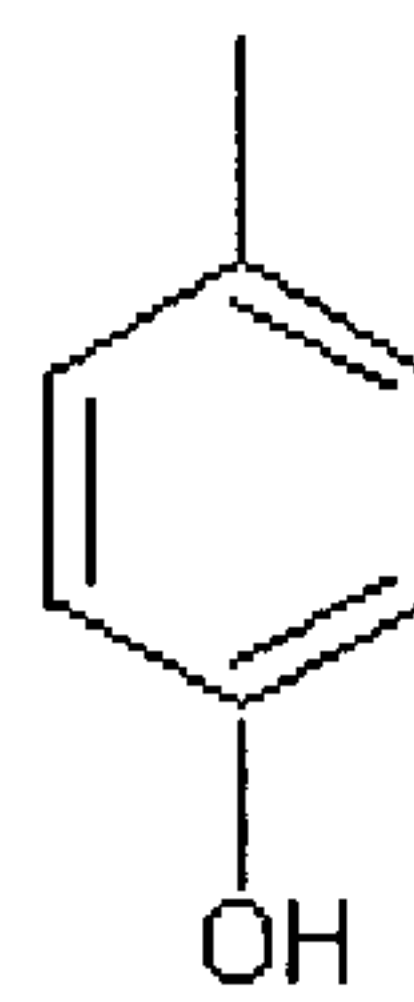
- any of  and  may independently be

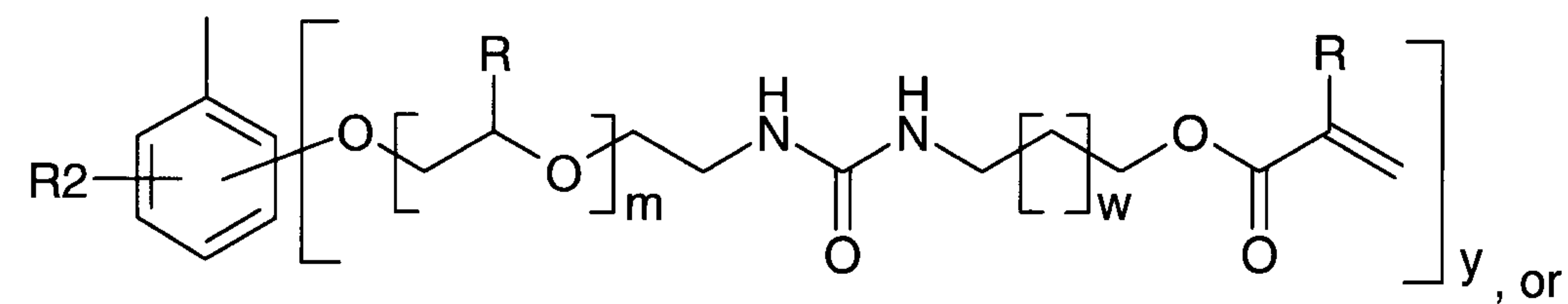
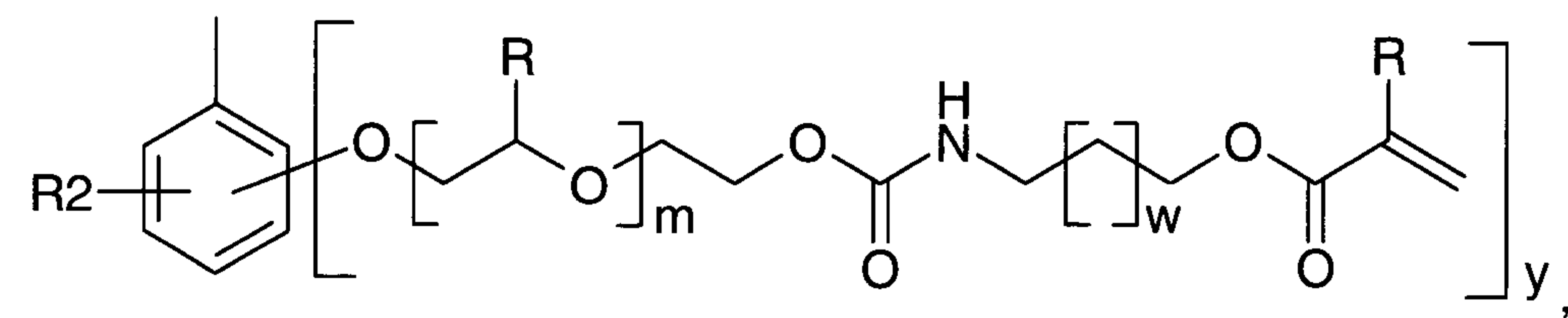
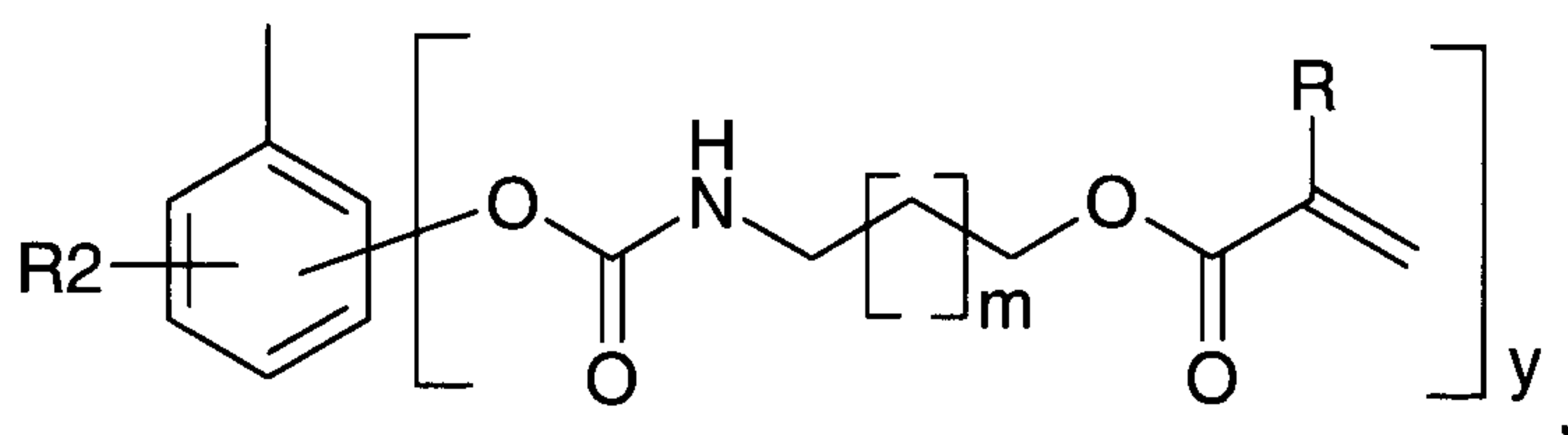
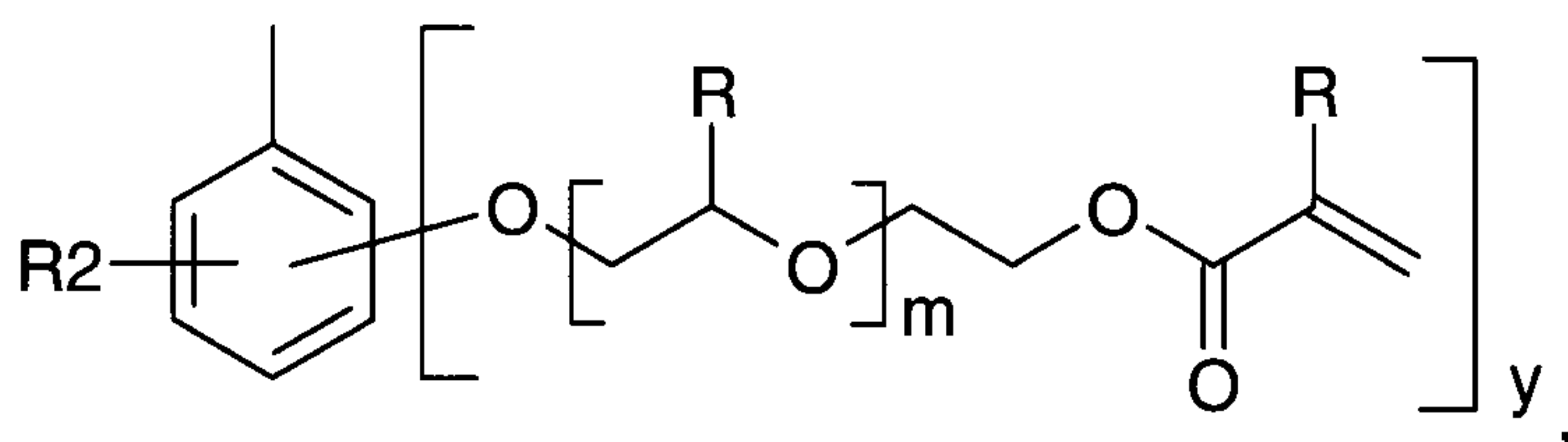
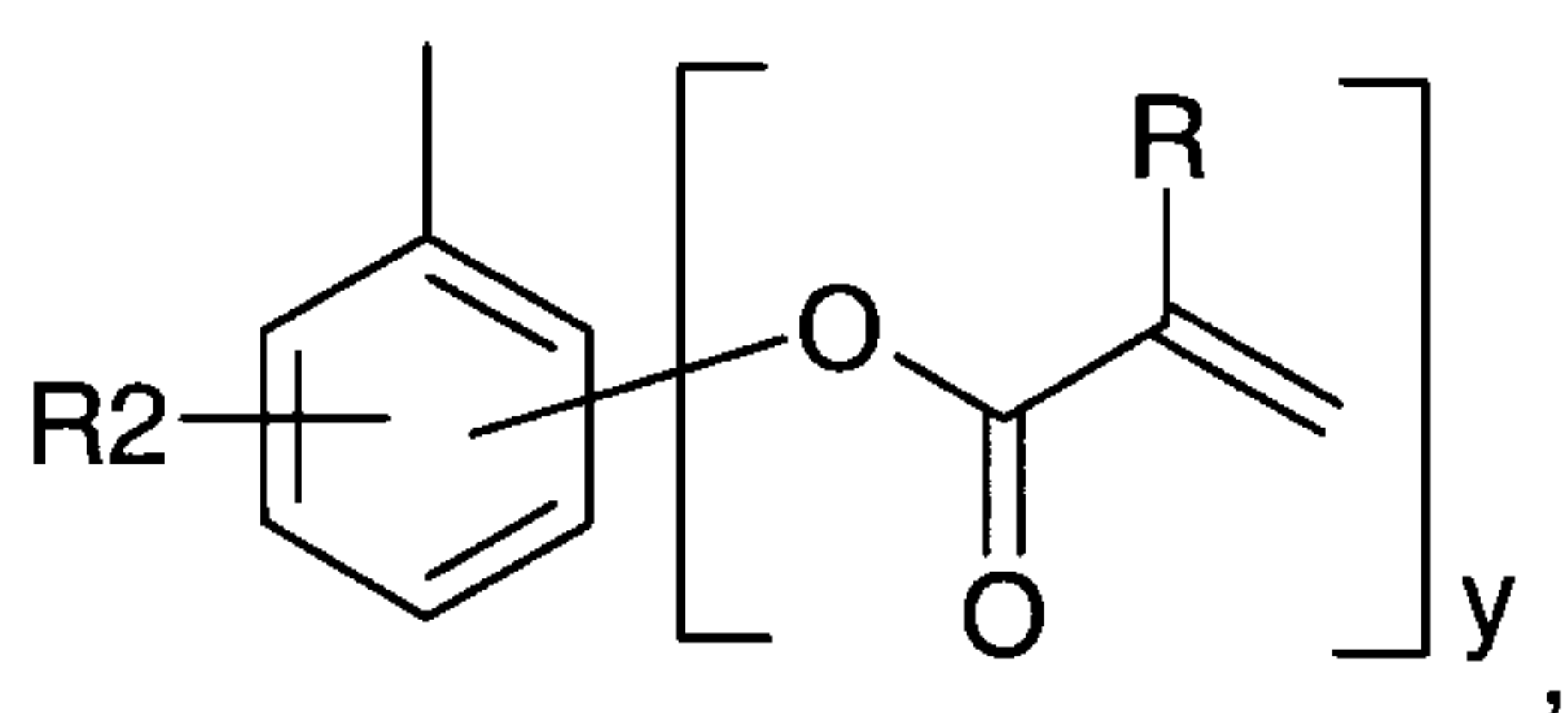
replaced by  ; and

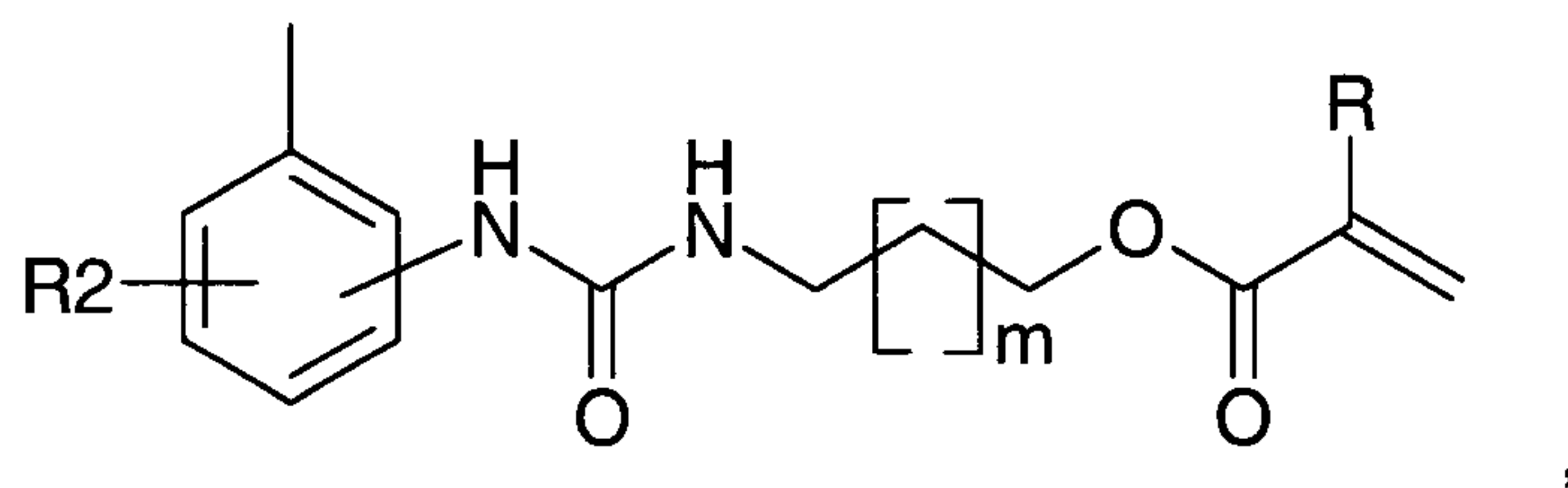
- said third functional group, if present, is attached to G2.

44. The coating solution of Claim 43, wherein G1 is linear alkyl, branched alkyl, linear aryl or branched aryl, wherein said linear alkyl, branched alkyl, linear aryl or branched aryl is substituted by a cyano, hydroxy, dialkylamino, trialkylammonium salts, ethylene oxide, propylene oxide methylbenzylsulfonyl-carbamate, carboxylic acid or phosphoric acid functional group.



45. The coating solution of Claim 43, wherein G1 is C₃H₇ or  .
46. The coating solution of any one of Claims 43 to 45, wherein G2 is linear alkyl, branched alkyl, linear aryl or branched aryl, wherein said linear alkyl, branched alkyl, linear aryl or branched aryl has attached thereto said third functional group.
47. The coating solution of Claim 46, wherein G2 is:

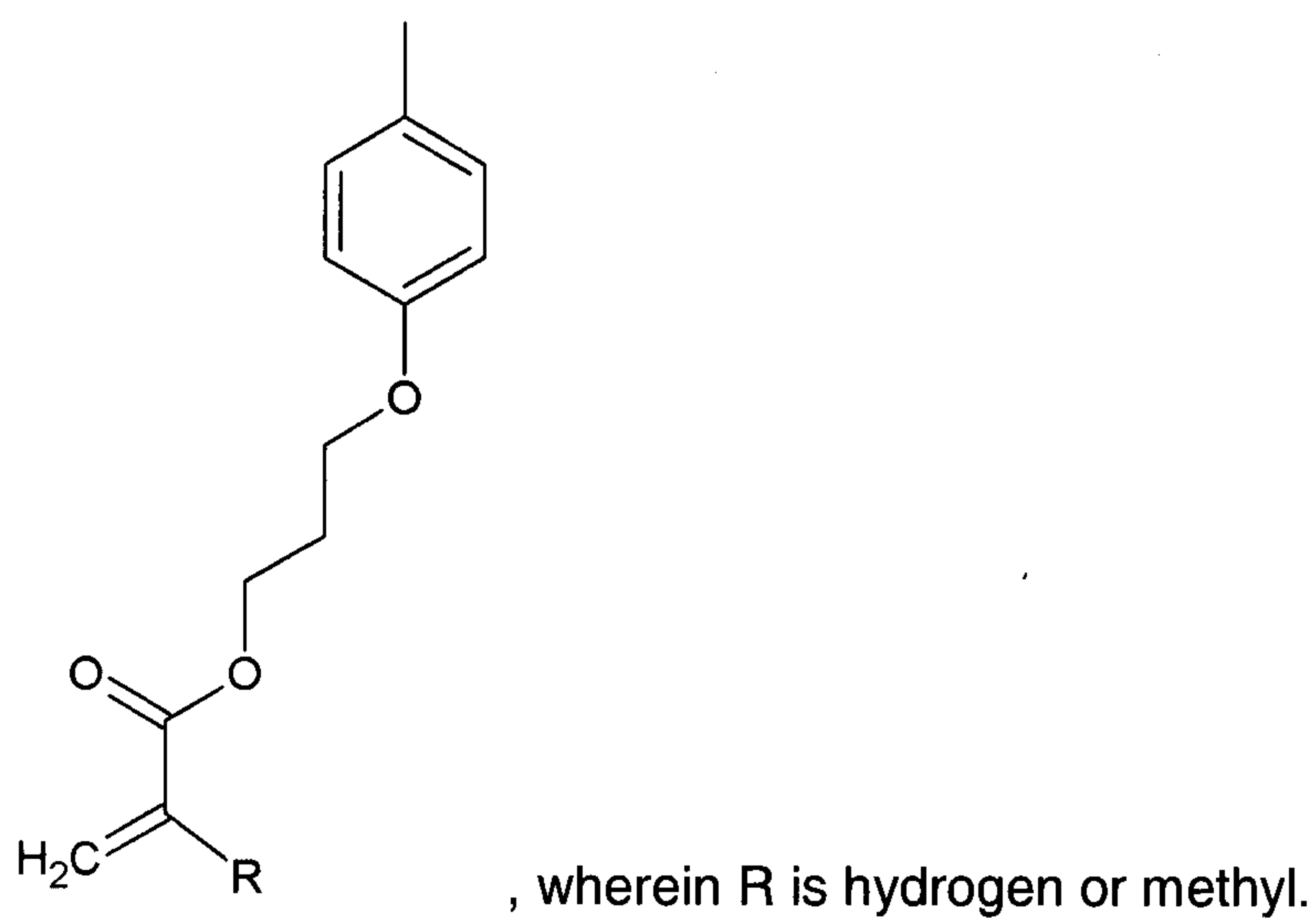
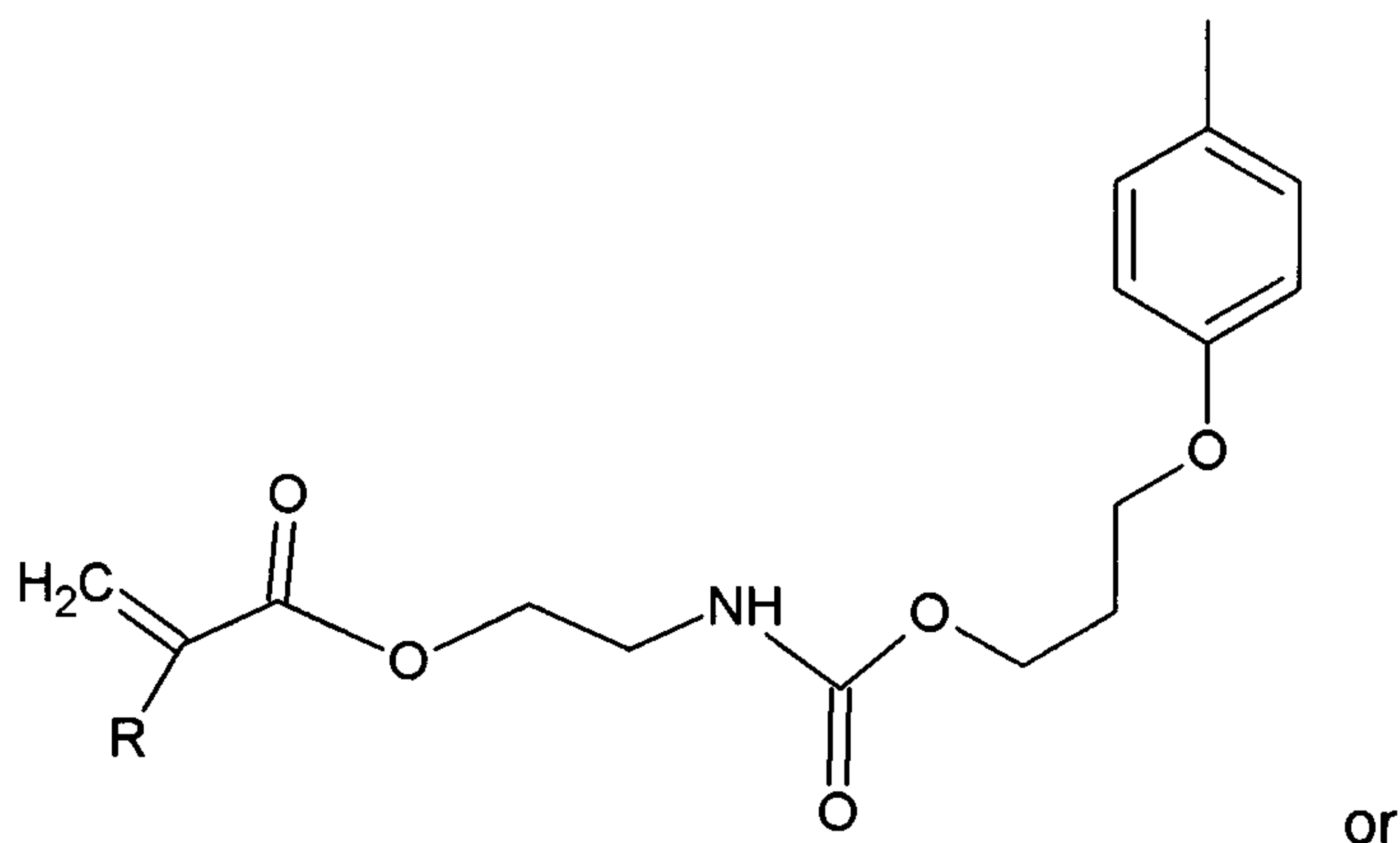




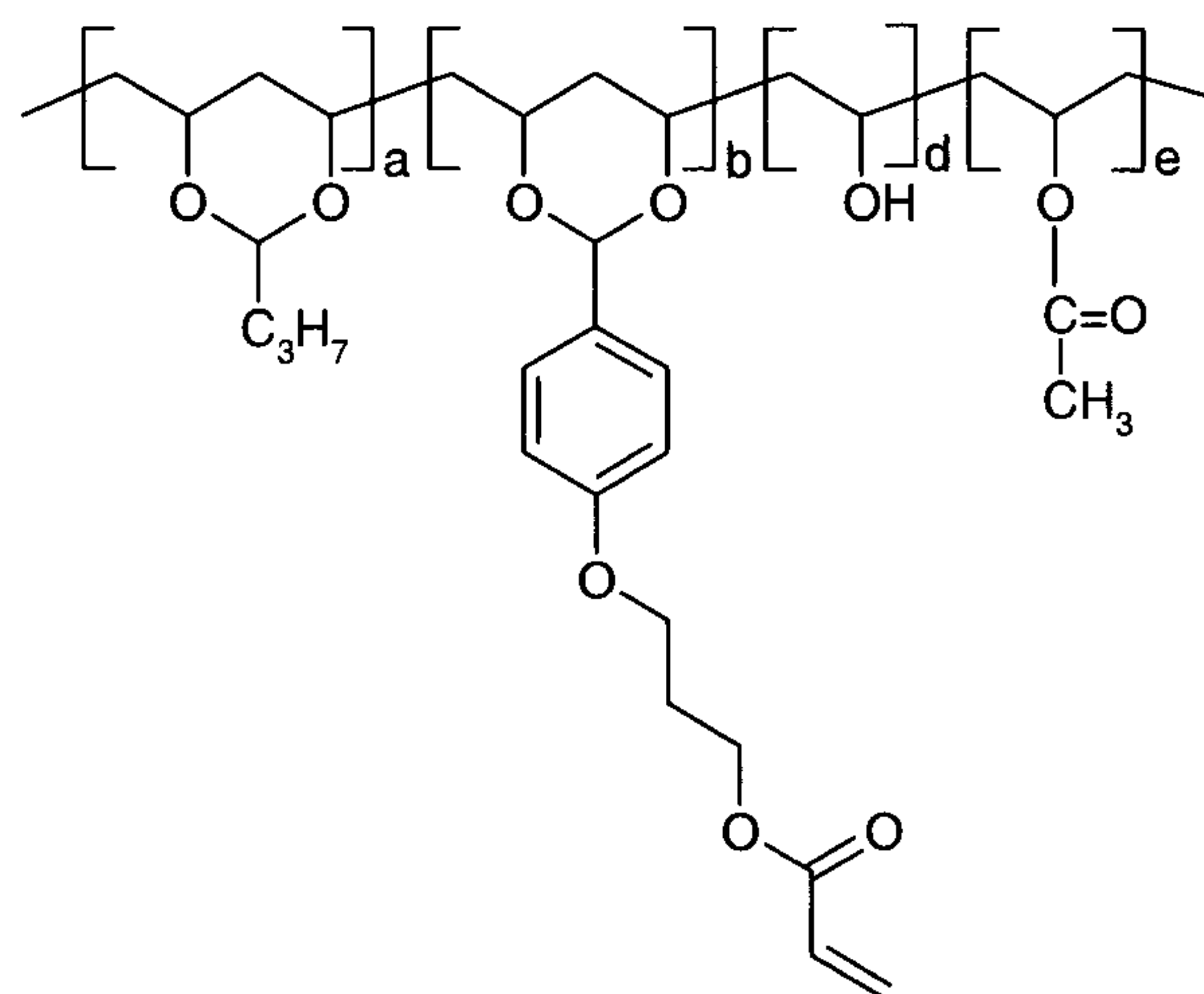
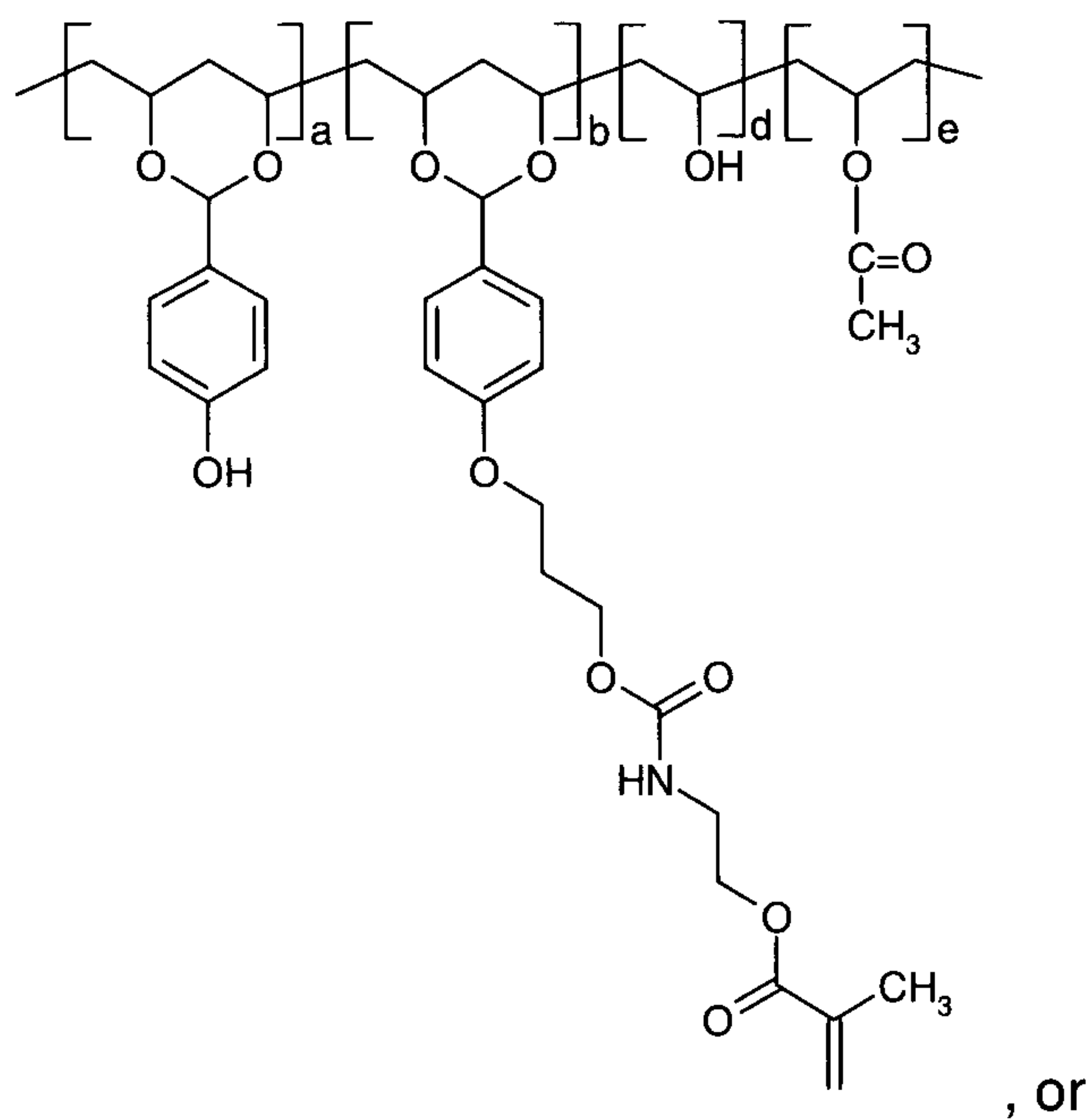
wherein:

- R is hydrogen or methyl;
- R2 is C₁₋₈ alkyl or alkoxy;
- m and w are integers varying between 0 and 50; and
- y is 1 or 2.

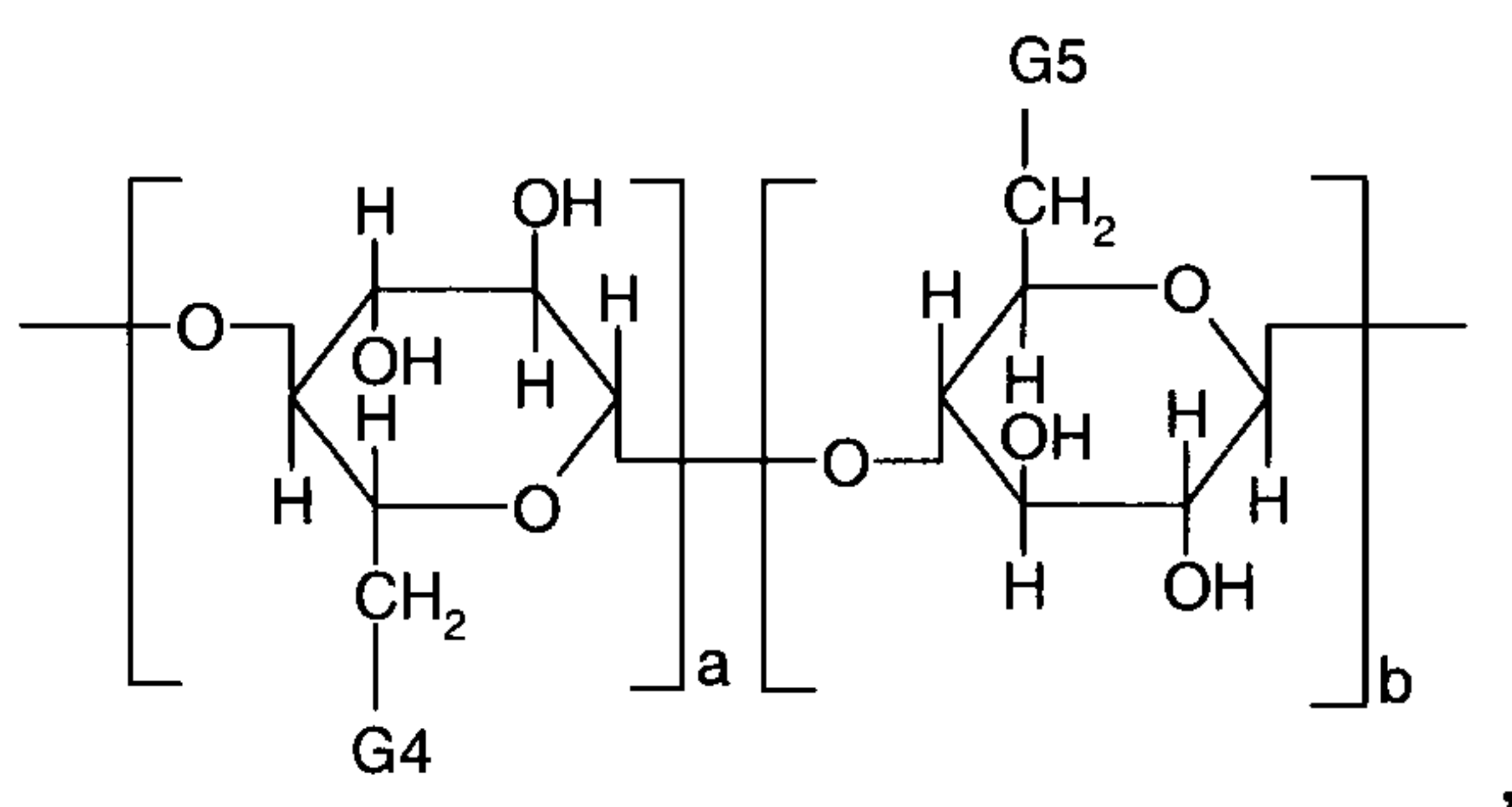
48. The coating solution of Claim 46, wherein G2 is:



49. The coating solution of Claim 48, wherein said polymer binder is:



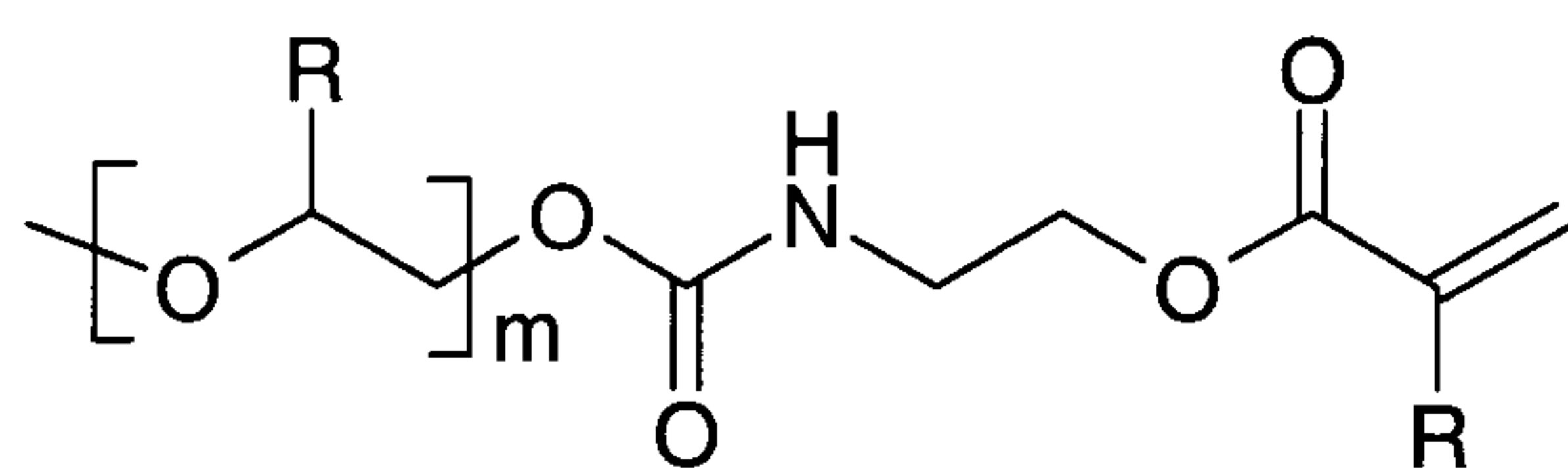
50. The coating solution of any one of Claims 40 or 41, wherein said polymer binder is selected from the group consisting of solvent-soluble cellulose ether and water-soluble cellulose ether or a mixture thereof, said cellulose ethers having attached thereto said third functional group.
51. The coating solution of Claim 50, wherein said cellulose ethers have been modified by reacting a hydroxymethyl, a hydroxyethyl or a hydroxypropyl group attached to said cellulose with a 2-isocyanato-ethyl methacrylate compound having attached thereto said third functional group.
52. The coating solution of Claim 50 or 51, wherein said polymer binder has the following structure:



wherein:

- a and b are molar ratios and may vary between about 0.01 and about, 0.99;
- G4 is hydroxy, hydroxyethyl or hydroxypropyl; and
- G5 comprises said third functional group.

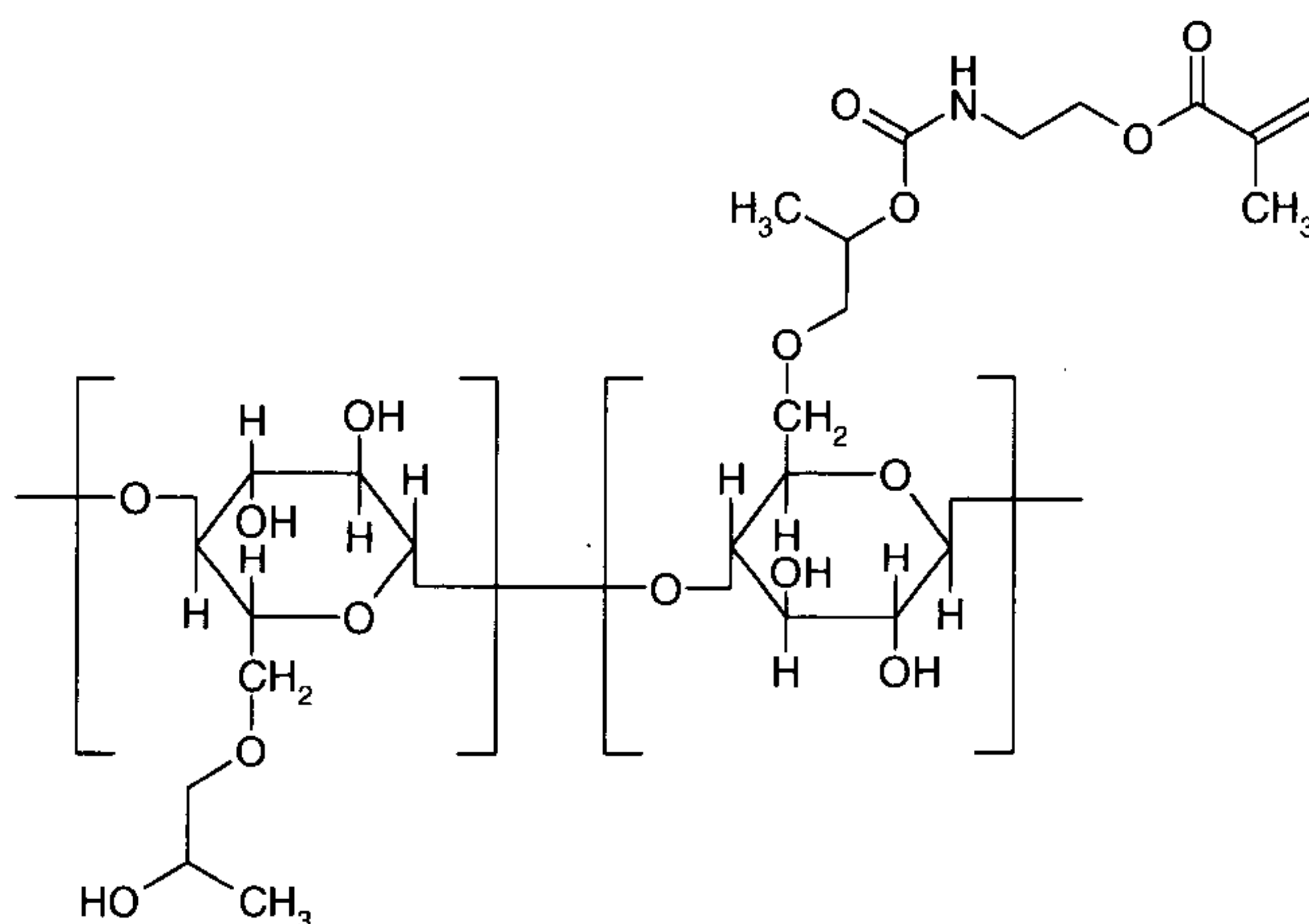
53. The coating solution of Claim 52, wherein G5 is



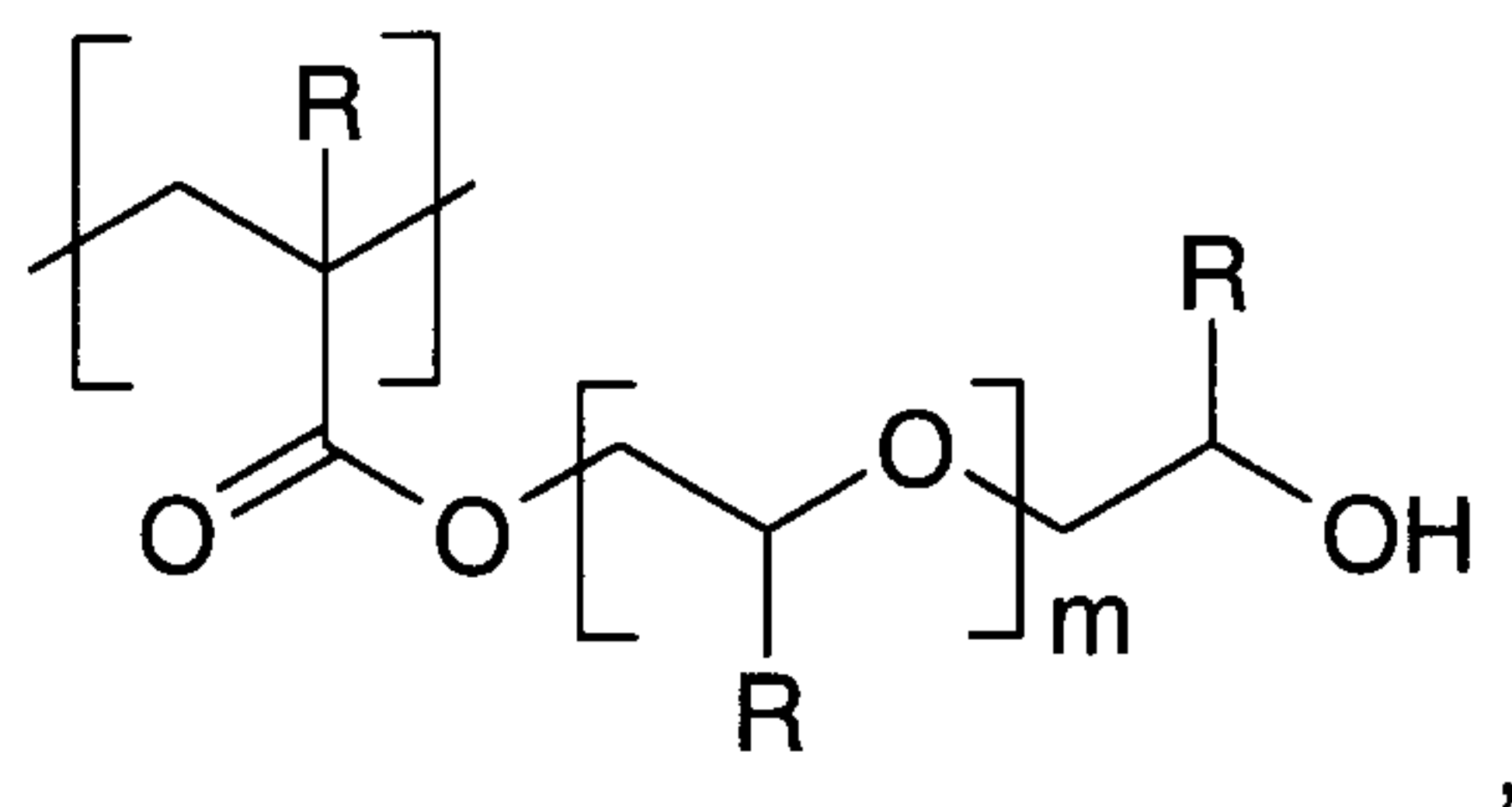
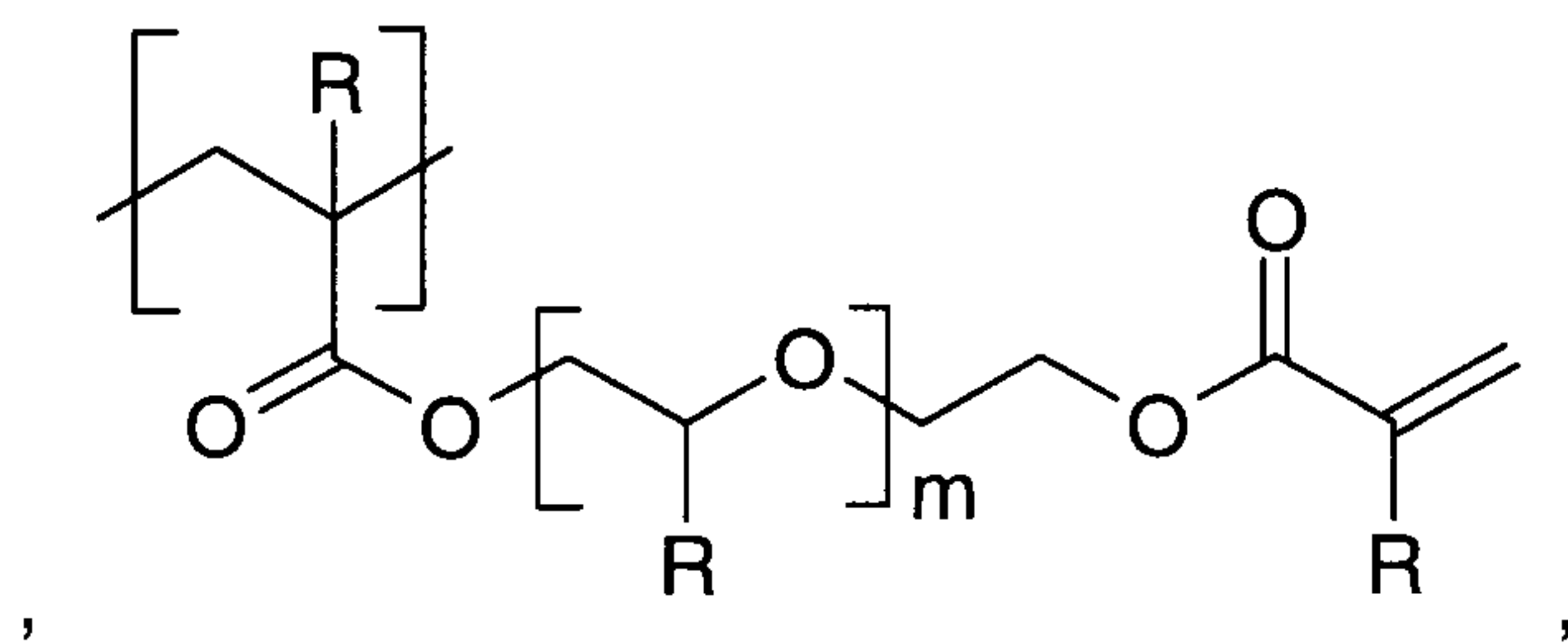
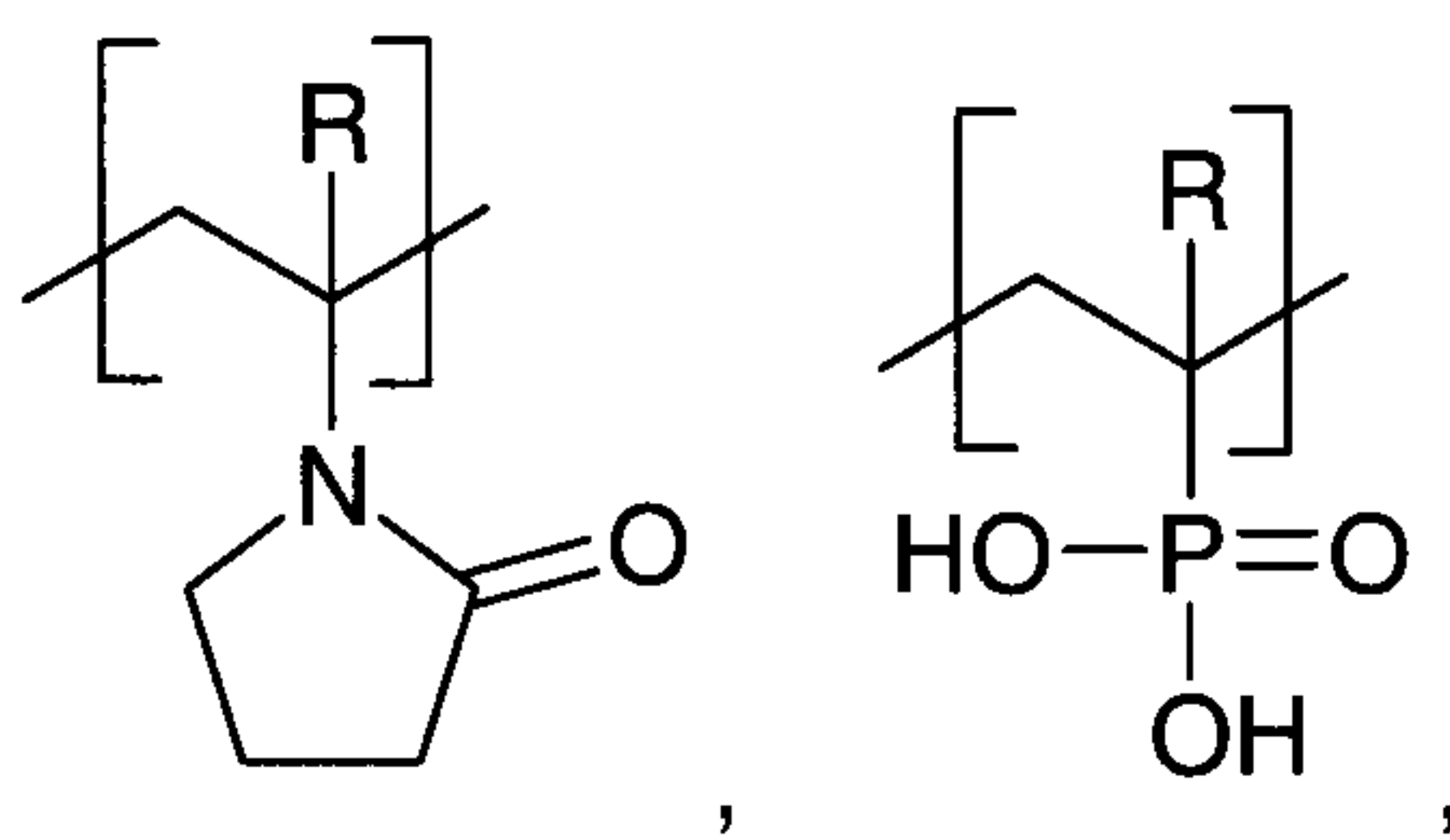
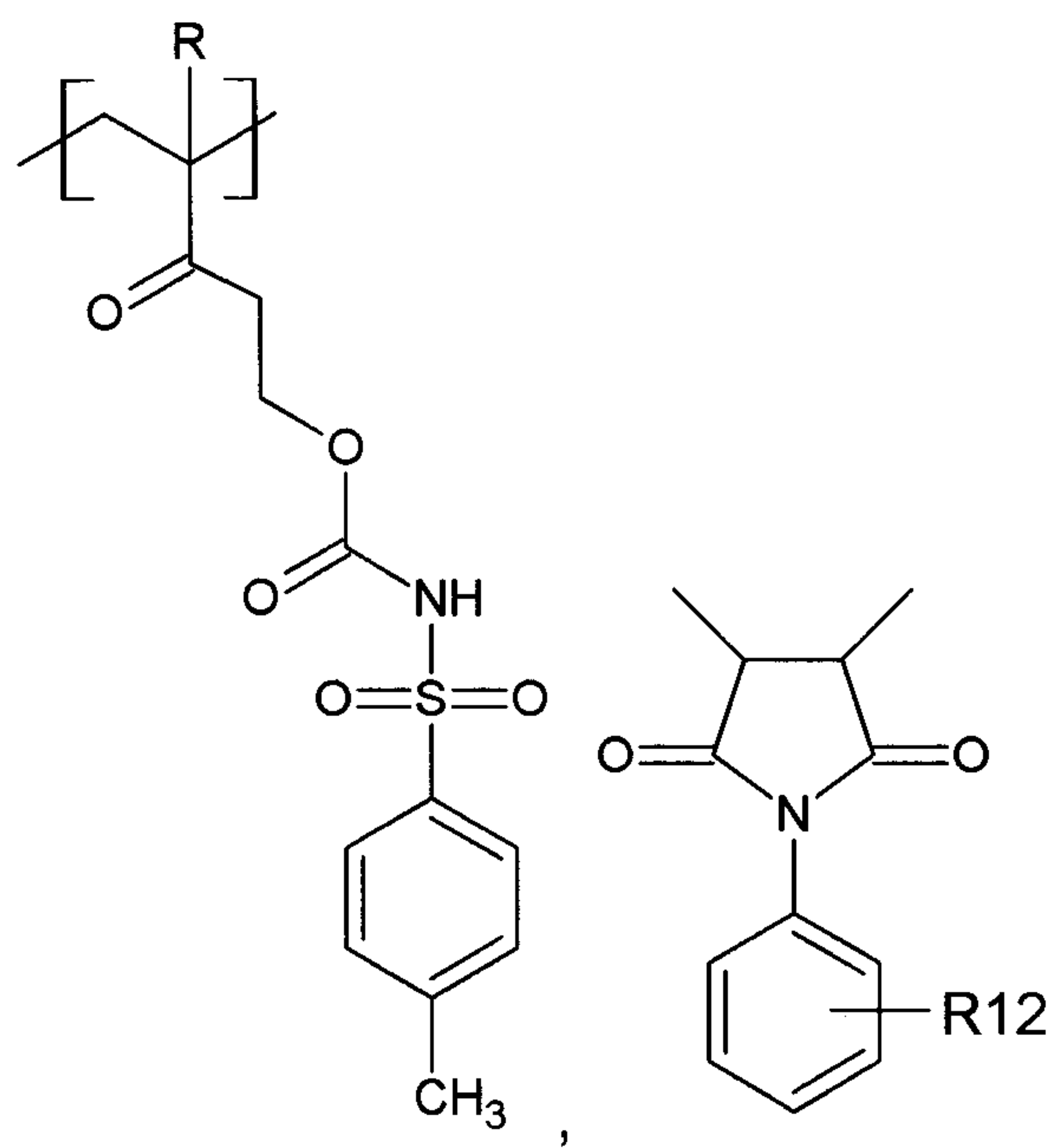
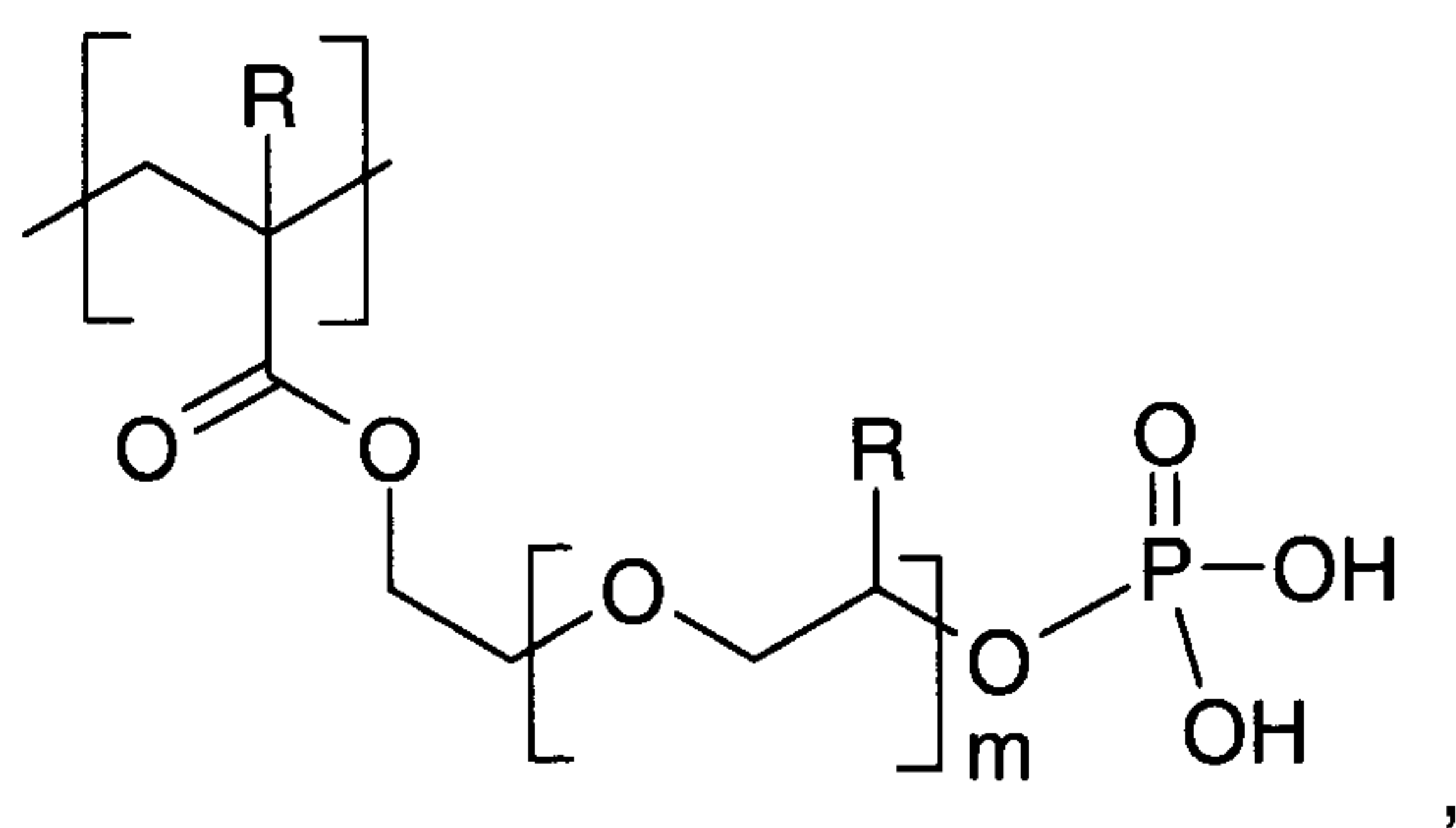
, wherein m is 0 or 1 and R is

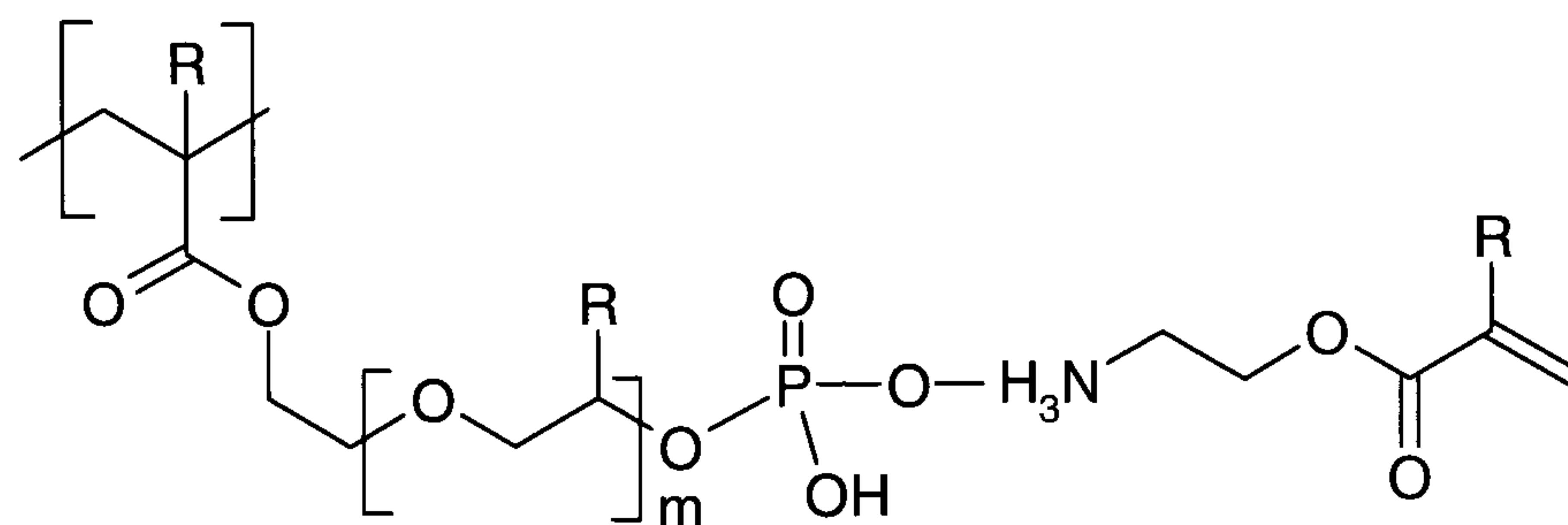
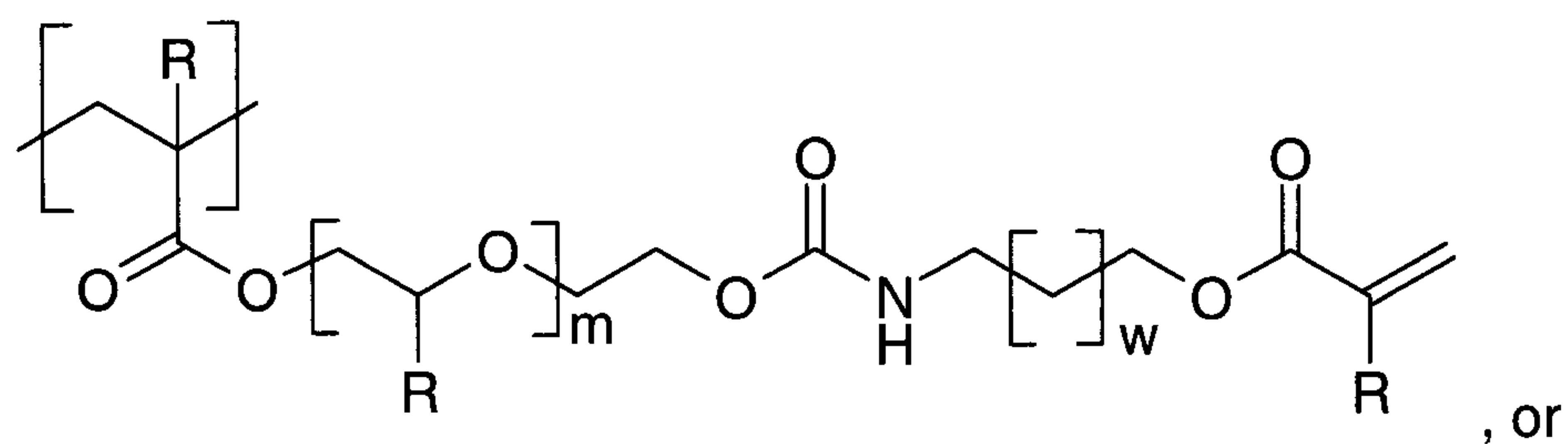
hydrogen or methyl.

54. The coating solution of Claim 53, wherein said polymer binder has the following structure:



55. The coating solution of Claim 40 or 41, wherein said polymer binder comprises one or more monomer of formula:

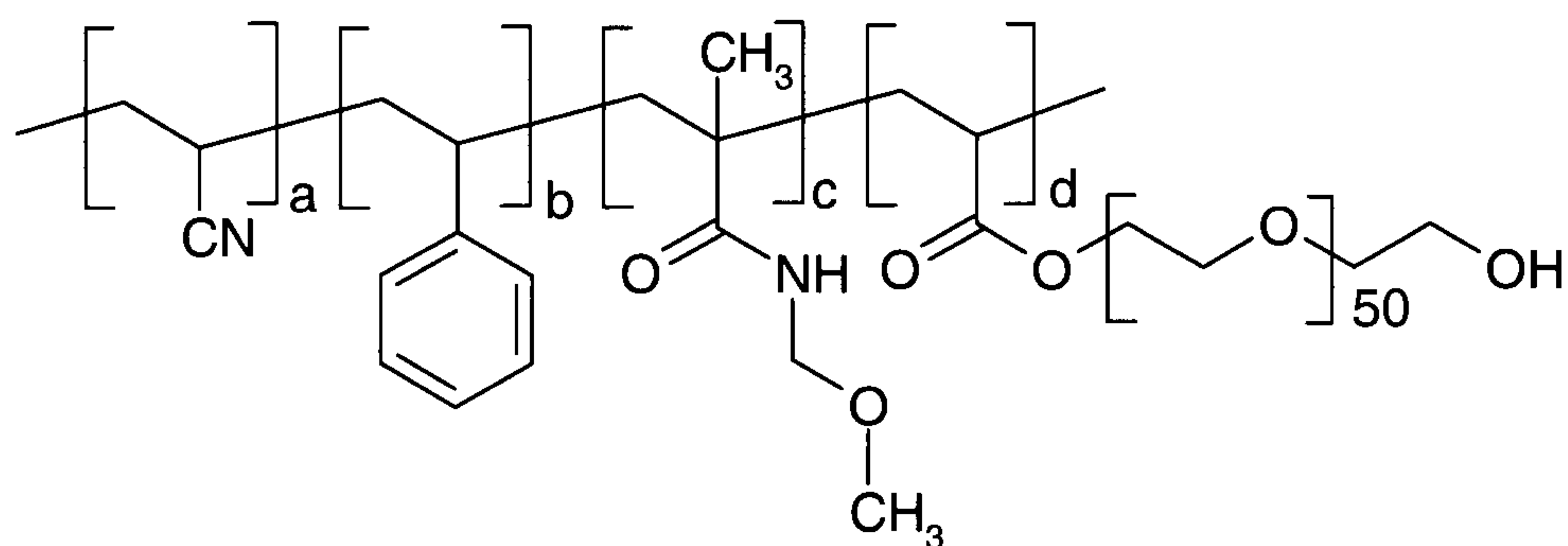
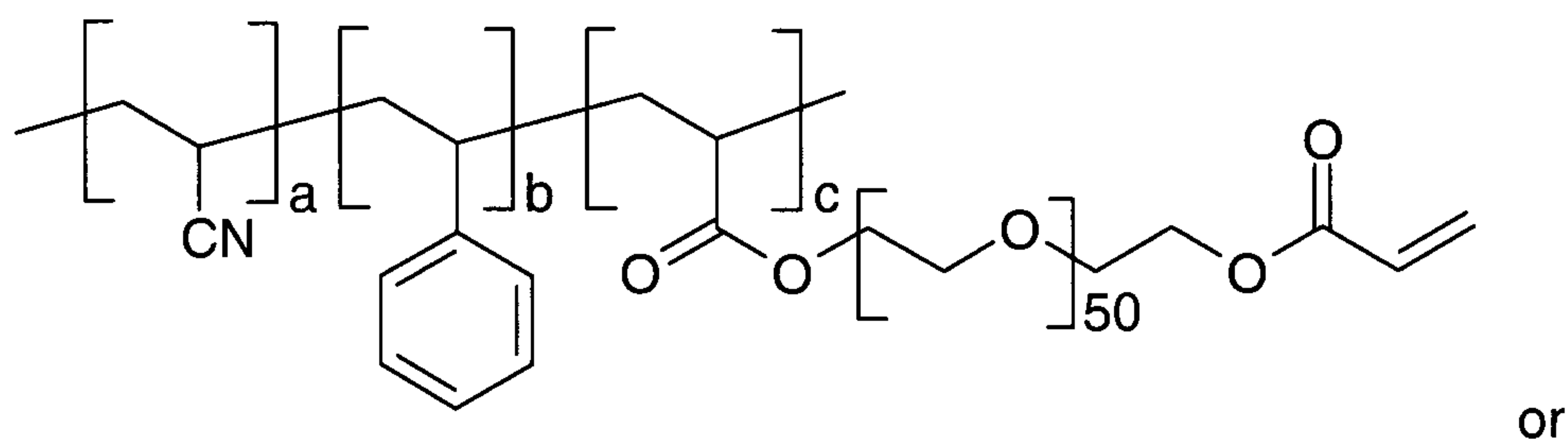




wherein:

- m and w may vary between 0 and 50;
- R is hydrogen or methyl; and
- R12 is alkyl, hydroxyl or carboxylic acid.

56. The coating solution of Claim 55, wherein said polymer binder is:

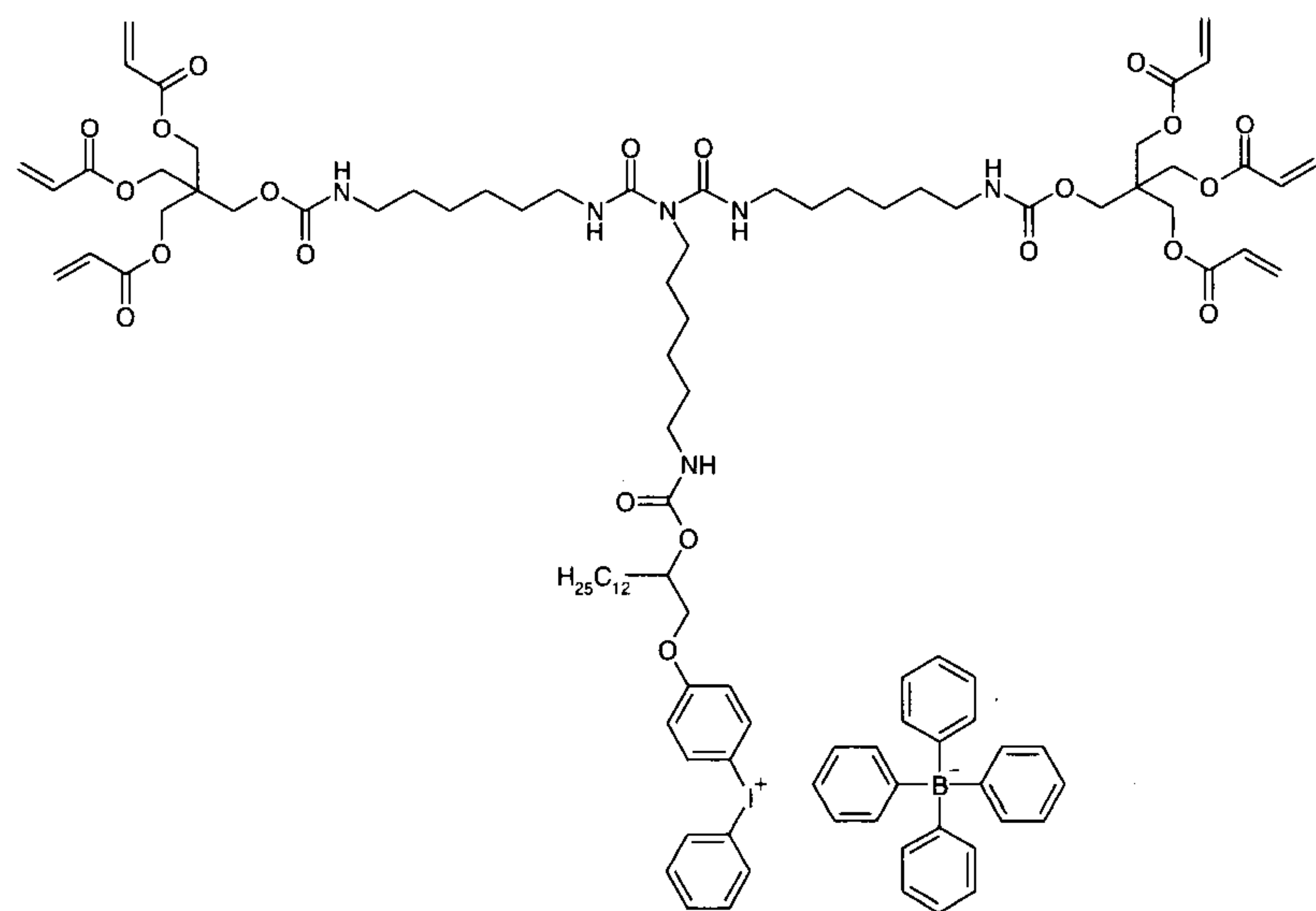
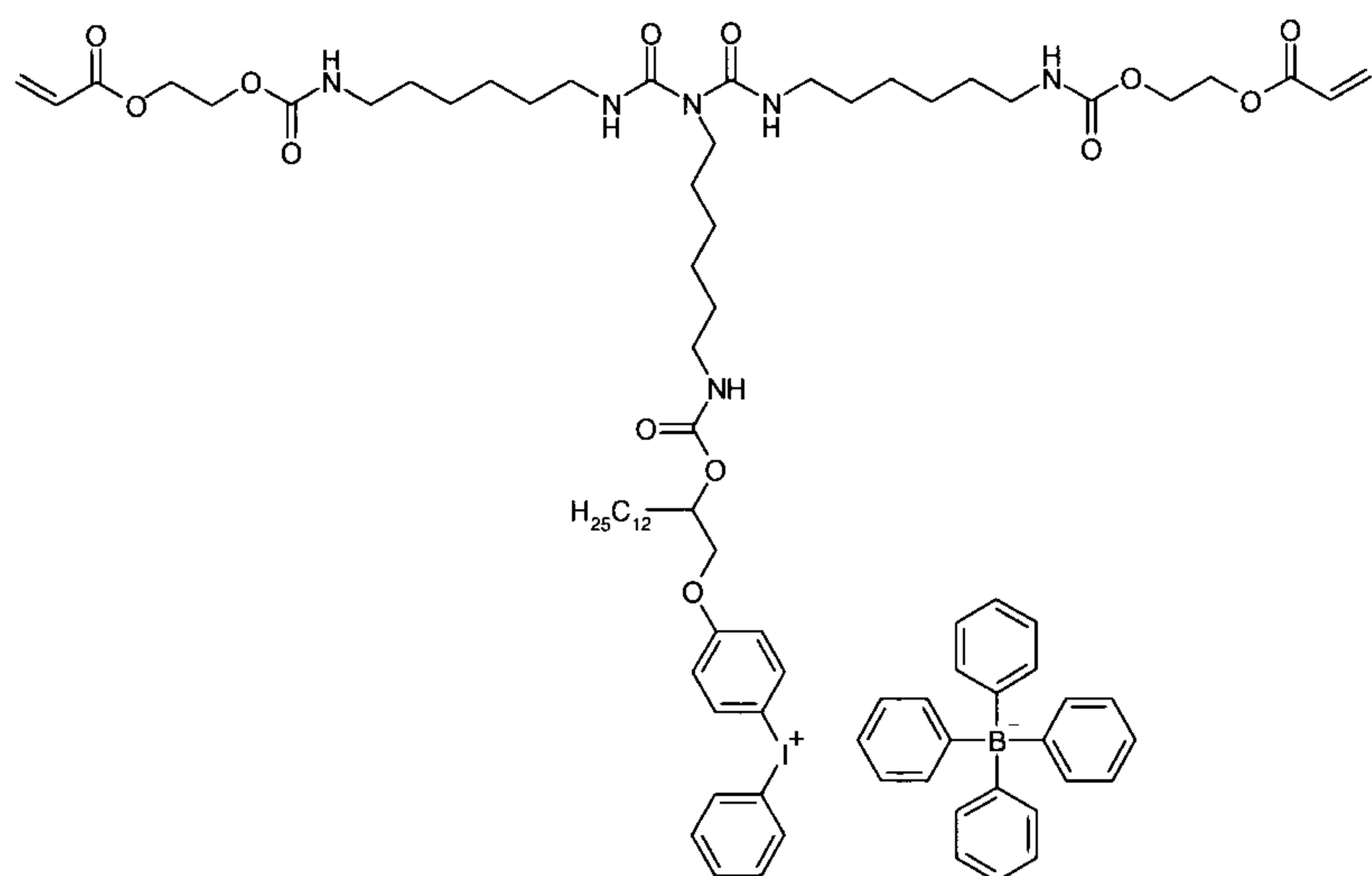


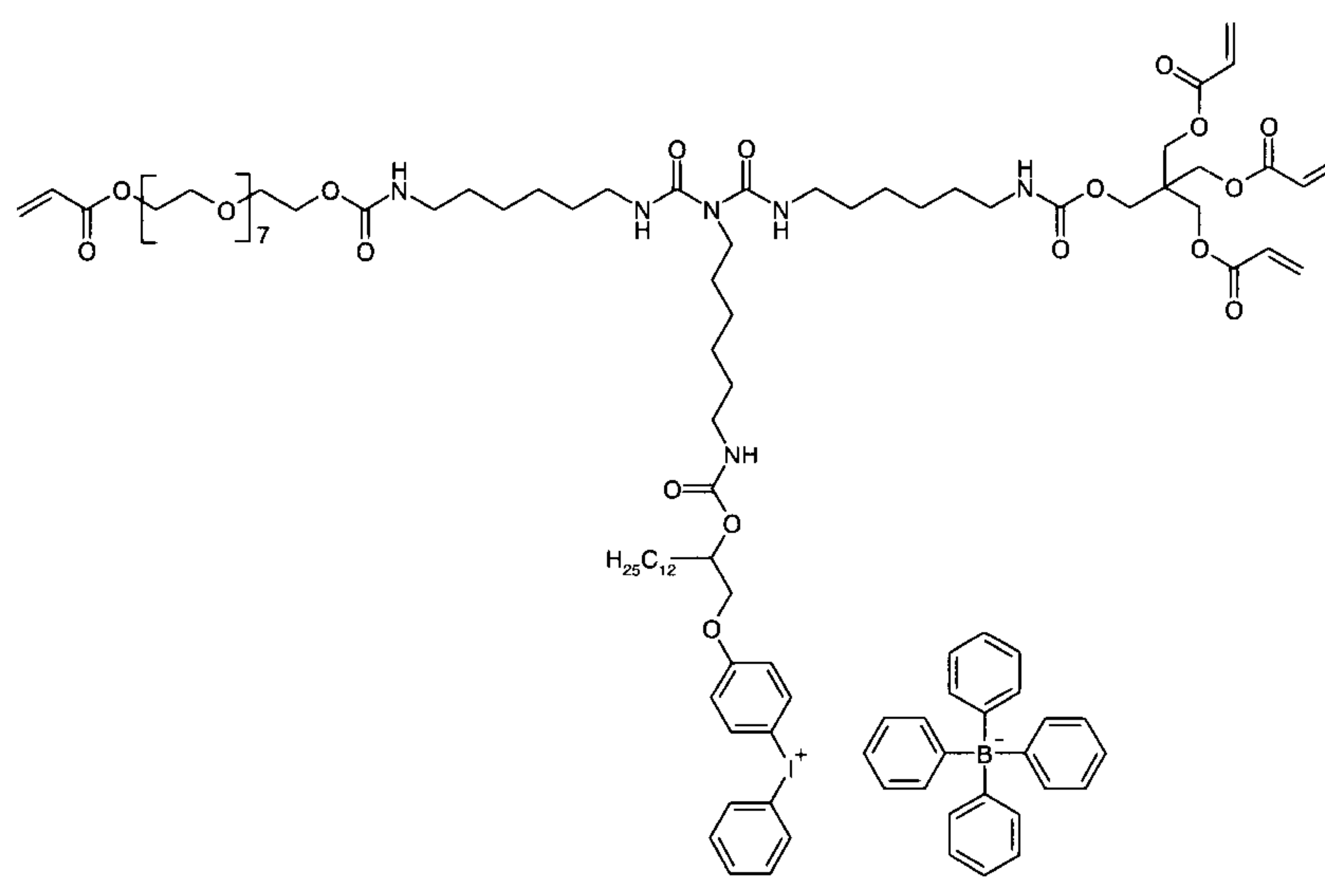
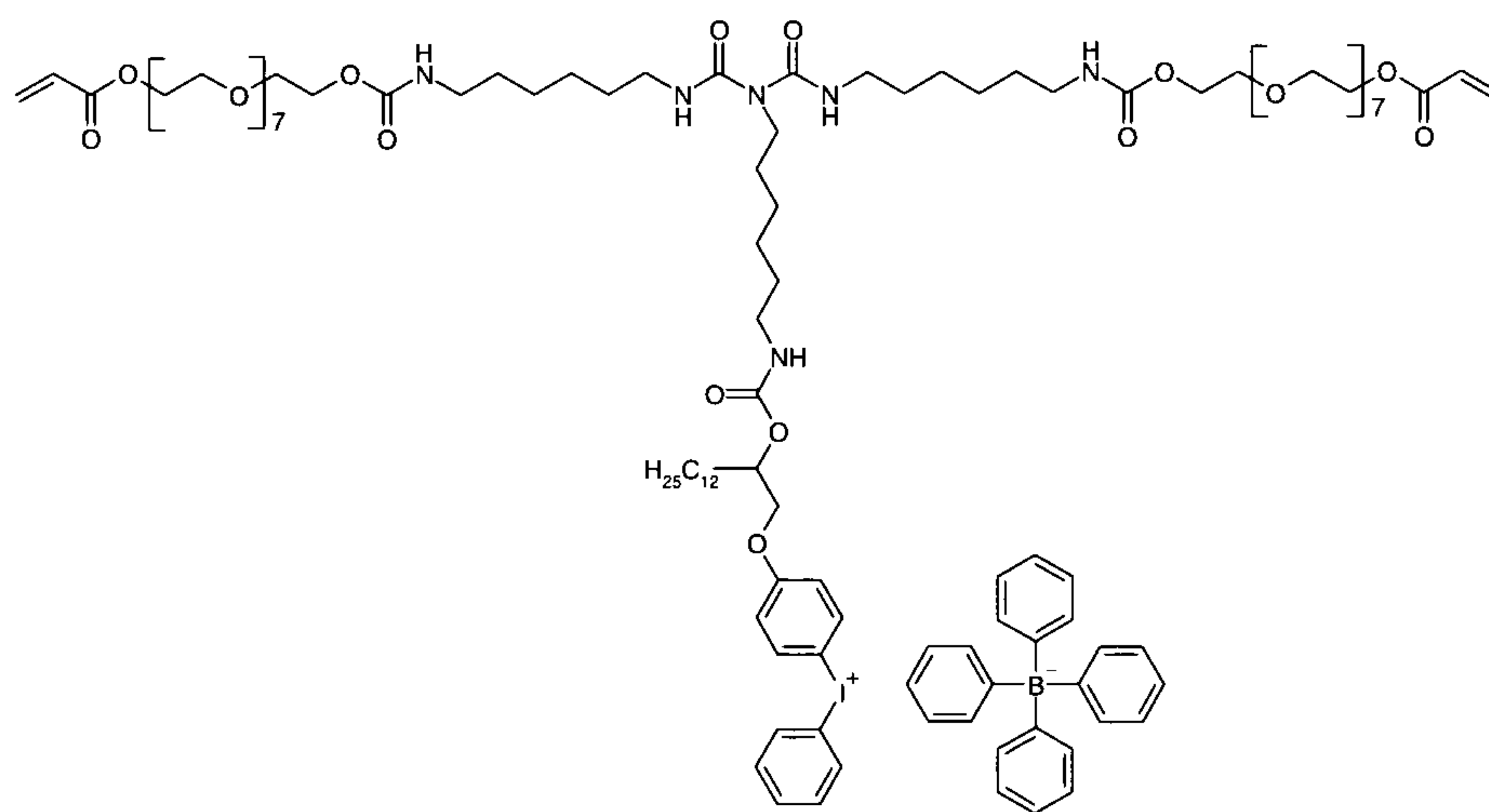
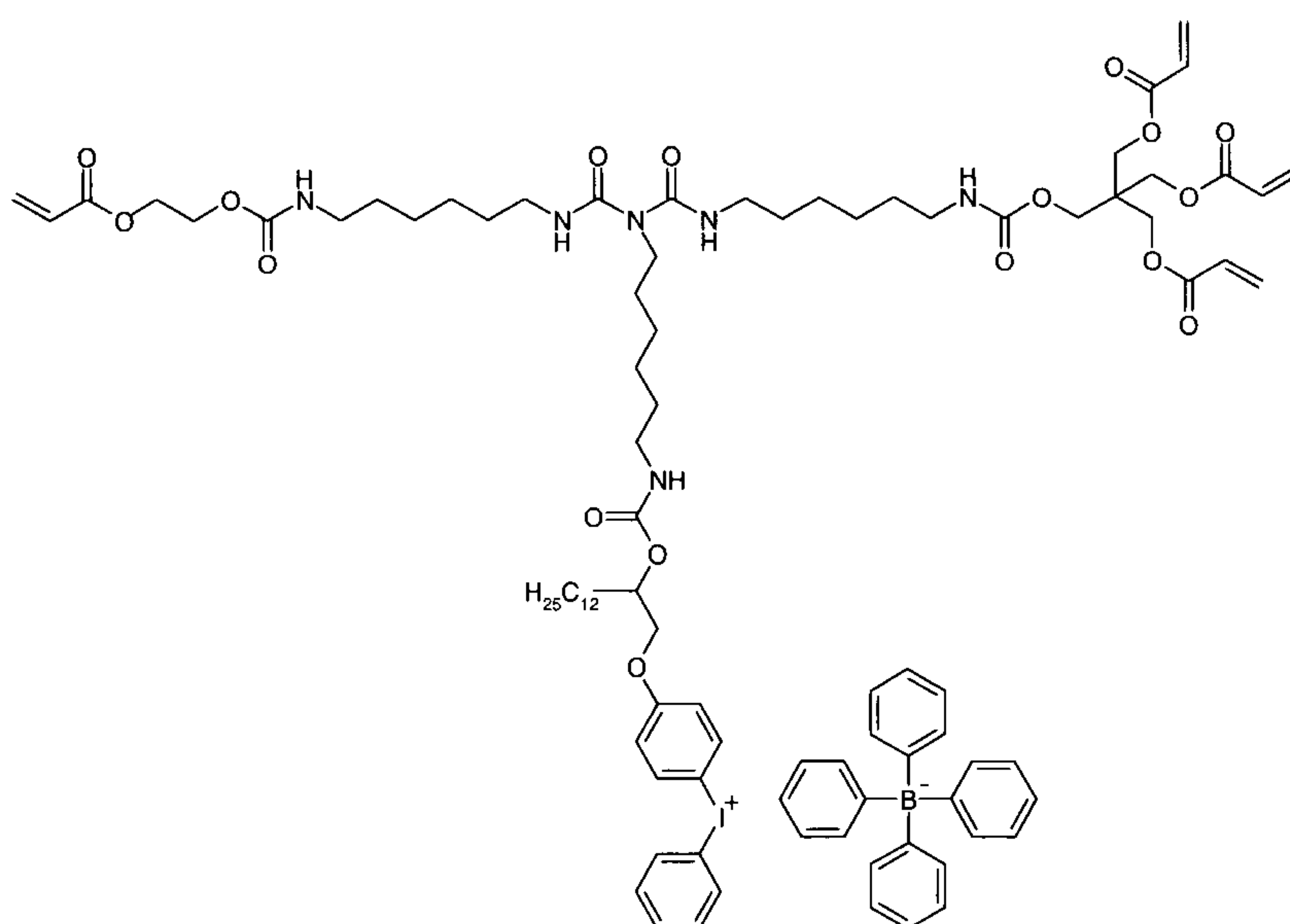
wherein a, b, c and d are molar ratios and may vary between about 0.01 and about 0.99.

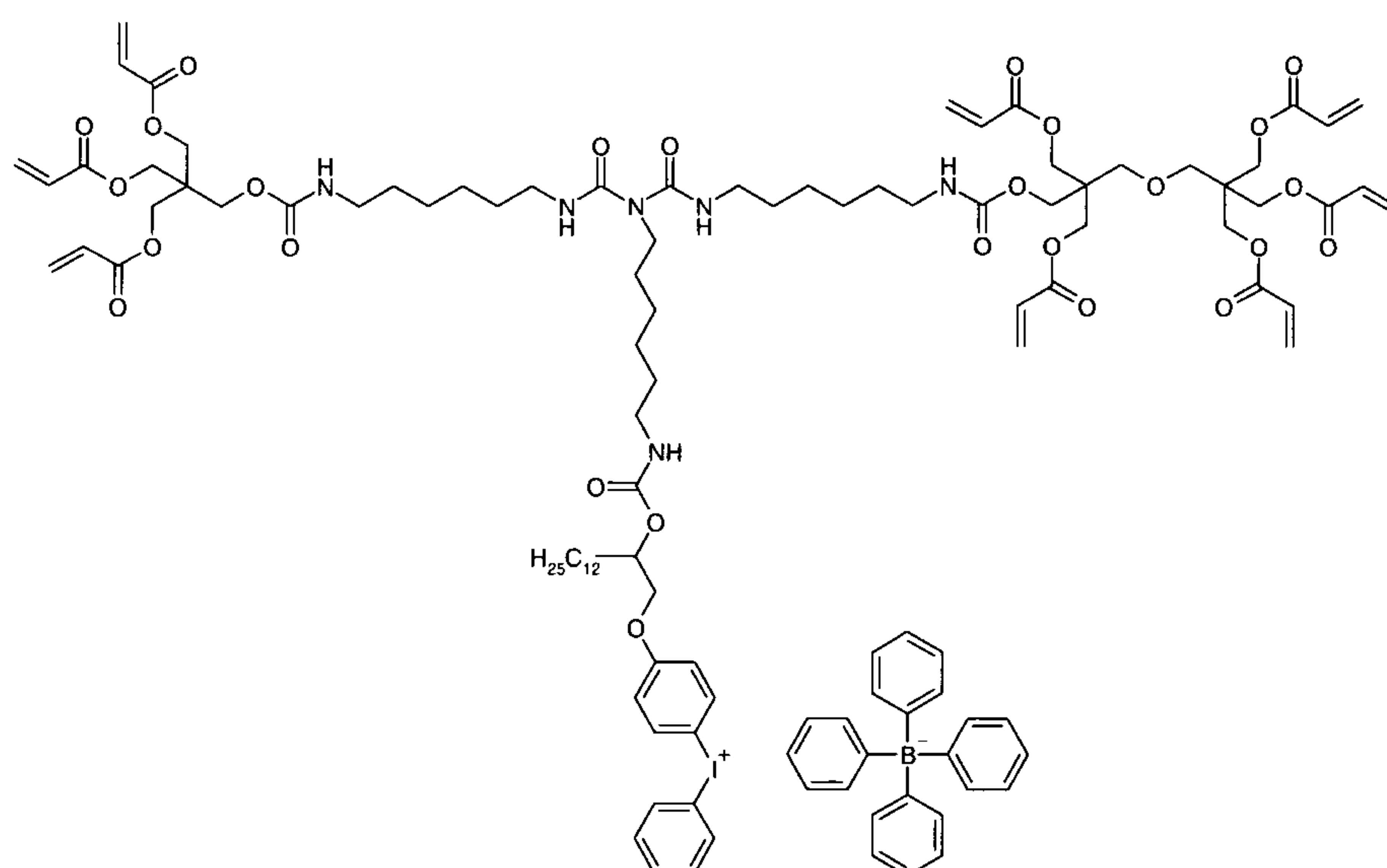
57. The coating solution of any one of Claims 18 to 56 further comprising a colorant.

58. The coating solution of Claim 57 comprising from about 0.5% to about 5 % by solid weight of said colorant.
59. The coating solution of Claim 57 or 58, wherein said colorant is triarylpyridine, xanthene or isobenzofuranone.
60. The coating solution of any one of Claims 57 to 59, wherein said colorant is initially colorless and becomes colored in the presence of free radical or acid.
61. The coating solution of any one of Claim 57 to 60, wherein said colorant is:
 - 3',6'-bis[N-[2-chlorophenyl]-N-methylamino]spiro[2-butyl-1,1-dioxo[1,2-benz isothiazole-3(3H),9'-(9H)xanthene]];
 - 3',6'-bis[N-[2-[methanesulfonyl]phenyl]-N-methylamino]spiro[2-butyl-1,1-dio xo[1,2-benzisothiazole-3(3H),9'-(9H)xanthene]];
 - 9-Diethylamino[spiro[12H-benzo(a)xanthene-12,1'(3'H)-isobenzofuran)-3'-one];
 - 2'-di(phenylmethyl)amino-6'-[diethylamino]spiro[isobenzofuran-1(3H),9'-(9H)-xanthen]-3-one ;
 - 3-[butyl-2-methylindol-3-yl]-3-[1-octyl-2-methylindol-3-yl]-1-(3H)-isobenzofuranone;
 - 6-[dimethylamino]-3,3-bis[4-dimethylamino]-phenyl-(3H)-isobenzofuranone;
 - 2-[2-Octyloxyphenyl]4-[4-dimethylaminophenyl]-6-phenylpyridine; or
 - leuco lactone dyes;
 - Blue-63™;
 - GN-169™; or
 - Red-40™.
62. The coating solution of any one of Claims 18 to 61 further comprising a stabilizer.
63. The coating solution of Claim 62 comprising from about 0.5% to about 5 % by solid weight of said stabilizer.
64. The coating solution of Claim 62 or 63, wherein said stabilizer is

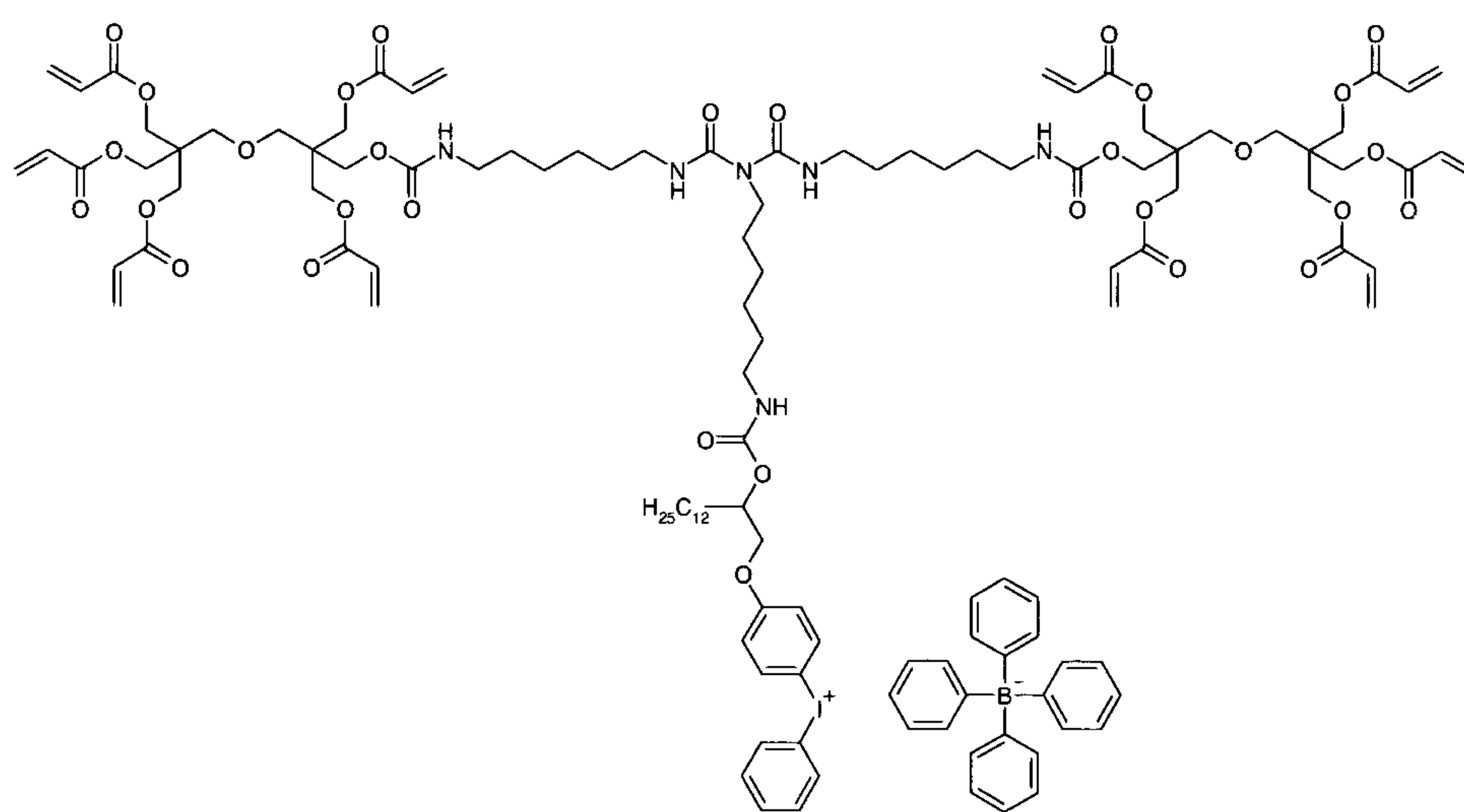
- C=CC(=O)OCCOCCOC(=O)NCCCCCCCCNC(=O)N(CCCCCCCCCNC(=O)OCCOC(=O)C=C)C(=O)NCCCCCCCCNC(=O)OCCOC(=O)C=C



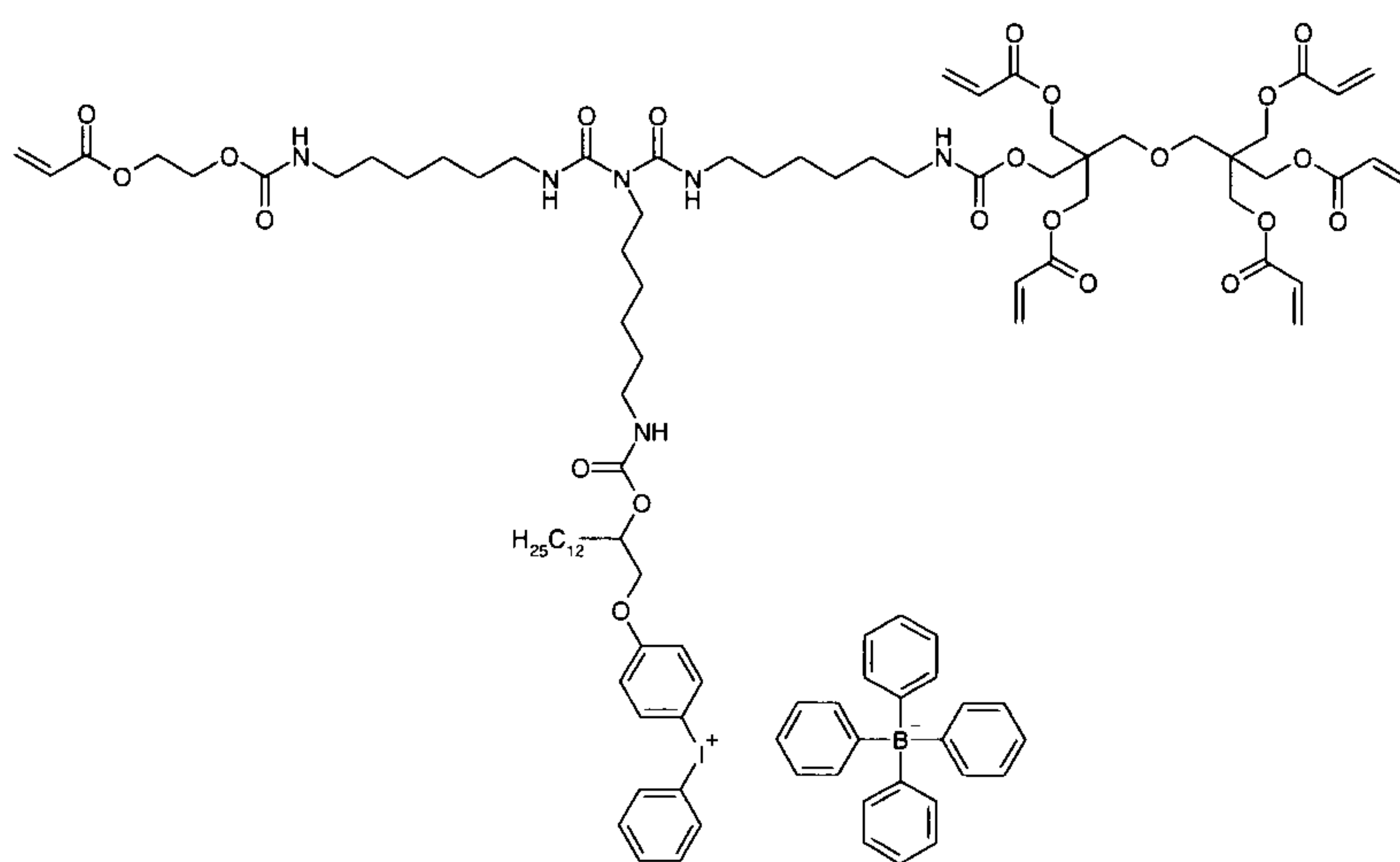




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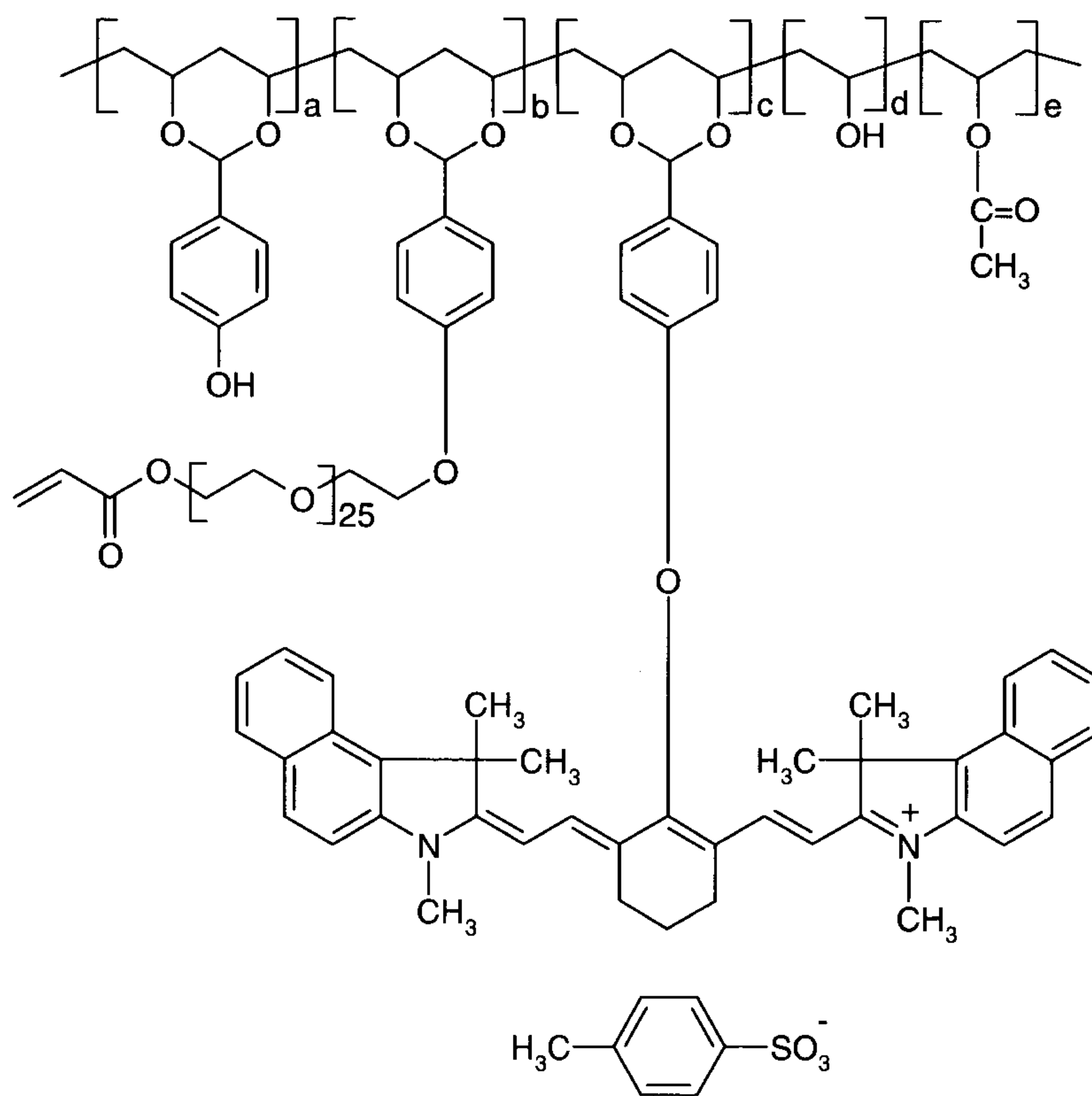
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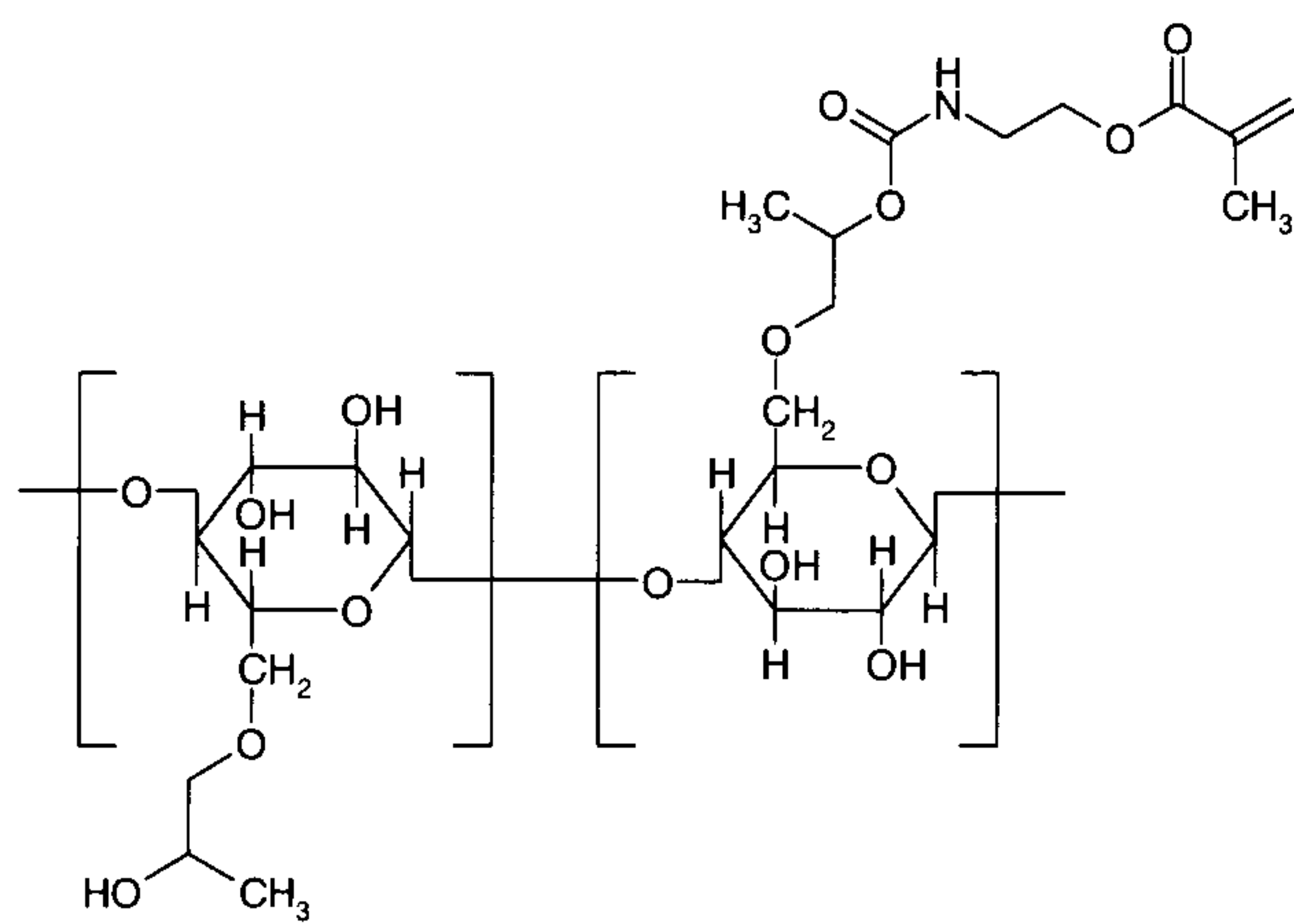
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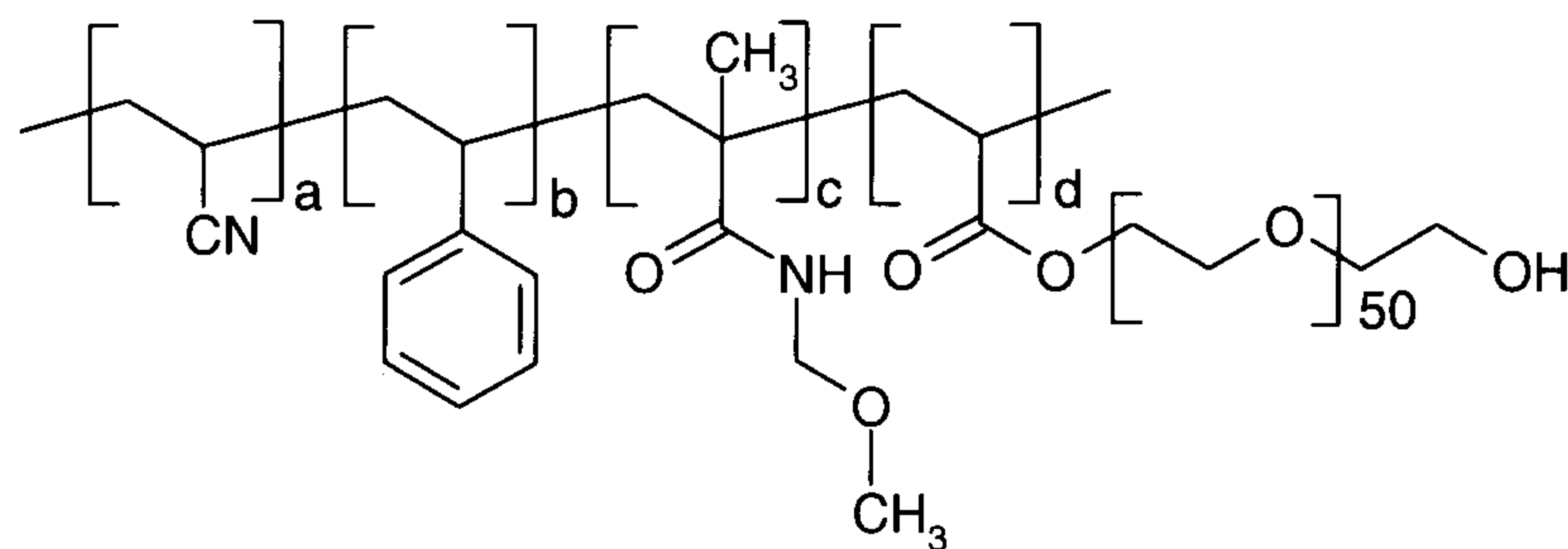
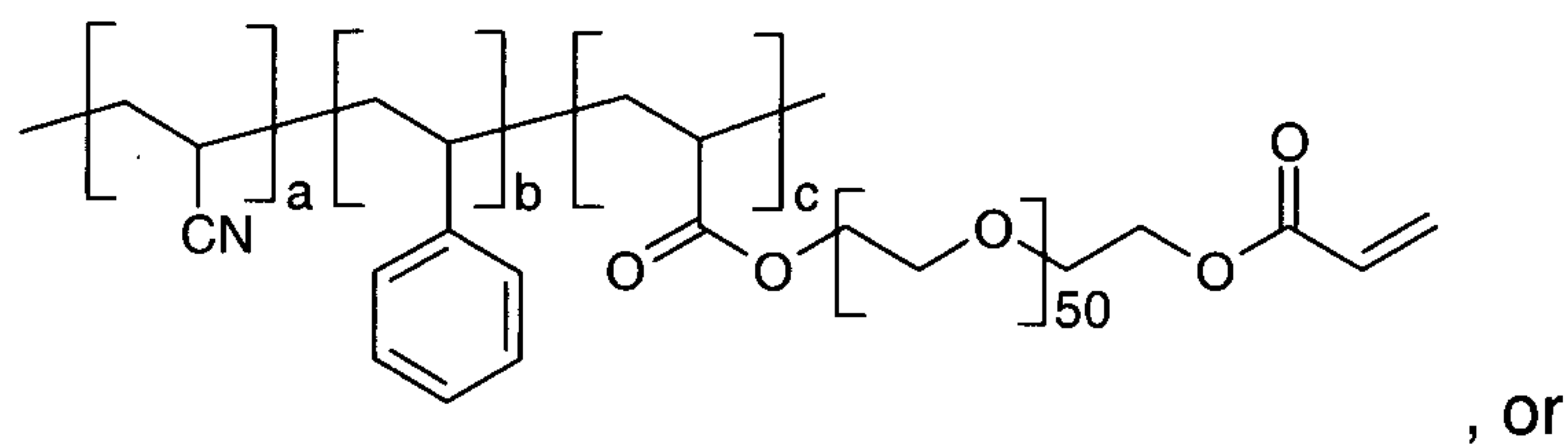
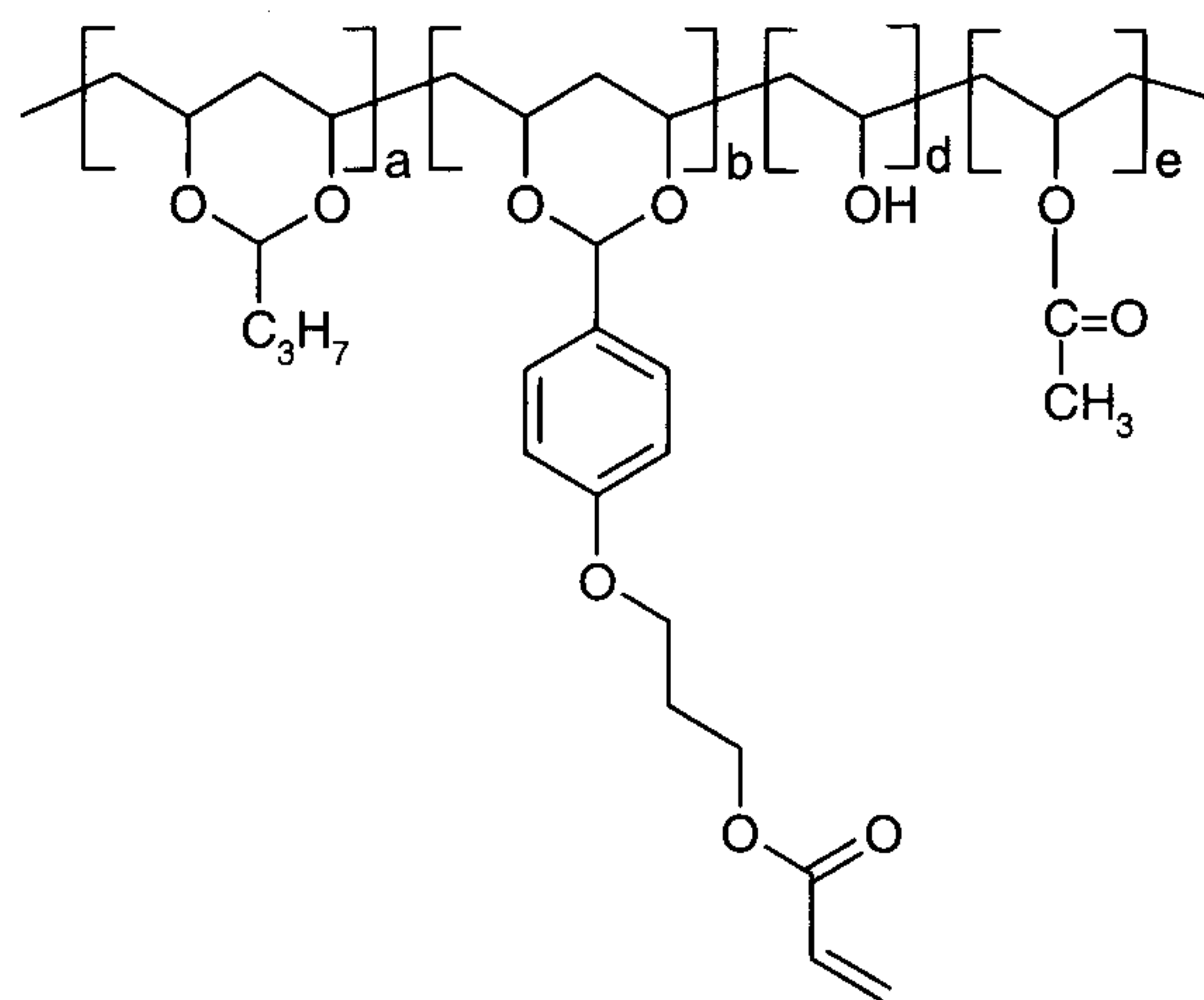
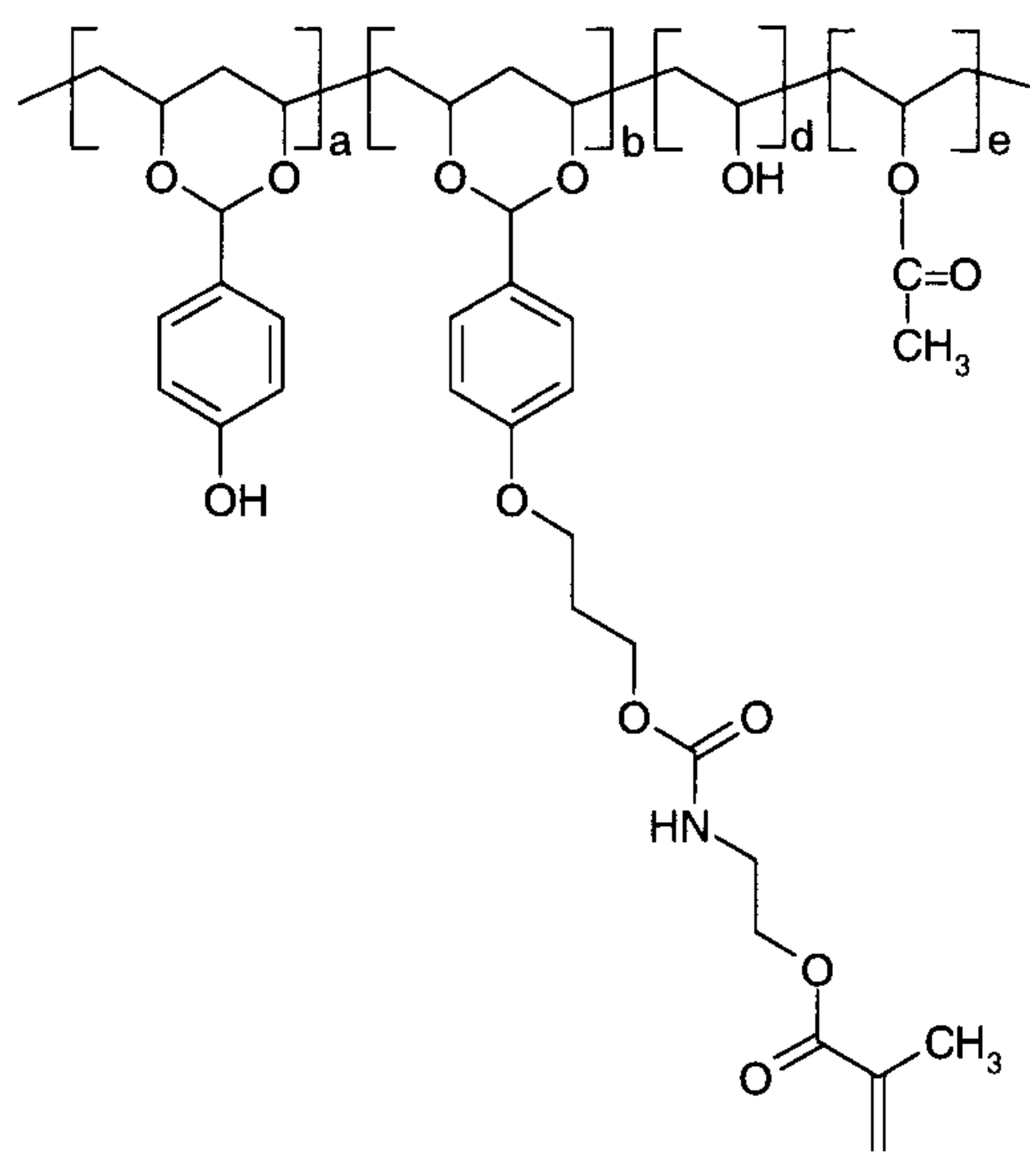






and a polymer binder of formula:





wherein a, b, c, d and e are molar ratios that may vary between about 0.01 and about 0.99.

66. Use of the coating solution of any one of Claims 18 to 65 in the preparation of a negative-working lithographic printing plate.

67. A negative working lithographic printing plate comprising a coating produced by depositing the coating solution of any one of Claims 18 to 65 onto a substrate.
68. The lithographic printing plate of Claim 67, wherein said coating weighs between about 0.5 and about 2.5 g/m².
69. The lithographic printing plate of Claims 67 or 68, wherein said substrate is anodized aluminum, plastic film, or paper.
70. The lithographic printing plate of Claim 69, wherein said anodized aluminum substrate has been brushed-grained or electro-grained before being anodized.
71. The lithographic printing plate of any one of Claims 67 to 70, wherein said lithographic printing plate further comprises a polymeric adhesion-promoting coating disposed between the substrate and the coating according to any one of claims 18 to 65.
72. The lithographic printing plate of Claim 71, wherein said polymeric adhesion-promoting coating comprises poly(acrylic acid) or poly(acrylic acid-co-vinylphosphoric acid).
73. The lithographic printing plate of Claim 71 or 72, wherein said polymeric adhesion-promoting coating weighs between about 0.1 and about 1.0 g/m².
74. The iodonium salt of Claim 9, wherein m is an integer varying between 0 and 7.

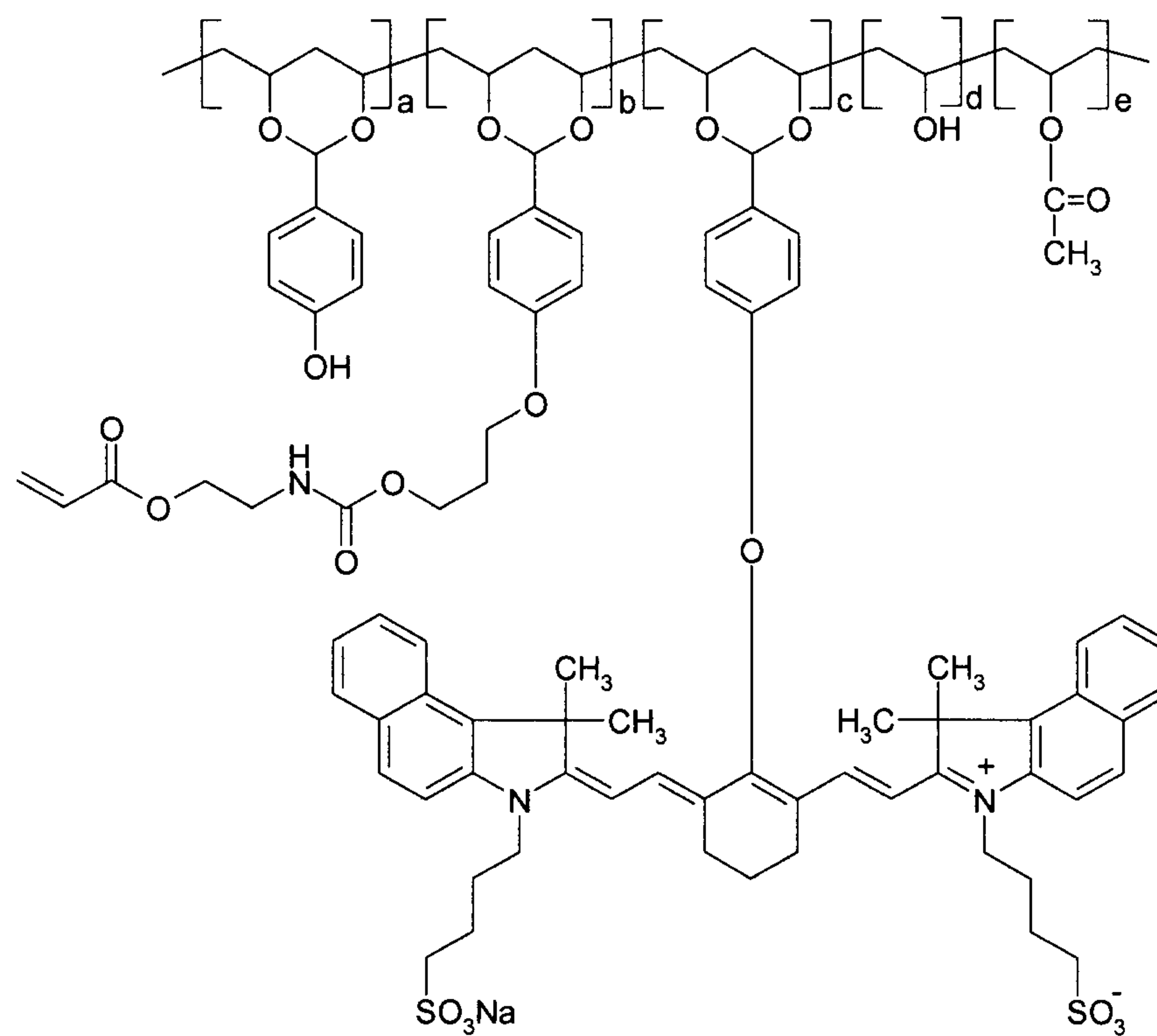


Figure 1

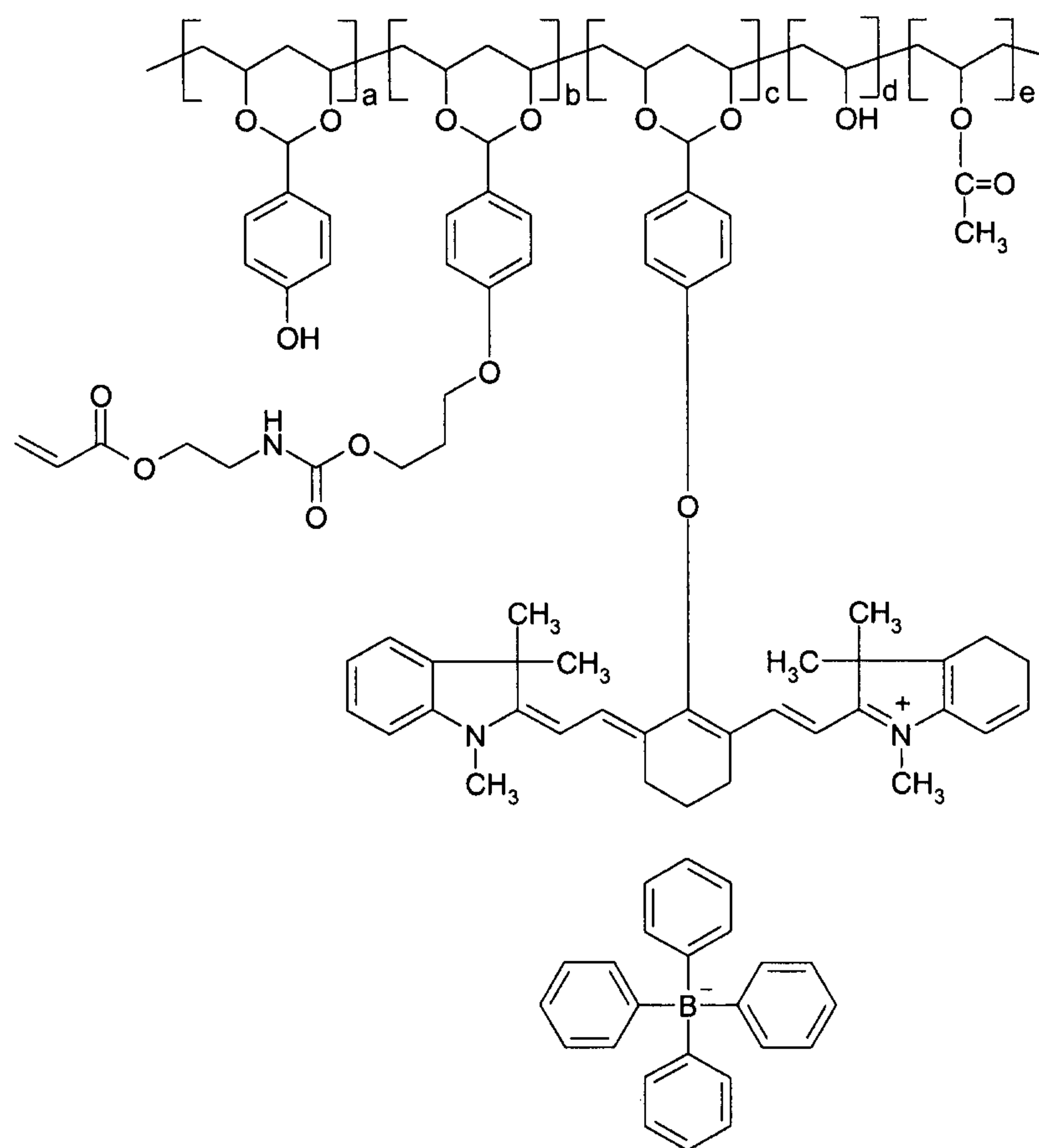


Figure 2

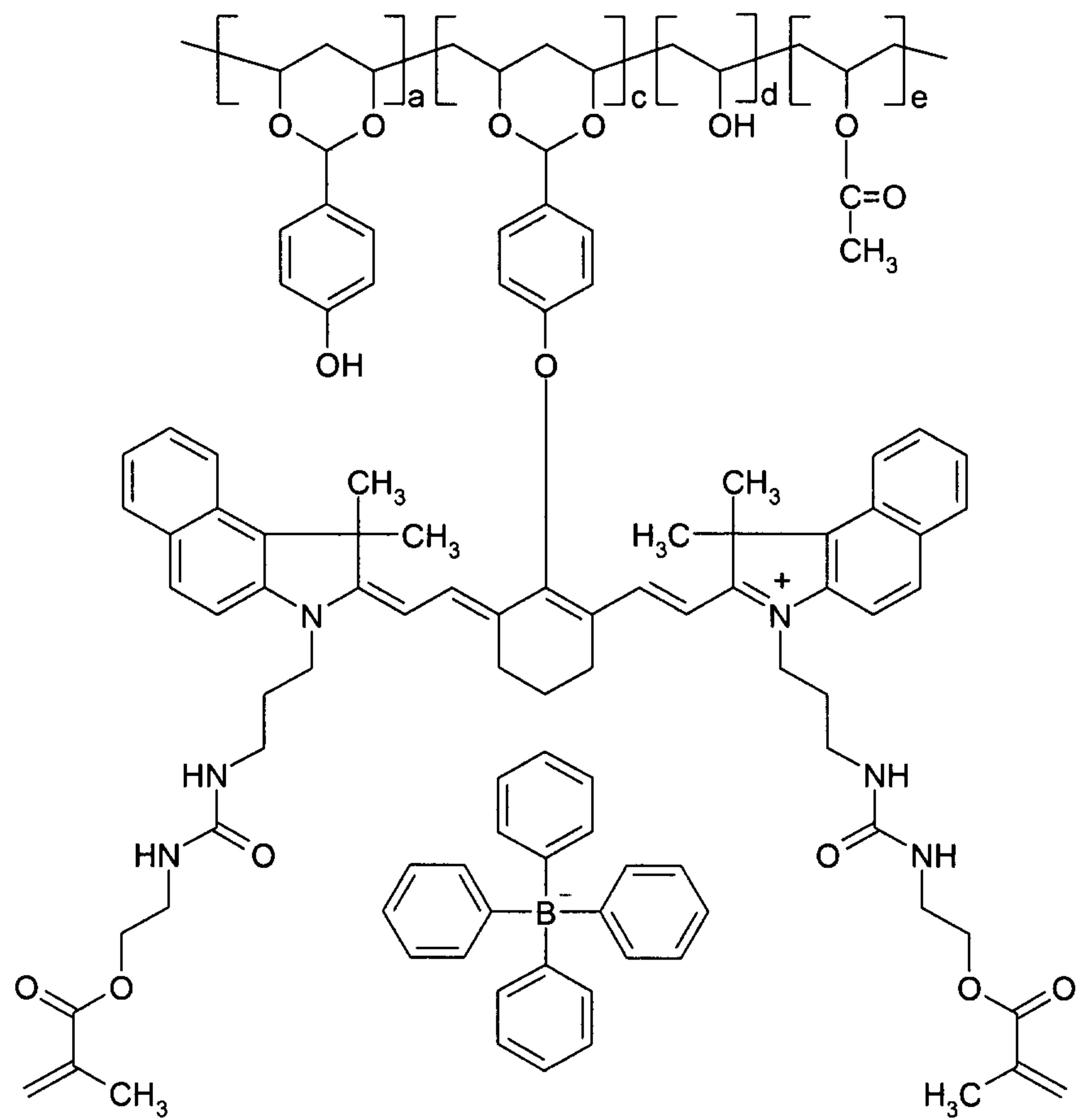


Figure 3

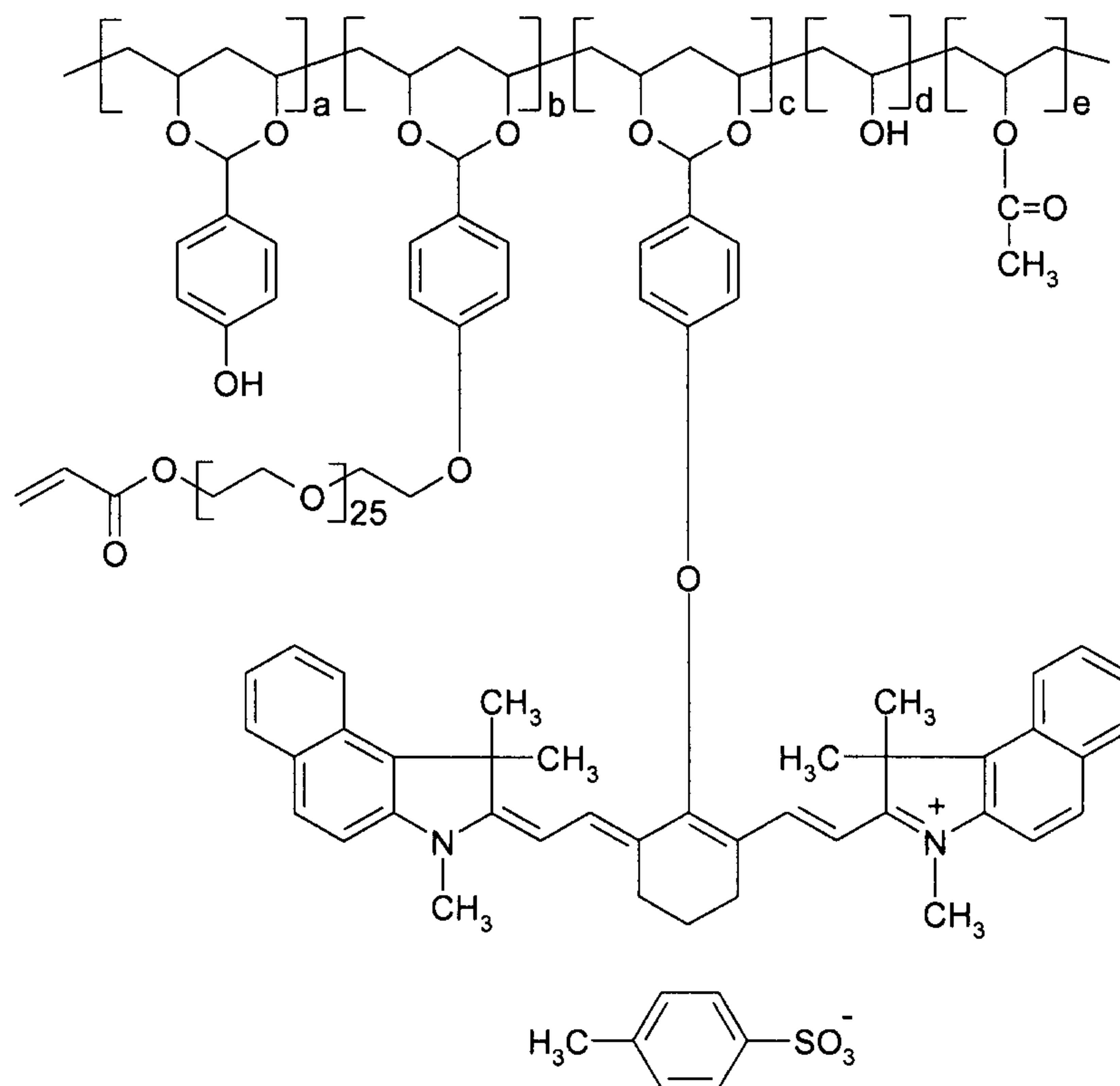


Figure 4

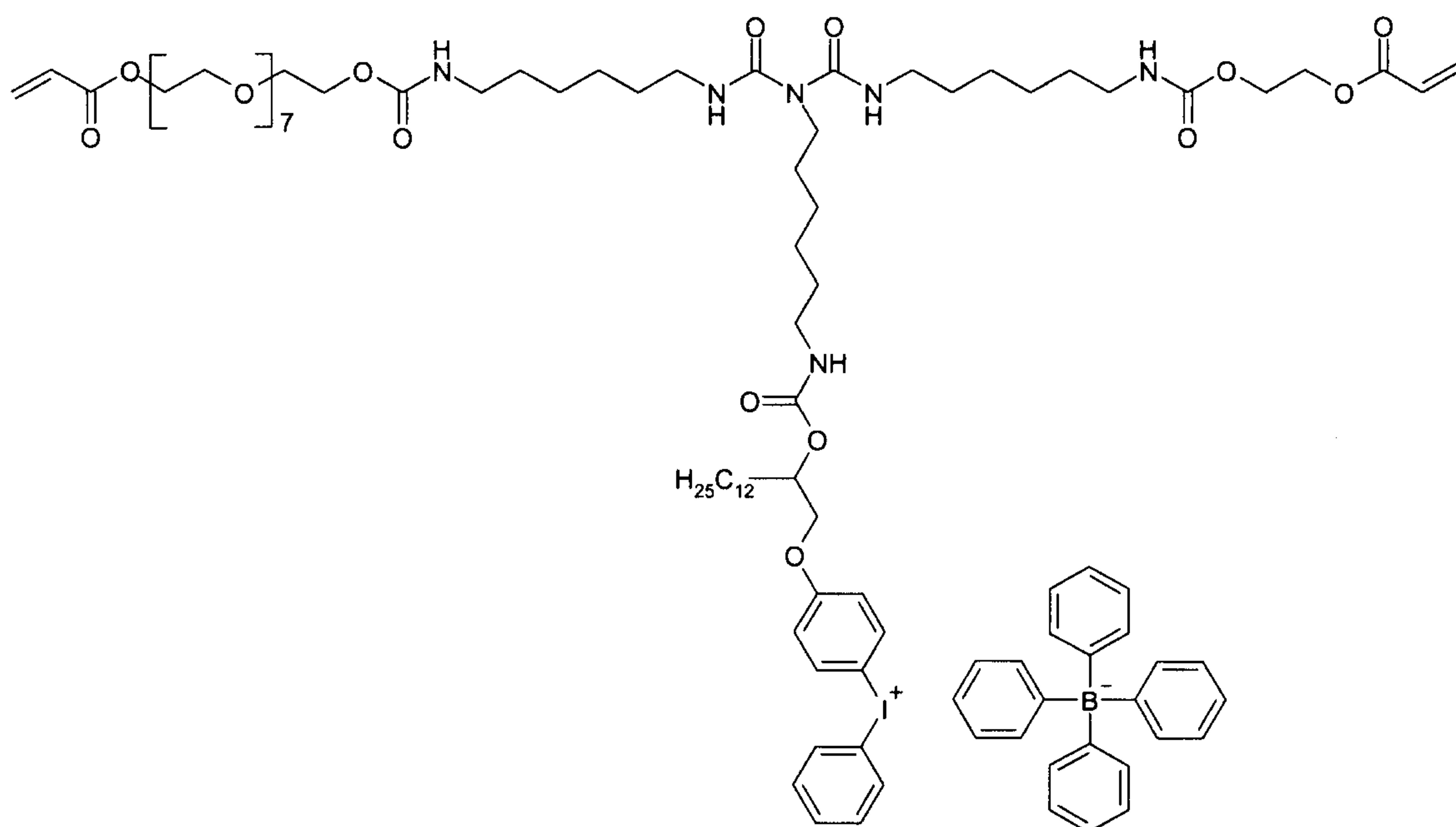


Figure 5

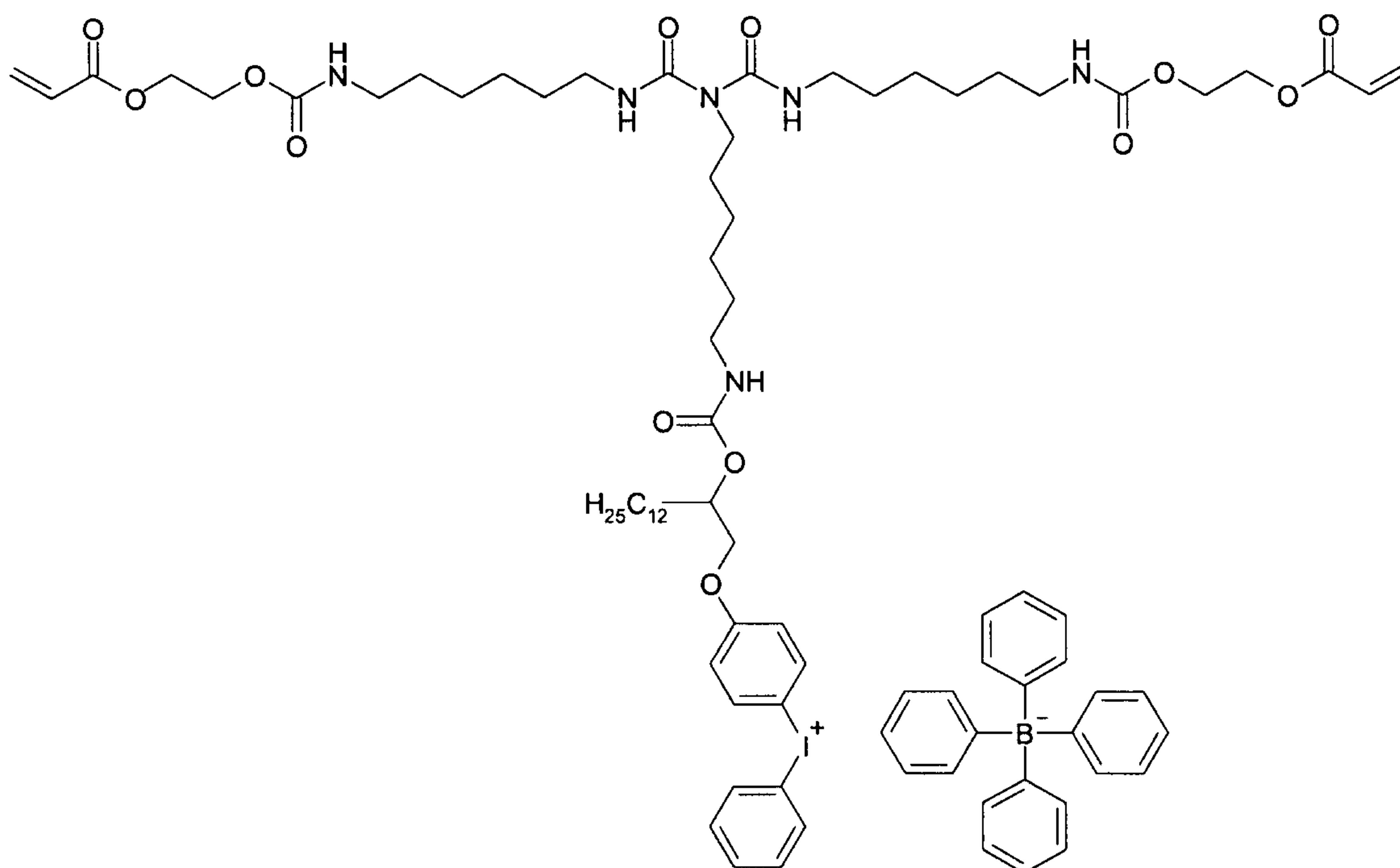


Figure 6

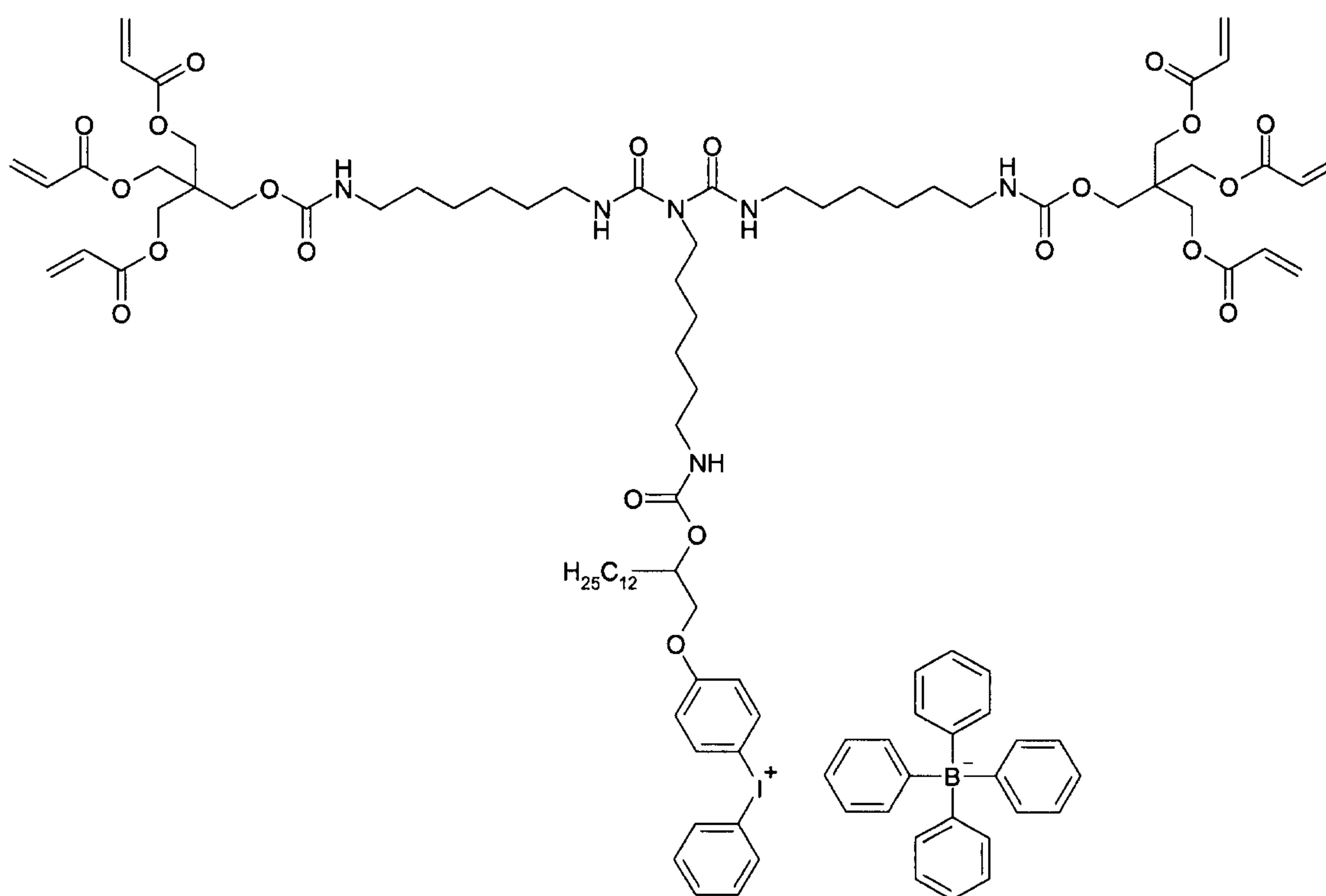
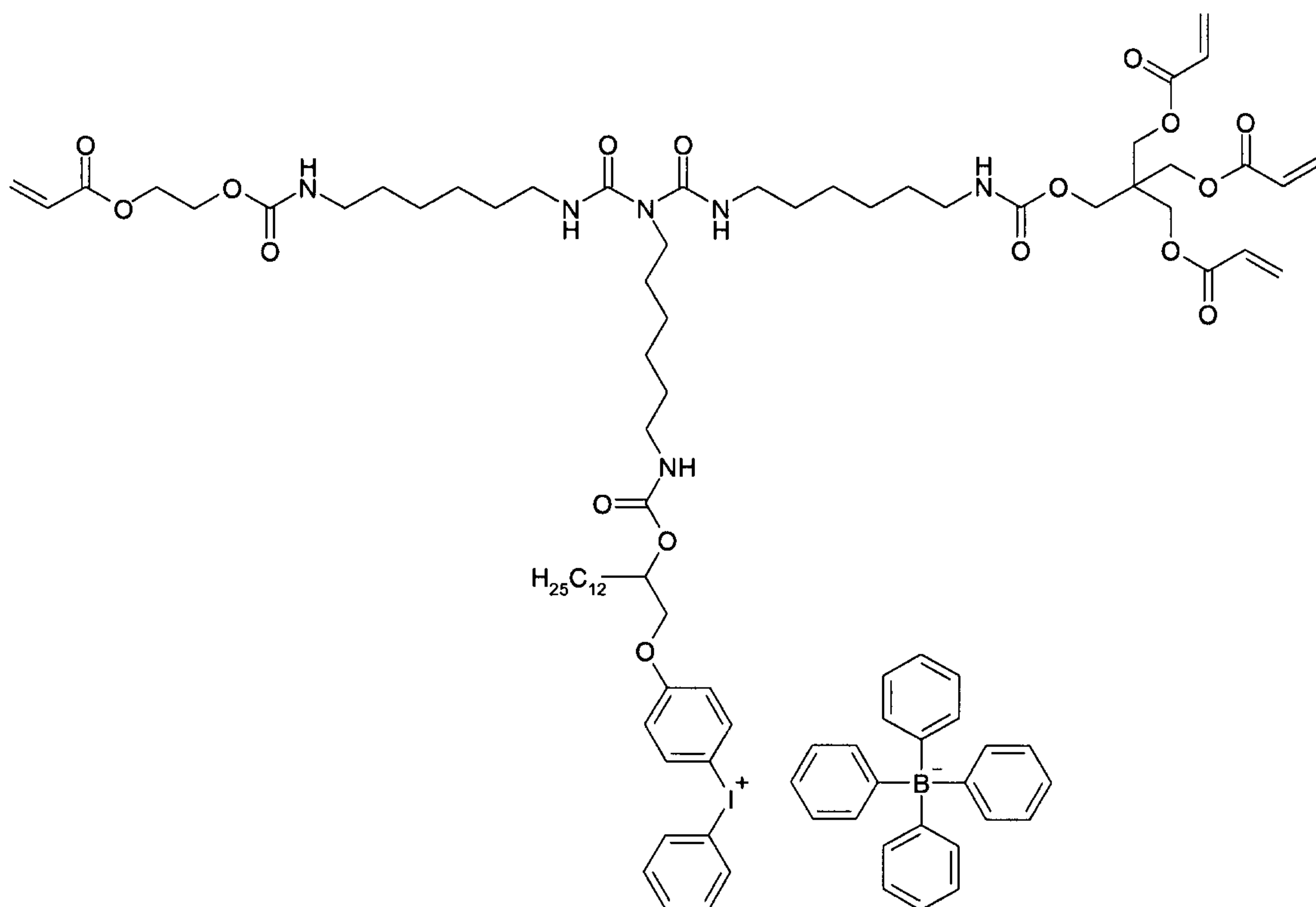
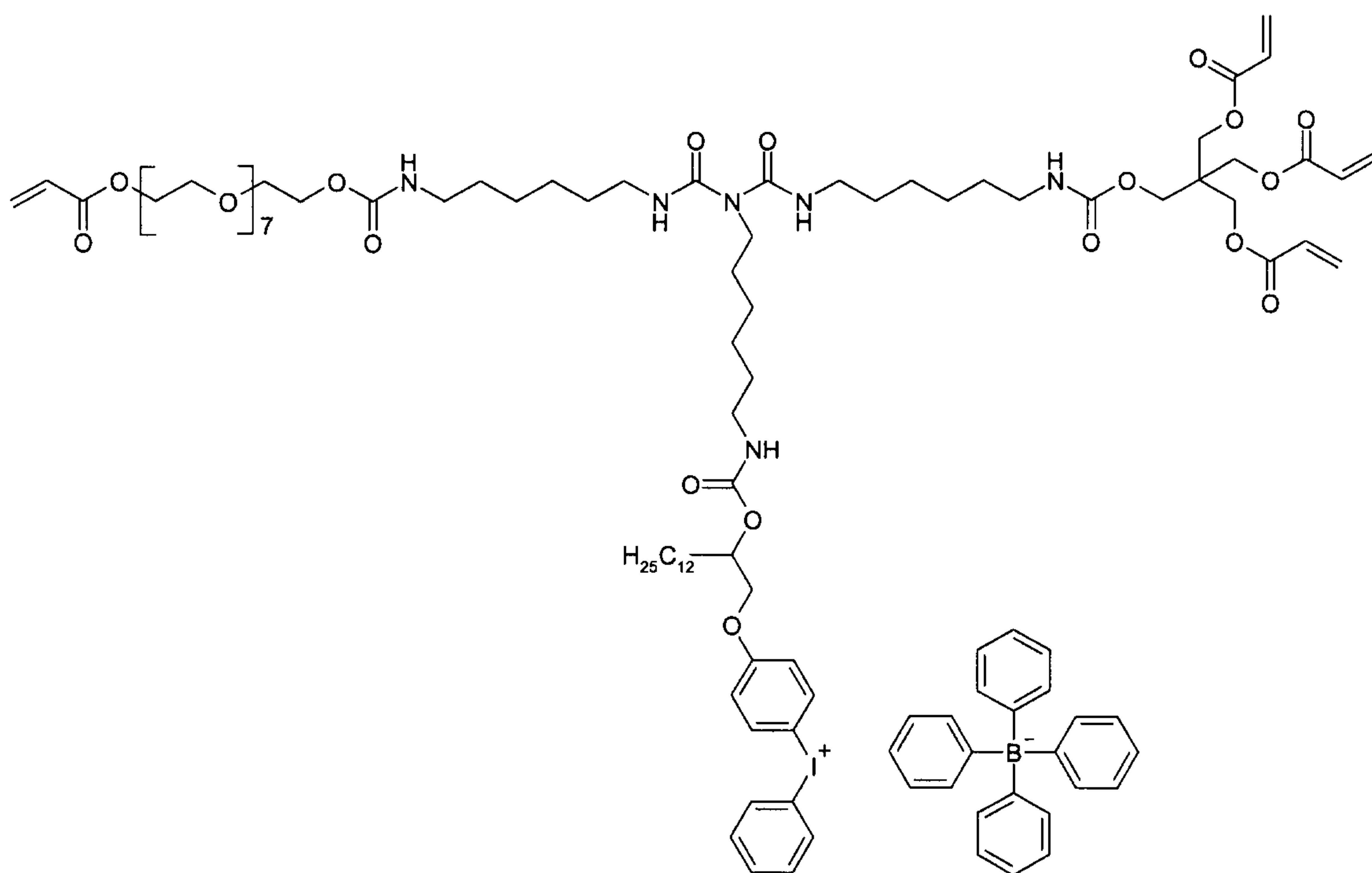


Figure 7

C=CC(=O)OCCOCCOC(=O)NCCCCCCCNC(=O)N(CCCCCCNC(=O)OCCOCCOC(=O)C=C)C(=O)NCCCCCCNC(=O)OCCOC(=O)C=C
CCCCCCCCCCCCCCCCCCCCCOCCOc1ccc(cc1)[I+]c2ccccc2.[B-](c3ccccc3)(c4ccccc4)c5ccccc5

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Chemical structure of the initiator 1, showing a central boron atom coordinated by four phenyl groups, with a positive charge on the boron and a negative charge on the nitrogen atom of the initiator chain.

Figure 11

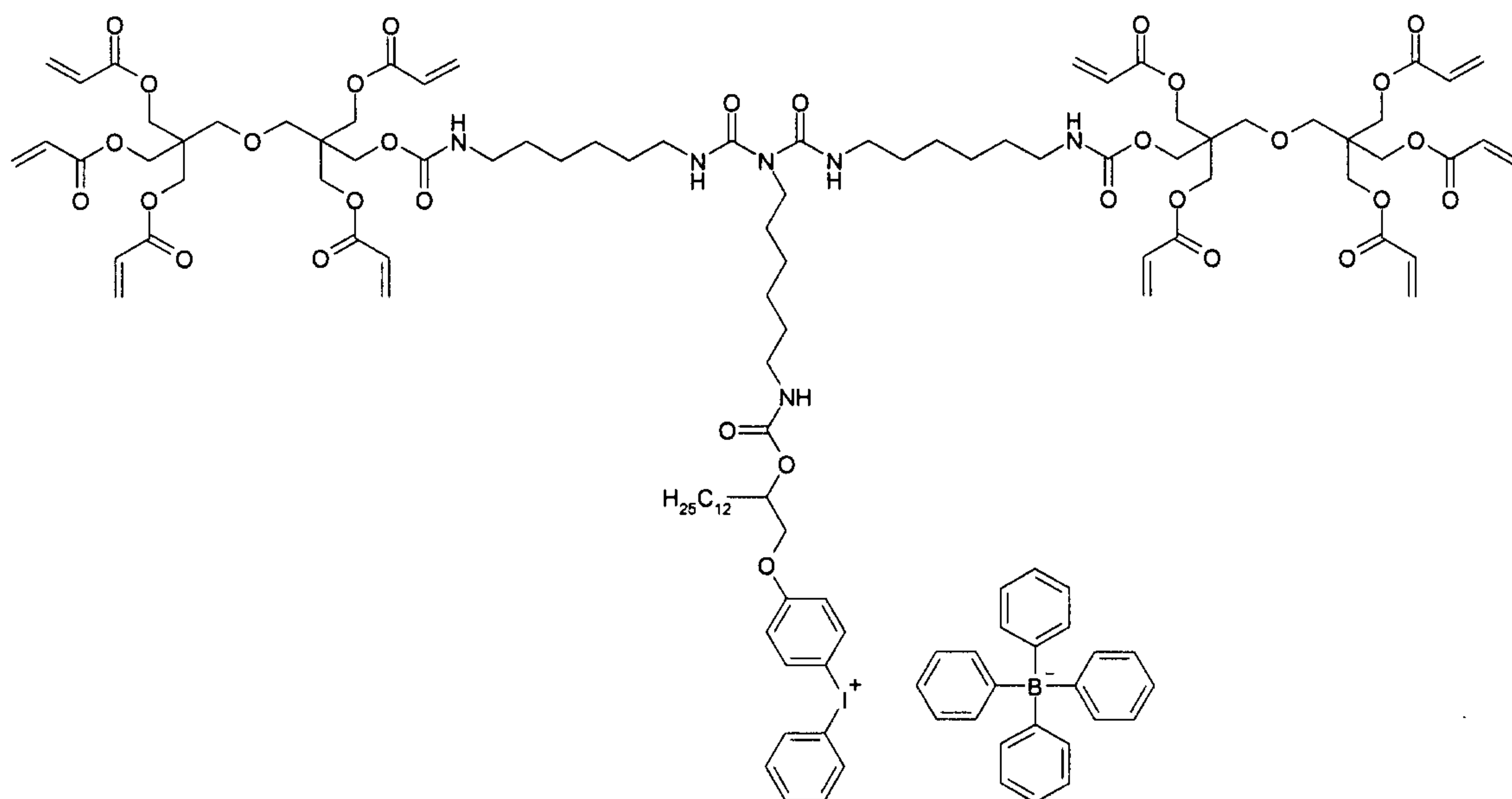


Figure 12

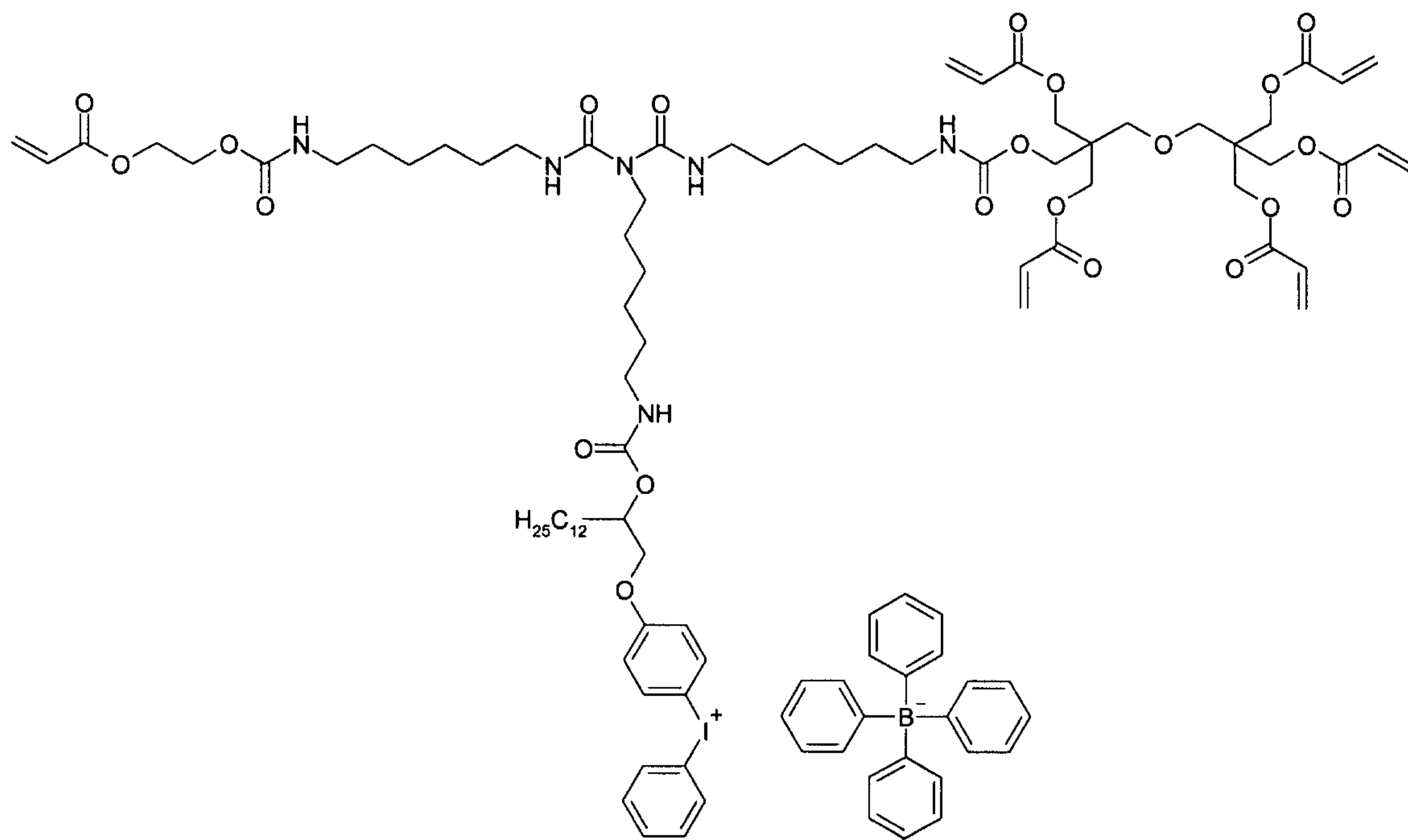
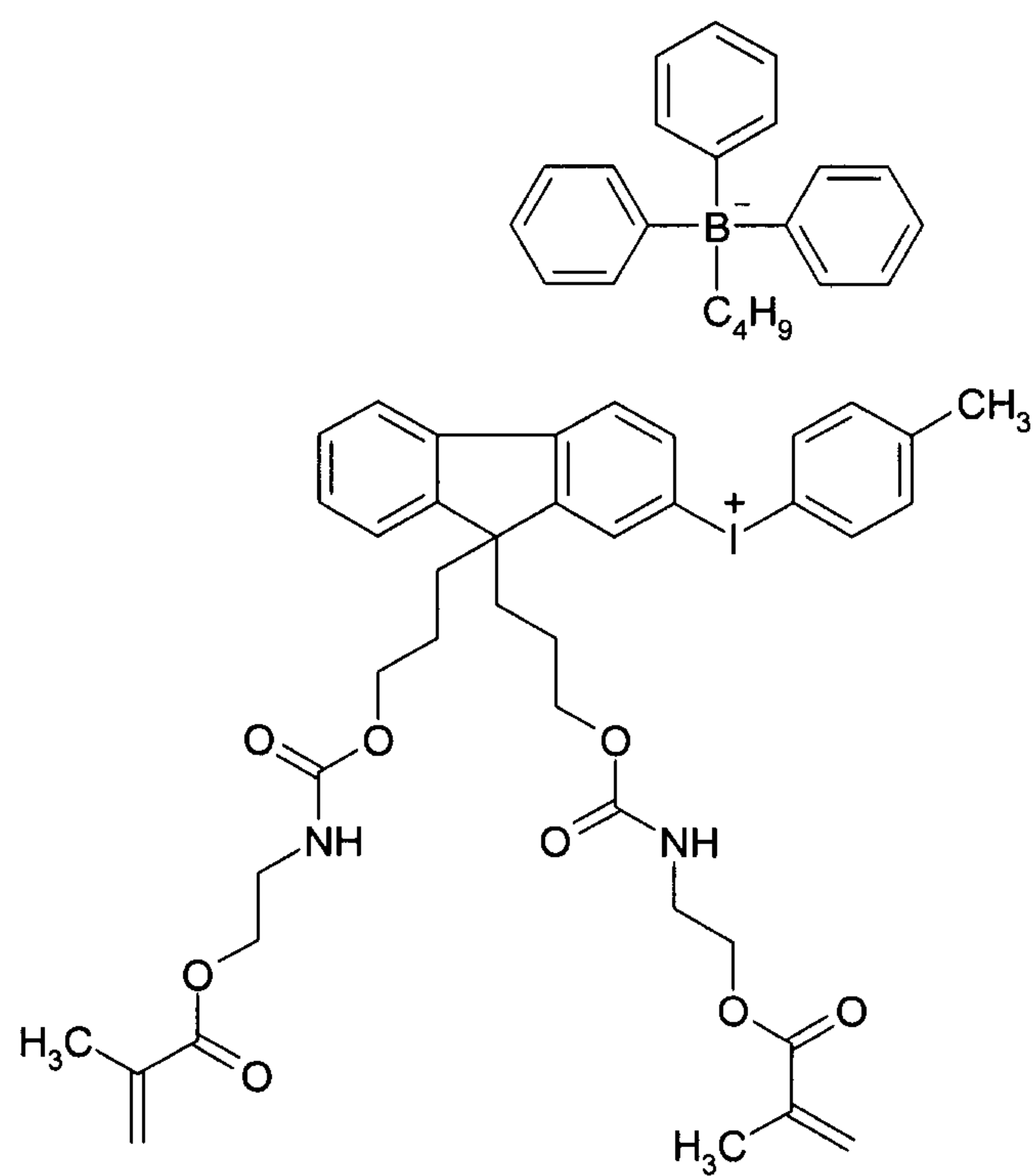


Figure 13

CC(=O)OCCOC(=O)NCCOC(=O)C(C)CO[C@H]1O[C@H](CO[C@@H]2[C@@H](O)[C@H](O)[C@@H](CO)O[C@H]2O)[C@H](O)[C@H](O)[C@H]1O

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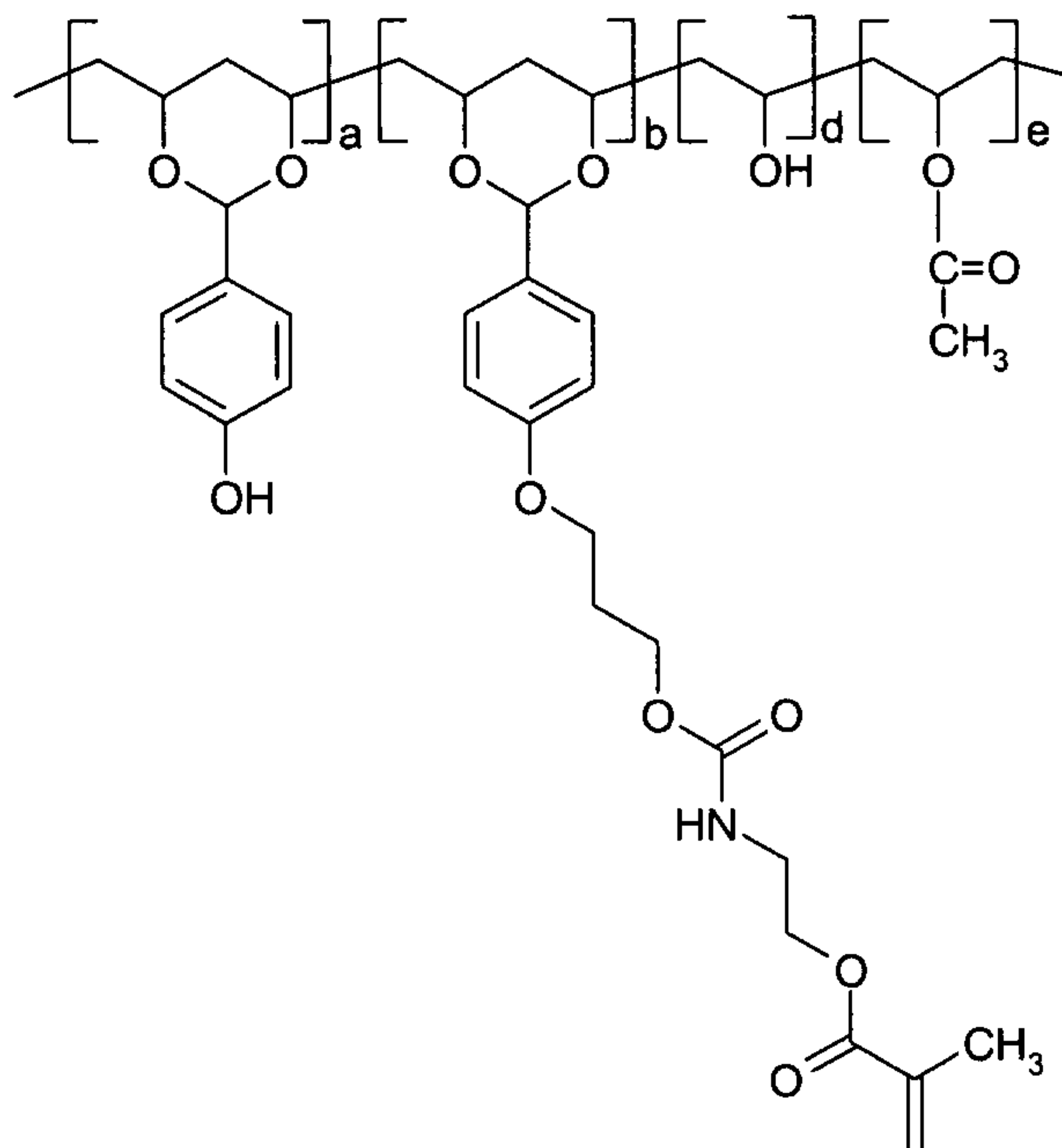


Figure 16

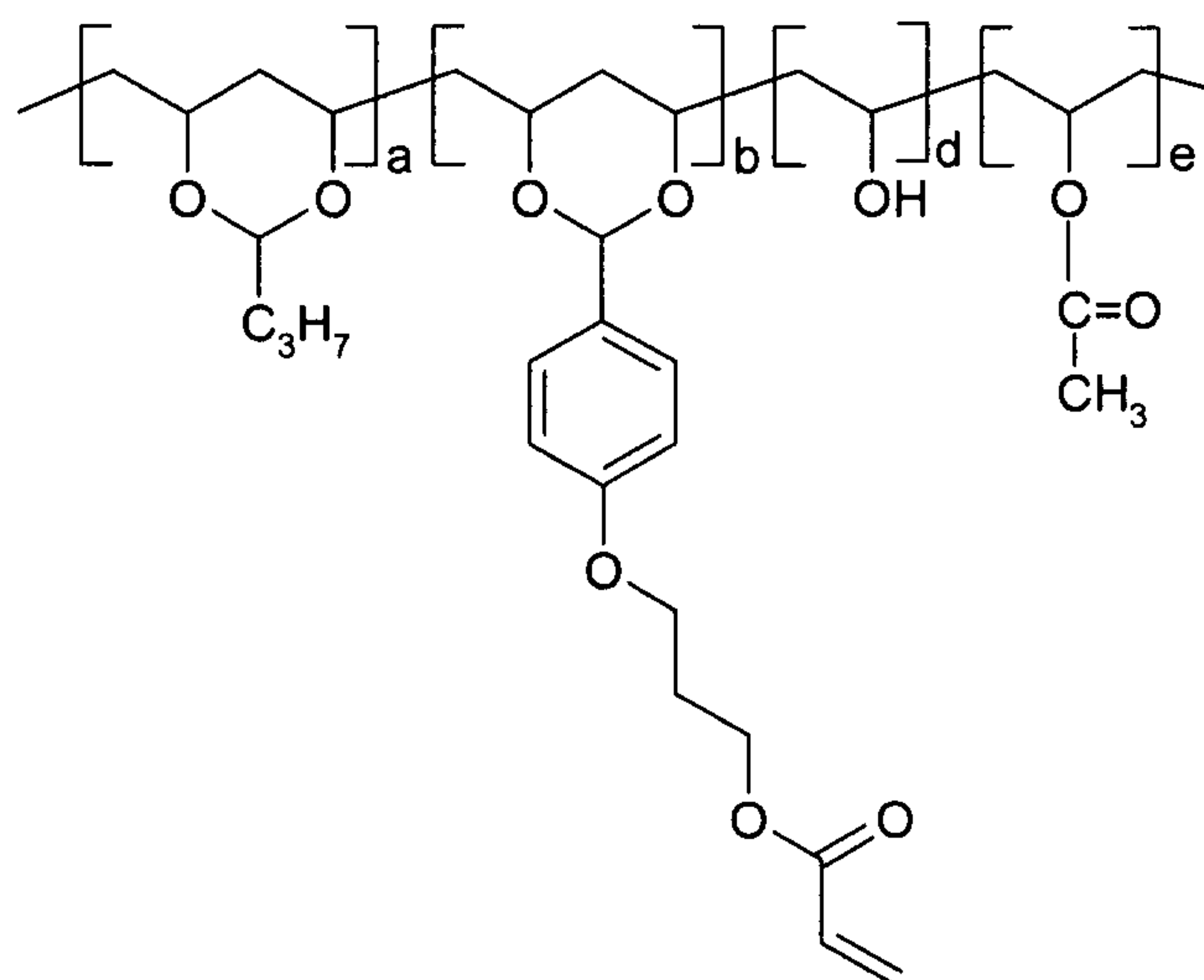


Figure 17

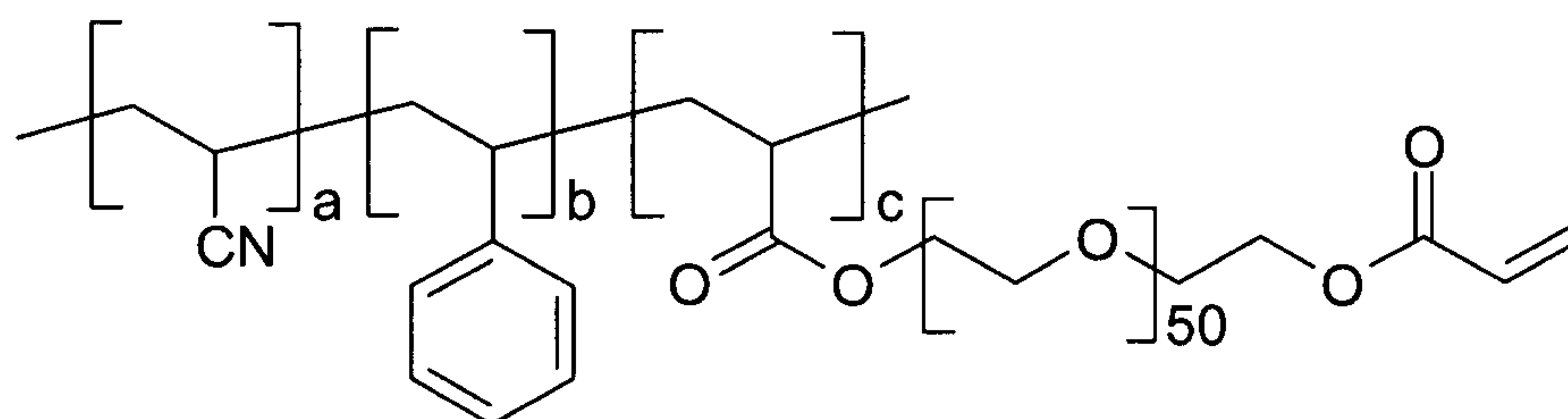


Figure 18

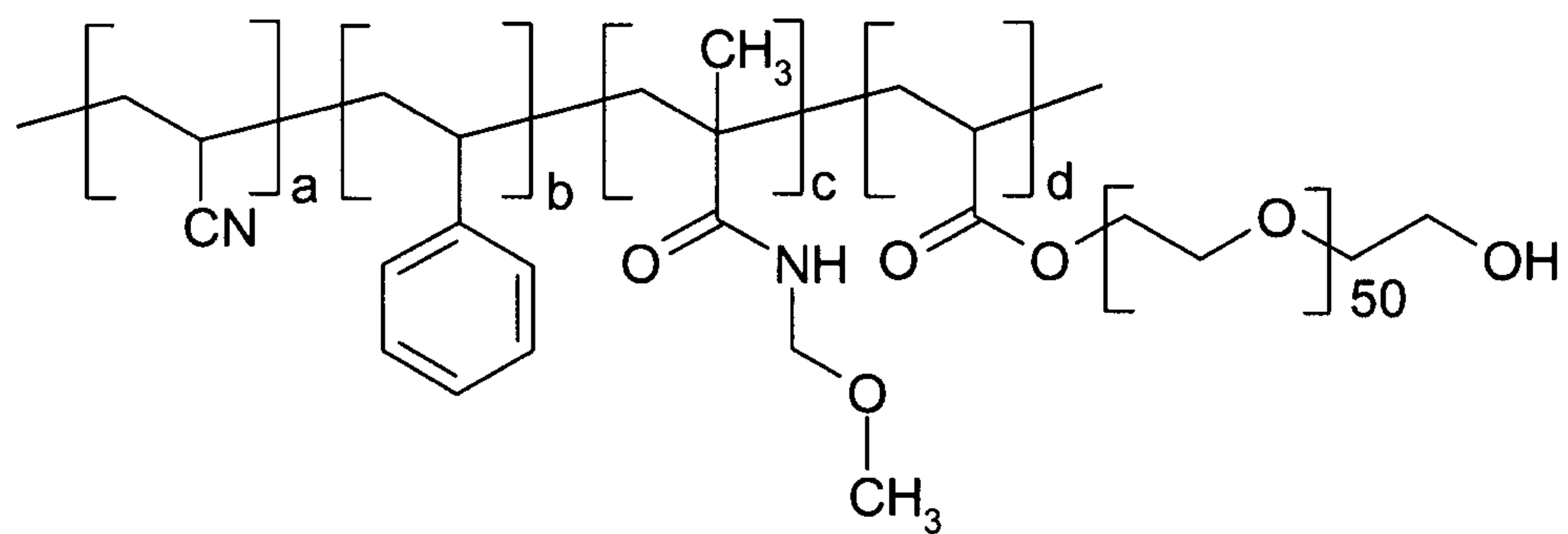


Figure 19

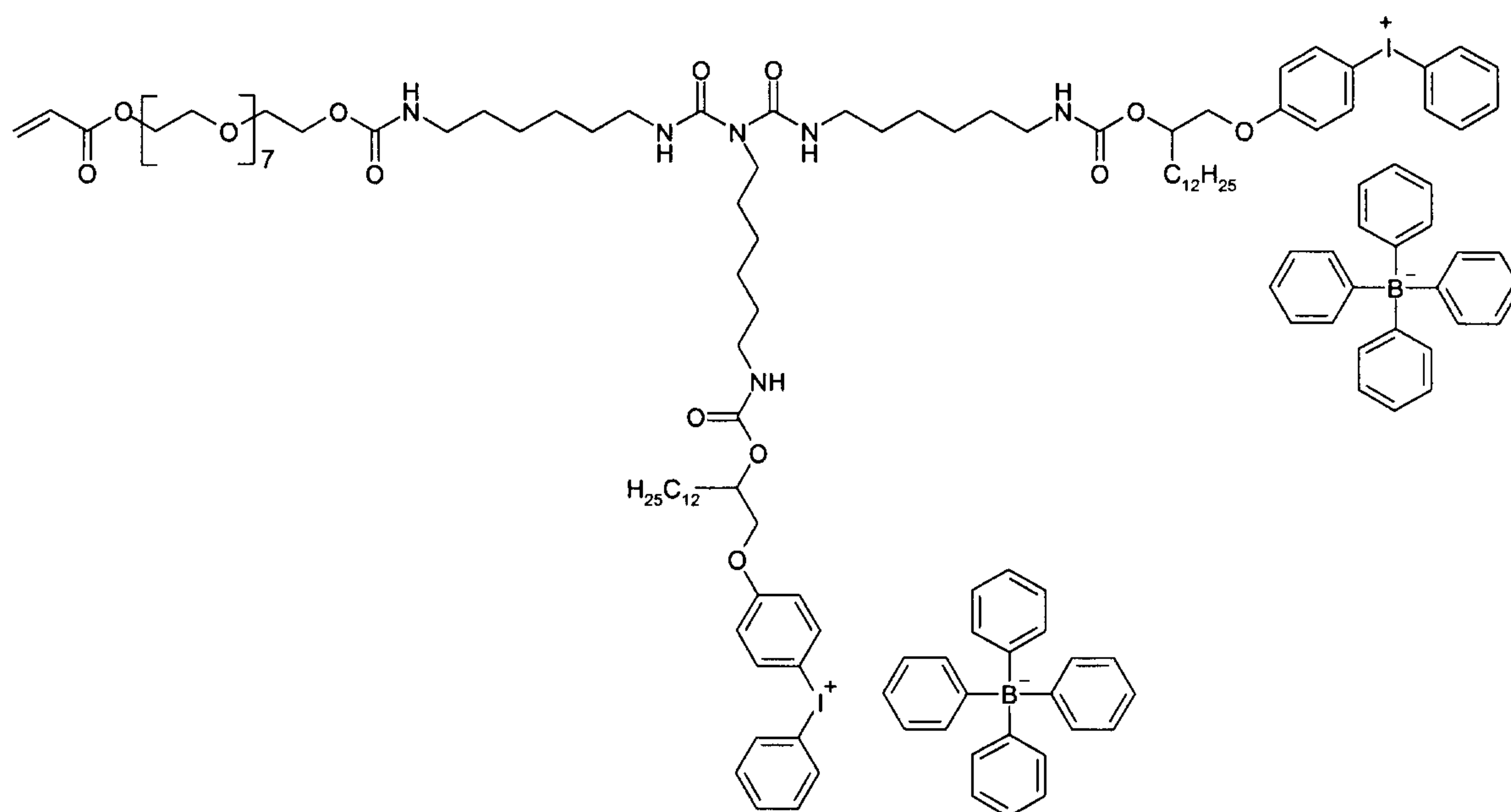


Figure 20

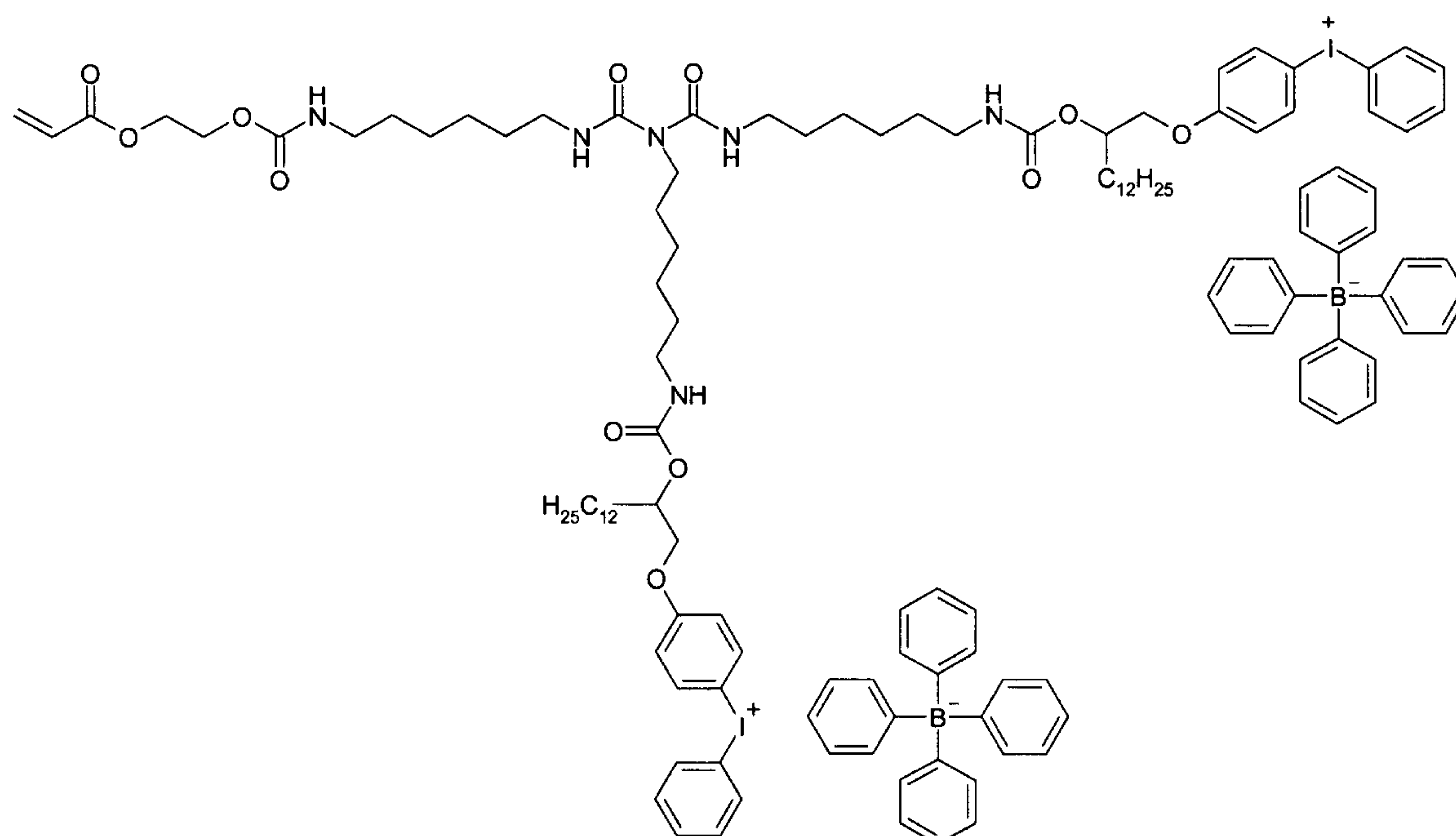


Figure 21

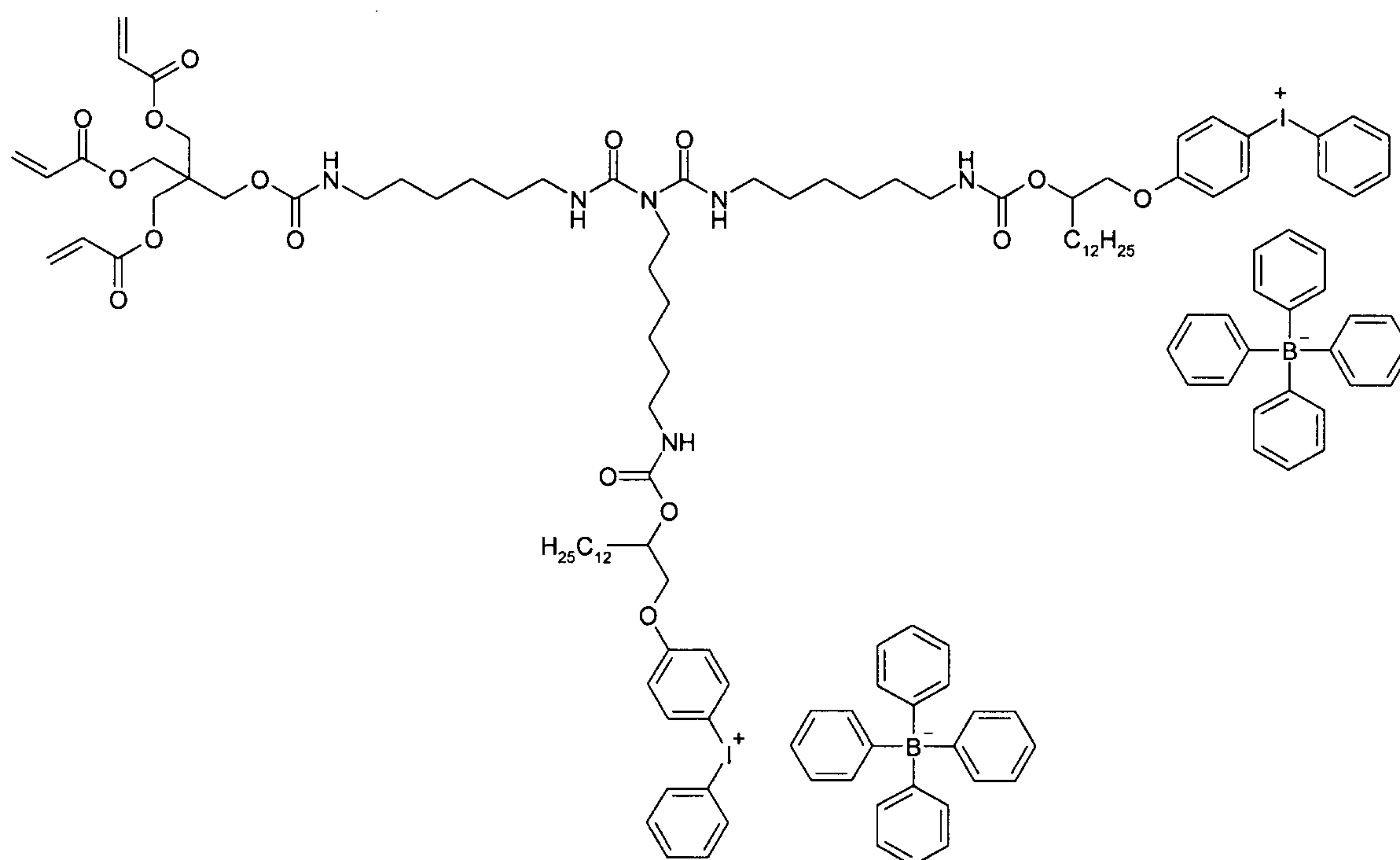


Figure 22

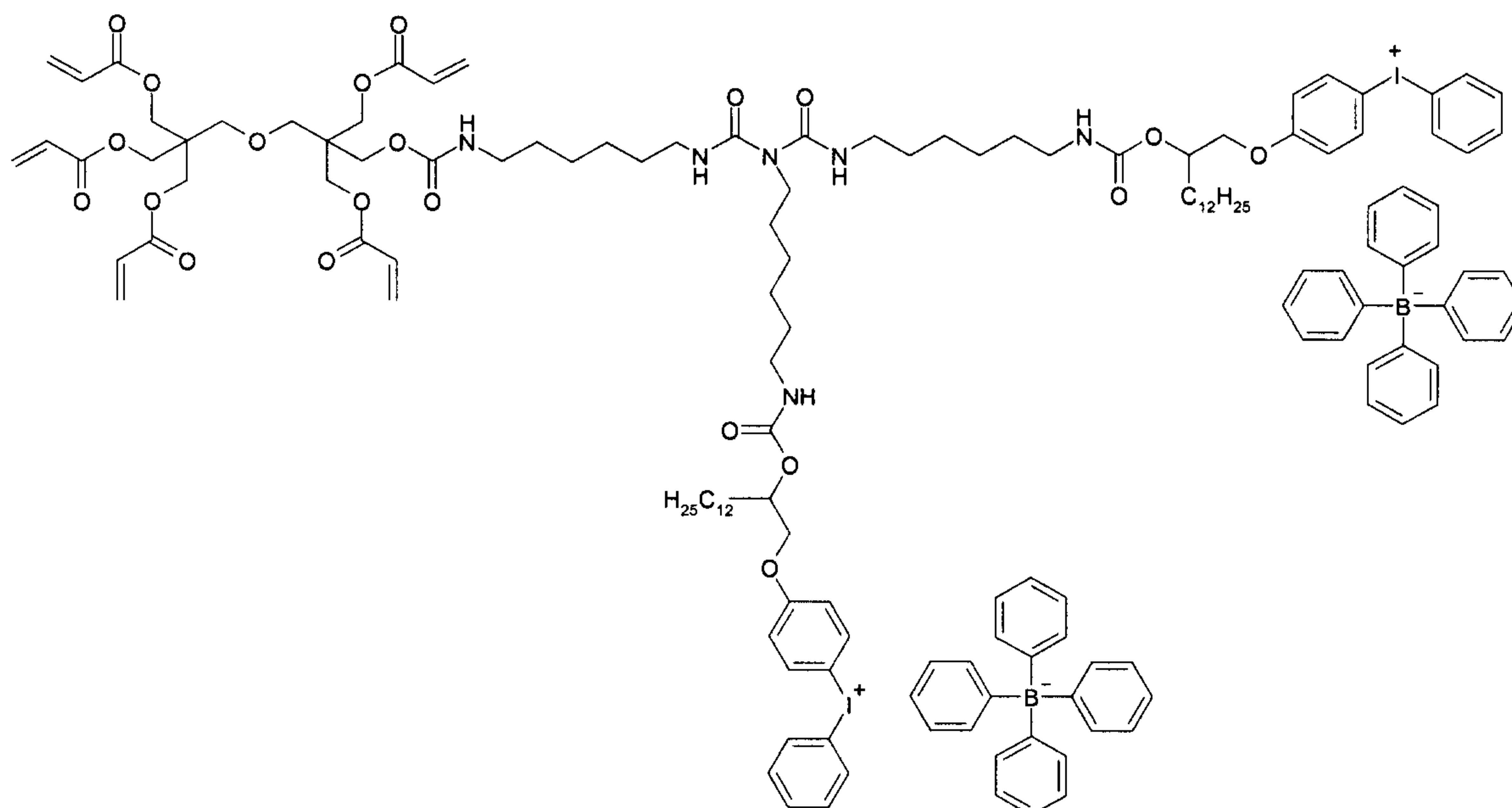


Figure 23

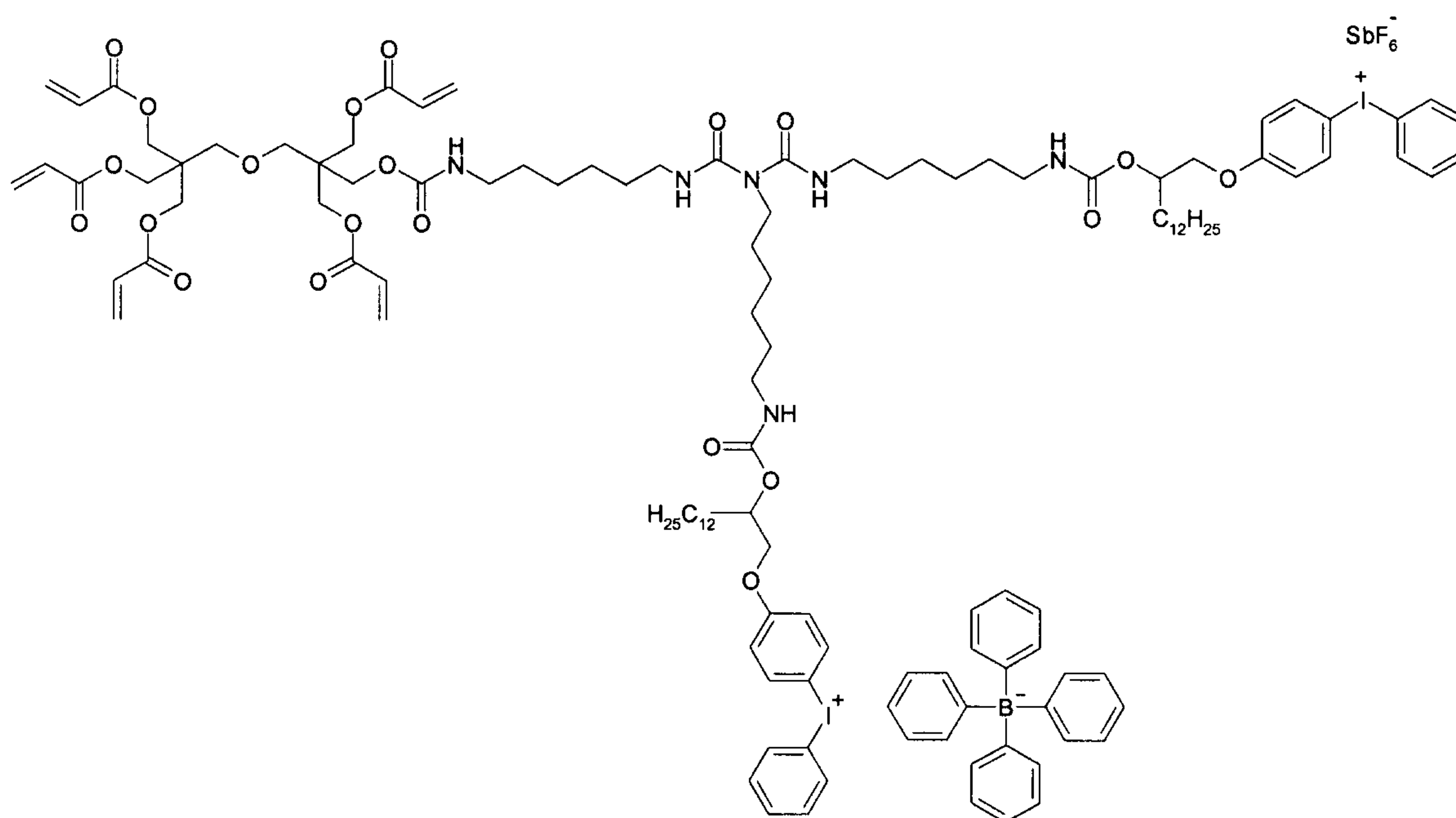


Figure 24

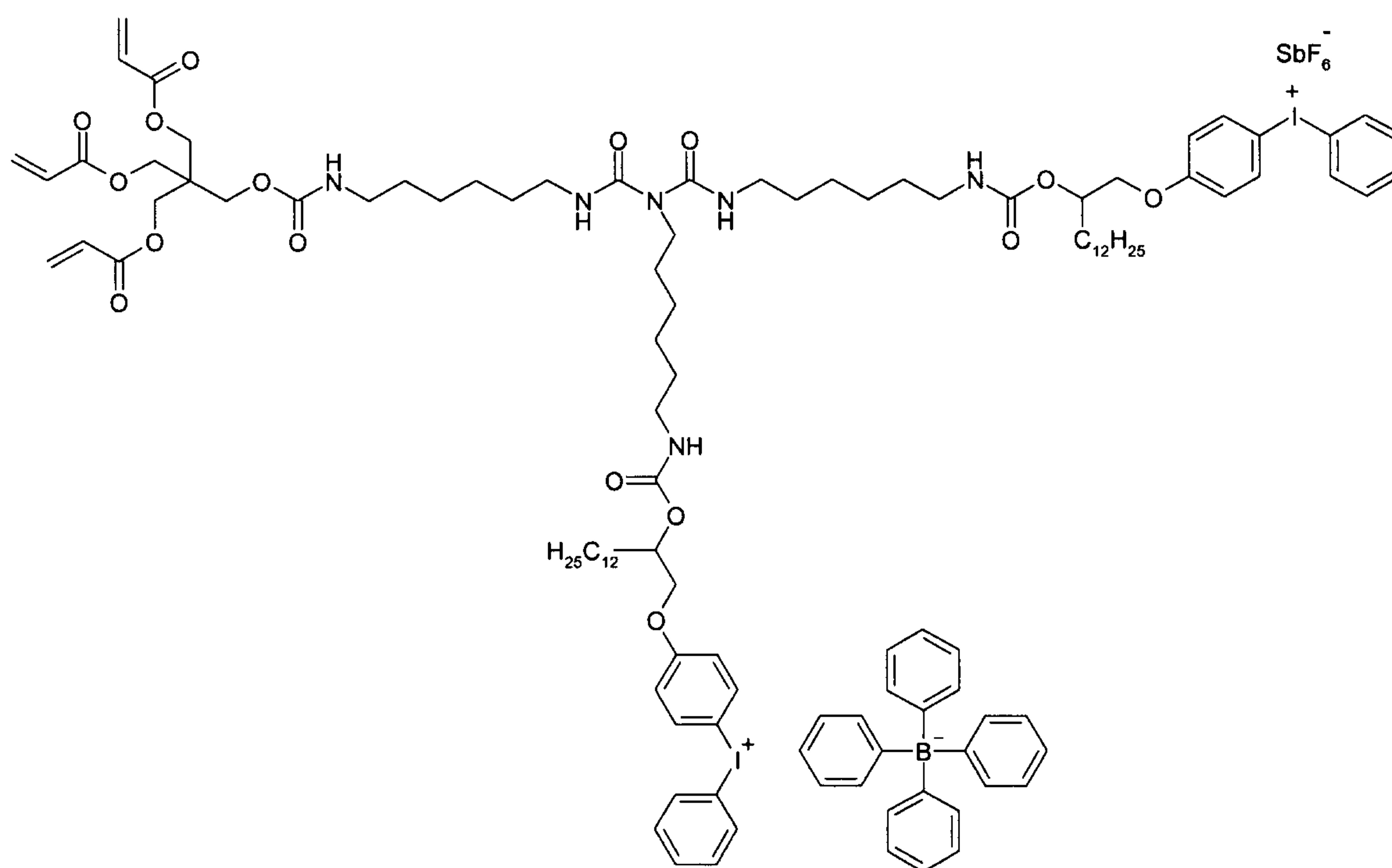


Figure 25

