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Economic Development Canada
Canadian Intellectual Property Office

CA 2960933 C 2021/03/30

(11)(21) **2 960 933**

(12) **BREVET CANADIEN**
CANADIAN PATENT

(13) **C**

(86) Date de dépôt PCT/PCT Filing Date: 2014/09/30
(87) Date publication PCT/PCT Publication Date: 2016/04/07
(45) Date de délivrance/Issue Date: 2021/03/30
(85) Entrée phase nationale/National Entry: 2017/03/10
(86) N° demande PCT/PCT Application No.: FR 2014/052475
(87) N° publication PCT/PCT Publication No.: 2016/051027

(51) Cl.Int./Int.Cl. *C08G 18/32* (2006.01),
C07C 323/12 (2006.01), *C08G 18/67* (2006.01)

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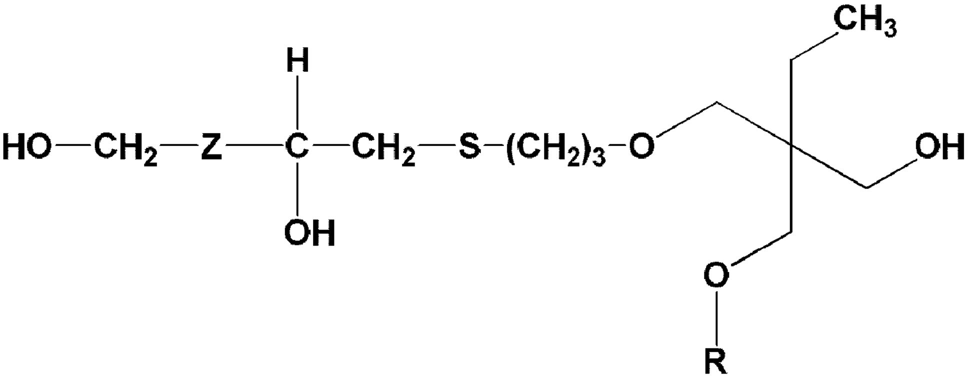
(54) Titre : COMPOSE POLYOL SOUFRE
(54) Title: SULPHUR-CONTAINING POLYOL COMPOUND



(I)

(57) Abrégé/Abstract:
The invention relates to a sulphur-containing polyol compound that can be used in particular as a monomer for the synthesis of polyurethane by polycondensation with a polyisocyanate, said polyol having formula (I) in which: Z represents an optional at-least-divalent linking group which comprises at least one carbon atom and can include a heteroatom; and R represents hydrogen or a hydrocarbon group, saturated or unsaturated, which can include a heteroatom.

(12) DEMANDE INTERNATIONALE PUBLIÉE EN VERTU DU TRAITÉ DE COOPÉRATION EN MATIÈRE DE BREVETS (PCT)

(19) Organisation Mondiale de la Propriété Intellectuelle
Bureau international

(43) Date de la publication internationale
7 avril 2016 (07.04.2016)

(10) Numéro de publication internationale
WO 2016/051027 A1

(51) Classification internationale des brevets :
C07C 323/12 (2006.01) ***C09J 175/04*** (2006.01)
C08G 18/67 (2006.01)

(21) Numéro de la demande internationale :
PCT/FR2014/052475

(22) Date de dépôt international :
30 septembre 2014 (30.09.2014)

(25) Langue de dépôt : français

(26) Langue de publication : français

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(81) États désignés *(sauf indication contraire, pour tout titre de protection nationale disponible)* : AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

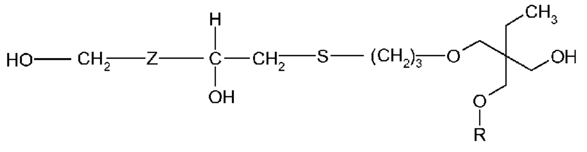
(84) États désignés *(sauf indication contraire, pour tout titre de protection régionale disponible)* : ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), eurasien (AM, AZ, BY, KG, KZ, RU, TJ, TM), européen (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Publiée :
— *avec rapport de recherche internationale (Art. 21(3))*

(54) Title : SULPHUR-CONTAINING POLYOL COMPOUND

(54) Titre : COMPOSÉ POLYOL SOUFRÉ

formule (I) :



(57) Abstract : The invention relates to a sulphur-containing polyol compound that can be used in particular as a monomer for the synthesis of polyurethane by polycondensation with a polyisocyanate, said polyol having formula (I) in which: Z represents an optional at-least-divalent linking group which comprises at least one carbon atom and can include a heteroatom; and R represents hydrogen or a hydrocarbon group, saturated or unsaturated, which can include a heteroatom.

(57) Abrégé : Composé polyol soufré, utilisable notamment comme monomère pour la synthèse d'un polyuréthane par poly condensation avec un polyisocyanate, ledit polyol répondant à la formule (I) : dans laquelle: - Z représente un groupement de liaison optionnel, au moins divalent, comportant au moins un atome de carbone et pouvant comporter un hétéroatome; - R représente l'hydrogène ou un groupe hydrocarboné, saturé ou insaturé, pouvant comporter hétéroatome.

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SULPHUR-CONTAINING POLYOL COMPOUND

1. FIELD OF THE INVENTION

The present invention relates to monomers capable of being used for the synthesis of polymers having urethane units (or polyurethanes), especially intended for adhesive systems for the adhesive bonding of glass or metal to rubber.

It more particularly relates to the above monomers of the sulphur-containing polyol type intended in particular for the synthesis of polyurethanes used in composites of the metal/rubber type for articles made of rubber, such as tyres.

2. PRIOR ART

Composites of the metal/rubber type, in particular for tyres, are well known. They are generally composed of a matrix made of unsaturated rubber, generally diene rubber, which can be crosslinked with sulphur, comprising metal reinforcing elements (or "reinforcers") such as wires, films or cords made of carbon steel.

As they are subjected to very high stresses during the rolling of the tyres, in particular to repeated actions of compression, bending or variation in curvature, these composites must, in a known way, satisfy a large number of sometimes contradictory technical criteria, such as uniformity, flexibility, flexural strength and compressive strength, tensile strength, wear resistance and corrosion resistance, and must maintain this performance at a very high level for as long as possible.

It is easily understood that the adhesive interphase between rubber and reinforcers plays a predominant role in the endurance of this performance. The conventional process for connecting the rubber compositions to carbon steel consists in coating the surface of the steel with brass (copper/zinc alloy), the bonding between the steel and the rubber matrix being provided by sulphurization of the brass during the vulcanization or curing of the rubber. In order to improve the adhesion, use is generally made, in addition, in these rubber compositions, of organic metal salts or metal complexes, such as cobalt salts, as adhesion-promoting additives.

In point of fact, it is known that the adhesion between the carbon steel and the rubber matrix is capable of weakening over time as a result of the gradual development of sulphides formed under the effect of the various stresses encountered, especially mechanical and/or thermal stresses, it being possible for the above decomposition process to be accelerated in the presence of moisture.

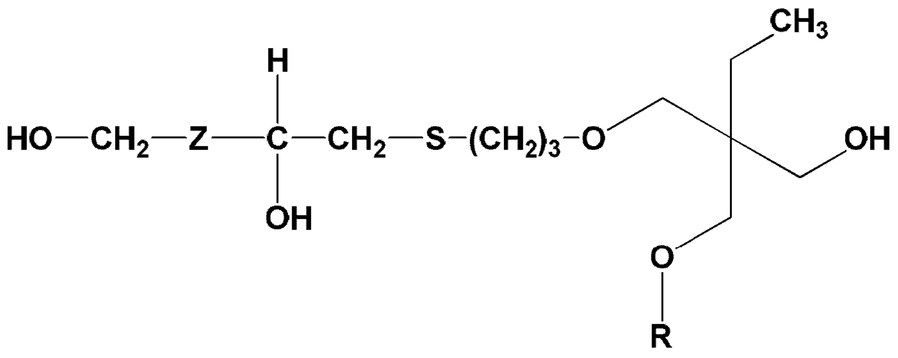
Moreover, the use of cobalt salts renders the rubber compositions more sensitive to oxidation and to ageing, and significantly increases the cost thereof, not to mention that it is desirable to eliminate, in the long run, the use of such cobalt salts in rubber compositions due to recent developments in European regulations relating to metal salts of this type.

For all the reasons set out above, manufacturers of metal/rubber composites, in particular tyre manufacturers, are seeking novel adhesive solutions in order to adhesively bond metal reinforcers to rubber compositions, while overcoming, at least in part, the above-mentioned disadvantages.

3. BRIEF DESCRIPTION OF THE INVENTION

In point of fact, during their research studies, the Applicants have found a novel polyol compound of sulphur-containing type which enables the synthesis of a polyurethane which meets such an objective.

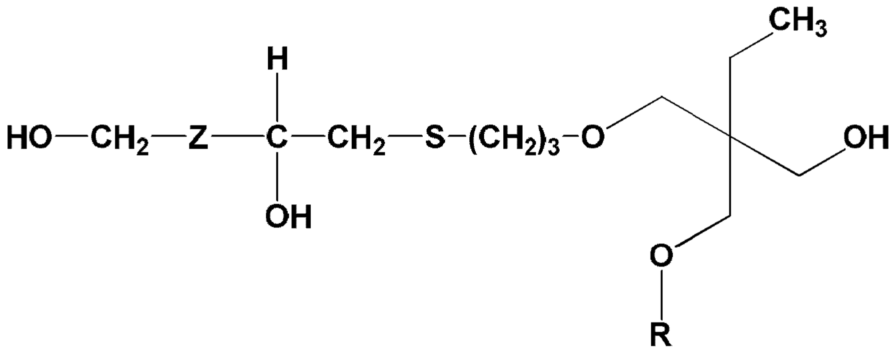
According to the invention, said sulphur-containing polyol compound corresponds to the formula (I) below:



in which:

- Z represents an optional, at least divalent, bonding group, comprising at least one carbon atom and possibly comprising a heteroatom;
- R represents hydrogen or a saturated or unsaturated hydrocarbon group, possibly comprising a heteroatom.

Another embodiment of the invention relates to a sulfur-containing polyol compound, preferably useful for the synthesis of a polyurethane by polycondensation with a polyisocyanate, said compound corresponding to the formula (I):



in which:

- Z represents an optional, at least divalent, bonding group selected from the group consisting of aliphatic groups comprising 1 to 20 carbon atoms, aliphatic groups comprising 1 to 20 carbon atoms and a heteroatom, cycloaliphatic group comprising from 3 to 20 carbon atoms, and cycloaliphatic groups comprising for 3 to 20 carbon atoms and a heteroatom; and
- R represents a hydrogen atom, a saturated hydrocarbon group, a saturated hydrocarbon group comprising a heteroatom, an unsaturated hydrocarbon group, or an unsaturated hydrocarbon group comprising a heteroatom.

By virtue of this sulphur-containing polyol (primary diol) compound in accordance with the invention comprising in particular, in addition to its two primary alcohol functional groups, on the one hand, at least one secondary alcohol functional group and, on the other hand, a thioether functional group in the alpha position with regard to this secondary alcohol functional group, it has proved to be possible to prepare a polyurethane which, used as adhesion primer on metal reinforcers, gives these reinforcers the major and unexpected advantage of being able to adhere to unsaturated rubber matrices by using simple textile adhesives, such as "RFL" (resorcinol-formaldehyde-latex) adhesives, or other equivalent adhesive compositions, or else directly (that is to say, without use of such adhesives) to these unsaturated rubber matrices when the latter comprise, for example, appropriate functionalized unsaturated elastomers, such as, for example, epoxidized elastomers.

The invention also relates to the use of a polyol compound in accordance with the invention in the manufacture of a polyurethane (polymer having urethane units) and also to any polyurethane resulting from at least one polyol compound in accordance with the invention.

The invention also relates to any process for the synthesis of a polyurethane by polycondensation of at least one polyol compound in accordance with the invention with a polyisocyanate compound.

The invention and its advantages will be easily understood in the light of the detailed description and exemplary embodiments which follow, and also of Figures 1 to 5 relating to these examples, which represent or diagrammatically represent:

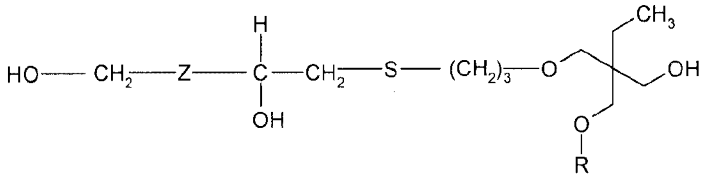
- a possible scheme for the synthesis of a polyol monomer (Monomer M1, also denoted A1 here) in accordance with the invention from two compounds (Compound 1 and Compound 2) (Fig.1);
- a possible scheme for the synthesis of a polyurethane polymer (Polymer P1) according to the invention, from Monomer A1 and from a diisocyanate monomer MDI (Monomer A2) (Fig. 2);
- a ^{1}H NMR spectrum (500 MHz) of Monomer A1 according to the invention and of its starting Compound 1 respectively, both dissolved in $CDCl_3$ (Fig. 3.1 and Fig. 3.2);
- another possible scheme for the synthesis, starting from Monomer A1 according to the invention and another diisocyanate monomer (Monomer A3; benzophenone-blocked MDI), of the same Polymer P1 (Fig. 4);
- a possible scheme for the synthesis, starting from Monomer A1 according to the invention and from two other monomers (A4 and A3), of another polyurethane (Polymer P2) according to the invention (Fig. 5).

4. DETAILED DESCRIPTION OF THE INVENTION

It will be recalled first of all here that a polyurethane is a polymer (by definition any homopolymer or copolymer, especially block copolymer) comprising a plurality of urethane (–O–CO–NH–) bonds resulting, in a known way, from the addition reaction of a polyol having at least two primary alcohol functional groups with a polyisocyanate (compound bearing at least two isocyanate –NCO functional groups), especially with a diisocyanate in the case of a polyurethane of the linear type.

The sulphur-containing polyol (primary diol) compound of the invention, which can be used especially for the synthesis of a polyurethane, thus corresponds to the formula:

(I)



in which:

- Z represents an optional (that is to say present or absent), at least divalent, bonding group, comprising at least one carbon atom and possibly comprising a (at least one) heteroatom;
- R represents hydrogen or a saturated or unsaturated hydrocarbon group, possibly comprising a (at least one) heteroatom.

This sulphur-containing primary diol compound according to the invention thus has the main essential characteristic of comprising a secondary alcohol functional group and a thioether (–S –) functional group in the α position (alpha position, that is to say, as a reminder and by convention, borne by a carbon adjacent to the carbon bearing the secondary alcohol functional group) with respect to this alcohol functional group. Stated otherwise, the polyol compound of the invention has the essential characteristic of comprising an α-hydroxy-thioether unit.

Another essential characteristic of this polyol according to the invention is that one of its two primary diol functional groups is borne by an end group also bearing an -OR group as defined above.

Optional Z is a bonding group, spacing unit, of organic type, preferably hydrocarbon, also commonly referred to as “separator” or “spacer” by those skilled in the art. It may be saturated or unsaturated.

It may be an aliphatic, cycloaliphatic or aromatic, substituted or unsubstituted hydrocarbon group, the aliphatic group preferably comprising 1 to 30 (more preferentially 1 to 20) carbon atoms, the cycloaliphatic group preferably comprising from 3 to 30 (more preferentially 3 to

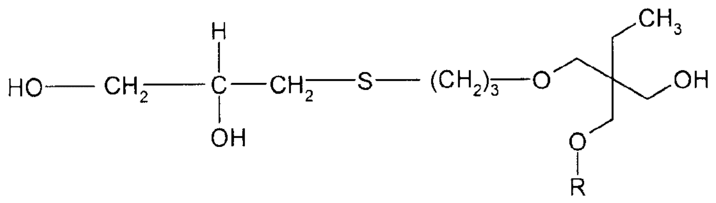
20) carbon atoms, the aromatic group comprising from 6 to 30 (more preferentially 6 to 20) carbon atoms.

Z more particularly represents an aliphatic bonding group having 1 to 20 atoms, more preferentially 1 to 12 carbon atoms, or a cycloaliphatic bonding group having 3 to 20 carbon atoms, more preferentially 3 to 12 carbon atoms. More particularly still, it is a C_1-C_{10}, especially C_1-C_5 alkylene.

Hydrocarbon Z may comprise at least one (that is to say one or more) heteroatom preferably selected from O, S, N or P, especially in the form of an ether (-O-) or thioether (-S-) bond, the latter possibly being present on the carbon chain (Z) itself or on a substituent of one of its carbon atoms.

According to another particular embodiment of the invention, Z is not present in formula (I), that is to say that the primary diol compound of the invention corresponds in this case to formula (II) below:

(II)



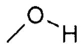
R thus represents hydrogen or an ethylenically saturated or unsaturated hydrocarbon group, possibly comprising at least one (that is to say one or more) heteroatom, such as, preferably, O, S, N or P.

R preferably represents hydrogen, an unsaturated hydrocarbon group or a saturated hydrocarbon group selected from C_1-C_{18} alkyls, C_5-C_{18} cycloalkyls and C_6-C_{18} aryls, the latter being more preferentially selected from C_1-C_6 alkyls, cyclohexyl and phenyl, in particular from C_1-C_4 alkyls, more particularly methyl or ethyl, all these groups possibly comprising at least one (that is to say one or more) heteroatom, such as, preferably, O, S, N or P.

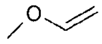
More preferentially still, R is hydrogen or an unsaturated hydrocarbon group, possibly comprising at least one (that is to say one or more) heteroatom, such as, preferably, O, S, N or P.

The unsaturated hydrocarbon group may be aliphatic, cycloaliphatic or aromatic. This unsaturated group, if it is aliphatic, preferably comprises 1 to 20, more preferentially 1 to 10, carbon atoms; if it is cycloaliphatic, it preferably comprises 3 to 30, more preferentially 3 to 20, carbon atoms; if it is aromatic, it preferably comprises from 6 to 30 carbon atoms, more preferentially 6 to 20 carbon atoms.

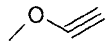
By way of examples of preferential -OR groups, mention may especially be made of the following groups:



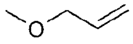
hydroxy



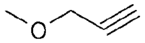
vinyloxy



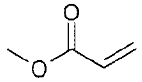
ethynyloxy



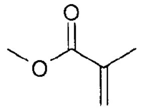
allyloxy



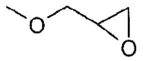
propynyloxy



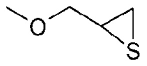
acryloyloxy



methacryloyloxy



2,3-epoxypropyloxy



2,3-thiiranepropyloxy

The formula of an example of (aliphatic) sulphur-containing polyol compound in accordance with the invention, denoted Monomer M1, has been represented in structural form, and also a synthesis scheme which can be used to obtain this compound has been represented, in the appended Figure 1.

This polyol compound (Monomer M1, subsequently also denoted Monomer A1) of Figure 1 is 3-[3-(2-allyloxymethyl-2-(hydroxymethyl)butoxy)propylsulphanyl]propane-1,2-diol. It can be obtained, for example, by reaction of trimethylolpropane diallyl ether and thioglycerol, as represented diagrammatically in Figure 1; this synthesis will be described in more detail in the exemplary embodiments which follow (Test 1 of section 5.1).

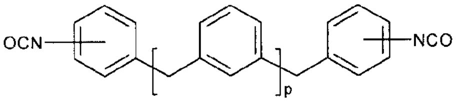
This sulphur-containing polyol compound of Figure 1 does indeed correspond to formulae (I) and (II) in which, for this example, optional Z is not present and R represents an allyloxy group.

The sulphur-containing polyol compound in accordance with the invention described above can be used for the synthesis of a polyurethane of the linear type, thus resulting essentially from the addition of this primary diol polyol and of a diisocyanate compound. The diisocyanate which can be used may be aromatic, aliphatic or cycloaliphatic; it may be a monomer, a prepolymer or a quasi-prepolymer, indeed even a polymer.

According to a preferential embodiment, the diisocyanate from which the polymer of the invention results is selected from the group consisting of the following aromatic compounds: diphenylmethane diisocyanate (abbreviated to "MDI"), toluene diisocyanate ("TDI"), naphthalene diisocyanate ("NDI"), 3,3'-bitoluene diisocyanate ("TODI"), para-phenylene diisocyanate ("PPDI"), their various isomers and the mixtures of these compounds and/or isomers.

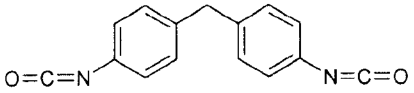
More preferentially, use is made of an MDI or a TDI, more preferentially still of an MDI.

All the isomers of MDI (in particular 2,2'-MDI, 2,4'-MDI and 4,4'-MDI) and their mixtures can be used, as well as what are referred to as polymeric MDIs (or "PMDIs") comprising oligomers of following formula (with p equal to or greater than 1):



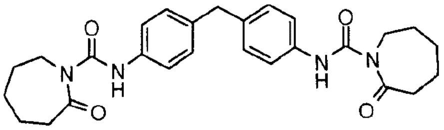
Diisocyanate compounds of the aliphatic type can also be used, such as, for example, 1,4-tetramethylene diisocyanate, 1,6-hexane diisocyanate ("HDI"), 1,4-bis(isocyanatomethyl)cyclohexane, 1,3-bis(isocyanatomethyl)cyclohexane, 1,3-bis(isocyanatomethyl)benzene, 1,4-bis(isocyanatomethyl)benzene, isophorone diisocyanate ("IPDI"), bis(4-isocyanatocyclohexyl)methane diisocyanate ("H12MDI") or 4,4'-dicyclohexylmethane diisocyanate ("H13MDI").

According to a particularly preferential embodiment, the diisocyanate used is 4,4'-MDI (4,4'-diphenylmethane diisocyanate), having the formula:

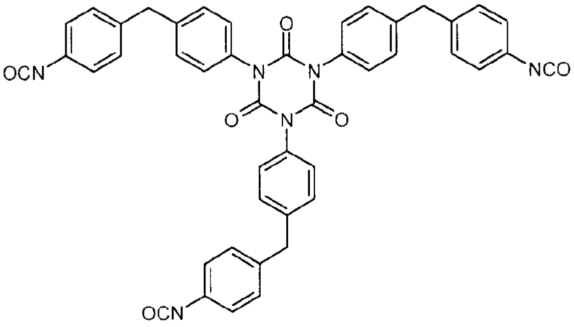


or, if several diisocyanates are used, constitutes the predominant diisocyanate by weight, preferably representing, in the latter case, more than 50% of the total weight of the diisocyanate compounds.

Use may also advantageously be made of a caprolactam-blocked 4,4'-MDI (for example the product in the solid form "Grilbond" IL-6 from EMS), of formula:

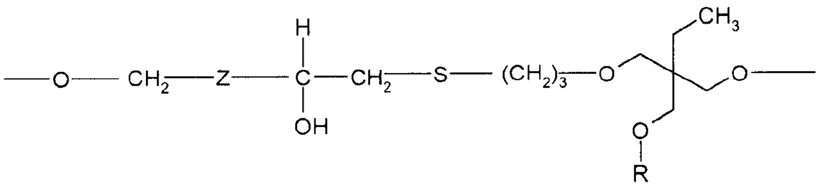


As the invention is not, however, limited to a polymer of the linear type (as a reminder, resulting from a diisocyanate), it will also be possible to use, especially with the aim of increasing the Tg of the polymer of the invention by formation of a three-dimensional network, a triisocyanate compound, such as, for example, an MDI trimer having a triazine nucleus of the following formula:



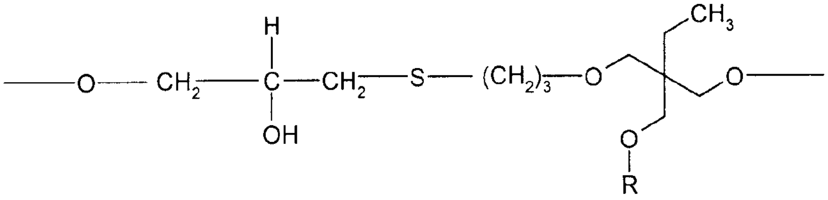
The polyurethane resulting from the polyol compound of the invention thus has the characteristic of comprising, in addition to its repeat base structural units having urethane (–O–CO–NH–) units contributed in a well-known way by the starting polyisocyanate compound, specific repeat additional units contributed by the polyol monomer according to the invention, these additional units comprising at least one unit of formula:

(III)



or, when optional Z is absent, of the following formula (IV):

(IV)



in which formulae Z and R have, of course, the main and preferential definitions given above.

Figures 2, 4 and 5 represent in detail preferential examples of polyurethanes resulting from polyols in accordance with the invention and also various possible schemes for the synthesis of these polyurethanes from polyols in accordance with the invention.

First of all, Figures 1 and 2 respectively illustrate possible processes for the synthesis of a polyol monomer in accordance with the invention (denoted Monomer A1) and then of a polymer (denoted Polymer P1) according to the invention of the polyurethane type starting from this Monomer A1 and from a diisocyanate monomer MDI (Monomer A2), which processes will be described in detail subsequently.

This example of Polymer P1 does indeed comprise a repeat unit of formula (V):

$$-O-C(O)-NH-Z'-NH-C(O)-O-A-$$

as defined above, in which Z' corresponds more particularly to the MDI residue divalent group and "A" corresponds to the formula (IV) above.

It is clearly visible in Figure 2 that, in accordance with the invention, the Polymer P1 contains, in addition to its urethane base units, additional repeat units comprising, on the one hand, an α-hydroxy-thioether ($-CH(OH)-CH_2-S-$) functional group, and on the other hand an -OR group with ethylenic unsaturation (here, an allyloxy functional group $-O-CH_2-CH=CH_2$).

Figure 4 illustrates another possible process for the synthesis of this same Polymer P1 according to the invention, this time starting from the preceding Monomer A1 and from another diisocyanate monomer (Monomer A3, caprolactam-blocked MDI), which process will be described in detail subsequently.

Figure 5 illustrates another process for the synthesis of another polymer (Polymer P2) in accordance with the invention starting from Monomer A1, Monomer A3 and another polyol monomer (not in accordance with the invention, Monomer A4), which process will be described in detail subsequently.

It is clearly visible in Figure 5 that, in accordance with the invention, the Polymer P2 comprises, in addition to its urethane base units (–O–CO–NH–), additional repeat units of general formula (II) having, on the one hand, a thioether (– S –) functional group in the α position relative to a secondary alcohol functional group (– CH(OH) –), and, on the other hand, an -OR group with ethylenic unsaturation (here, an allyloxy functional group – O – $CH_2 - CH = CH_2$).

The polyurethane which can be synthesized starting from a sulphur-containing polyol compound in accordance with the invention may comprise from ten to several hundred, preferably from 20 to 200, structural repeat units as described above. Its glass transition temperature Tg, measured by DSC (*Differential Scanning Calorimetry*), for example according to Standard ASTM D3418, is preferably greater than 50°C, more preferentially greater than 100°C, in particular between 130°C and 250°C.

By virtue of the primary diol compound of the invention, this polyurethane exhibits a high flexibility and a high elongation at break and has furthermore displayed effective hydrophobic properties and corrosion-resistance properties.

It can advantageously be used as hydrophobic coating on any type of substrate, especially made of metal or glass, or else as adhesion primer on any type of metal reinforcer, such as, for example, a thread, a film, a plate or a cord made of carbon steel coated or not coated with brass, intended in particular to reinforce an unsaturated rubber matrix, such as natural rubber.

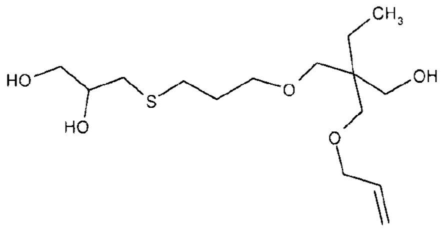
5. EXEMPLARY EMBODIMENTS OF THE INVENTION

In the present application, unless expressly indicated otherwise, all the percentages (%) shown are percentages by weight.

Test 1 - Synthesis of the Monomer A1

The monomer A1 (or M1) is 3-[3-(2-allyloxymethyl-2-(hydroxymethyl)-butoxy)propylsulphanyl]propane-1,2-diol, in accordance with the invention. This monomer was synthesized according to the procedure represented diagrammatically in Figure 1, as described in detail hereinafter: 4.76 g of Compound 1 (90% pure trimethylolpropane diallyl ether, from Sigma Aldrich), then 2.16 g of Compound 2 (thioglycerol) were placed in a 50 ml glass round-bottomed flask provided with a magnetic stirrer, the mixture being covered with a glass stopper to avoid any losses by evaporation; the reaction mixture was stirred at room temperature (20°C) for 4 hours, then overnight (around 12 hours) at a temperature of 80°C.

A transparent, viscous liquid is obtained in this way, the NMR spectrum of which (reproduced in Fig. 3.1), compared to the NMR spectrum of starting Compound 1 (reproduced in Fig. 3.2), taking as reference the transition of the methyl group at 0.86 ppm (3 protons) and following the reduction in the integrals corresponding to the protons of the vinyloxy group, does indeed confirm to those skilled in the art that it is Monomer A1, of formula:



The ^1H NMR analysis (500 MHz, $CDCl_3$) (Fig. 5.1) of the product gave the following results: *0.85 (m, 3H), 1.39 (m, 2H), 11.86 (m, 1H), 2.65 (m, 3H), 3.46 (m, 8 H), 3.73-3.75 (s, 2H), 3.98 (d, 2H), 5.16-5.19 (d, 1H), 5.28 (d, 1H), 5.88 (m, 1H).*

Finally, the molecular weight of the product, as measured by "ESI" (*Electrospray Ionization*) mass spectrometry in a 1/1 water/acetonitrile mixture (with traces of NaCl), was evaluated in negative mode ($[M + Cl]^-$ anion) at 357.3 (calculated theoretical value equal to 357.5) and in positive mode ($[M + Na]^+$ cation) at 345.2 (calculated theoretical value equal to 345.5).

5.2. Test 2- Synthesis of Polymer P1 by reacting Monomers A1 and A2

This test gives a detailed description of the synthesis of Polymer P1 according to the invention starting from Monomers A1 and A2, according to the procedure represented diagrammatically in Figure 2.

3.40 g of Monomer A1 were placed into a dry 50 ml round-bottomed flask then, as polymerization catalyst, 18.1 mg (0.3% by weight) of bismuth neodecanoate and 100 ml of γ-butyrolactone solvent, all under an inert atmosphere (nitrogen stream). A solution (itself under an inert atmosphere) of 2.64 g of Monomer A2 (solid MDI dissolved in 20 ml γ-butyrolactone) was then added into the 50 ml round-bottomed flask by means of a dropping funnel. The transparent reaction mixture was stirred and heated at 80°C for 4 hours.

3 ml of the solution of Polymer P1 thus obtained was then deposited on a glass sheet (10 x 10 cm); the glass sheet was placed under vacuum at 80°C for 1 hour until the solvent (γ-butyrolactone) had evaporated. The transparent film of Polymer P1 thus obtained was analysed by "ATR-FTIR" (*Attenuated Total Reflection InfraRed*) spectroscopy: the synthesis of a polyurethane is indeed confirmed by the appearance of the peak visible at 1700 cm^{-1}, characteristic of the -OCONH- bond.

Incidentally, it was noted that Polymer P1 thus obtained exhibited excellent adhesion to the glass (impossibility of separating by pulling the polymer from the glass).

In order to measure its molecular weight, the polymer dissolved in a mixture (1:20) of γ-butyrolactone and THF (tetrahydrofuran) was then subjected to GPC (*Gel Permeation Chromatography*) analysis (C18 column-reversed phase and THF as mobile phase): a molecular weight (Mw) of approximately 140 000 was thus determined (polystyrene controls with molecular weight between 500 and 500 000). The same synthesis without polymerization catalyst led to a very broad elution profile with a predominant distribution centred at around 17 000.

Finally, the same synthesis carried out with 1% by weight of catalyst and in DTP solvent (1,3-dimethyl-3,4,5,6-tetrahydro-2(*1H*-pyrimidinone – CAS 7226-23-5) led to a Tg value equal to approximately 93°C (DSC from -80°C to 200°C (10°C/min), 2nd pass).

5.3. Test 3- Synthesis of Polymer P1 by reacting Monomers A1 and A3

Polymer P1 in accordance with the invention was also synthesized from monomers A1 and A3 (caprolactam-blocked MDI) according to the simple procedure represented diagrammatically in Figure 4.

226.4 mg of Monomer A1 and 334.6 mg of Monomer A3 ("Grilbond" IL-6) were placed in a glass container, then 8 ml of γ-butyrolactone solvent were added and the mixture was heated under a stream of hot air (120°C) until a clear solution was obtained.

3 ml of this solution were then deposited uniformly on a glass sheet (10 x 10 cm) and everything was then placed in an oven at 190°C for 15 min under vacuum so as to eliminate any traces of solvent. The transparent film of Polymer P1 thus obtained was characterized as above (ATR-FTIR) and gave virtually the same infrared spectrum. DSC analysis (second pass) from -80°C to 200°C (10°C/min) gave a Tg equal to approximately 120°C.

5.4. Test 4 - Test of adhesion of Polymer 1 in a metal/rubber composite

In this test, a new sample of Polymer P1 according to the invention was synthesized as indicated in the preceding test, the γ-butyrolactone solvent being simply replaced with DTP.

A thin film of Polymer P1 thus obtained was deposited (at room temperature) uniformly on the surface of a brass sheet. Everything was then covered with a layer of conventional textile adhesive of the RFL type (resorcinol-formaldehyde-latex). After a 5 min pre-drying operation at 100°C, everything was then treated for 10 min in the oven at 190°C.

The brass sheet thus coated with the film of Polymer P1 and coated with RFL adhesive was subsequently placed in a matrix of conventional rubber composition (in the raw, non-vulcanized state) for a belt reinforcement of a passenger vehicle tyre, based on natural rubber, on carbon black and silica as filler and on a vulcanization system (sulphur and sulphenamide accelerator), this composition being devoid of cobalt salt.

The metal/rubber composite test specimen thus prepared was then placed under a press and everything was cured (vulcanized) at 165°C for 30 min under a pressure of 20 bar. After vulcanization of the rubber, excellent adhesive bonding between the rubber matrix and the metal sheet was obtained, despite the absence of cobalt salt in the rubber matrix; this is because, during peel tests carried out both at room temperature (23°C) and at high temperature (100°C), it was found that the failure occurred systematically in the rubber matrix itself and not at the interphase between metal and rubber.

5.5. Test 5- Synthesis of Polymer P2 by reacting Monomers A1, A3 and A4

This test describes the synthesis of Polymer P3 in accordance with the invention starting from Monomers A1, A3 and A4, according to the procedure represented diagrammatically in Figure 5.

1.34 g of Monomer A1, 0.61 g of Monomer A5 (BHBA, 2,2-bis(hydroxymethyl)propionic acid) then 7.90 g of Monomer A3 (caprolactam-blocked MDI "Grilbond" IL-6 50%-F) were added successively into a glass flask. The suspension was stirred by mechanical vibration (vortex device) while gently increasing the temperature to approximately 50°C (stream of hot air). 2.3 g of the suspension obtained were then distributed homogeneously on a (10 x 10 cm) glass sheet which was then treated in an oven for 10 min at 190°C until a yellow-coloured clear film was obtained; 10 additional minutes of treatment were carried out under vacuum so as to eliminate the gaseous components (i.e. total treatment time of 20 min at 190°C). A thin yellow film of Polymer P2 according to the invention was thus obtained, which film adheres very well to the glass (impossibility of separating by pulling the polymer from the glass).

150 mg of the above suspension were also placed on a brass sheet (3 x 3 cm) and treatment was subsequently carried out in an oven at 190°C for 10 min and then for an additional 10 min under vacuum (i.e., a total treatment at 190°C of 20 min); excellent adhesion of the polymer according to the invention to the metal could also be confirmed, with impossibility of separating by pulling the polymer from the brass sheet.

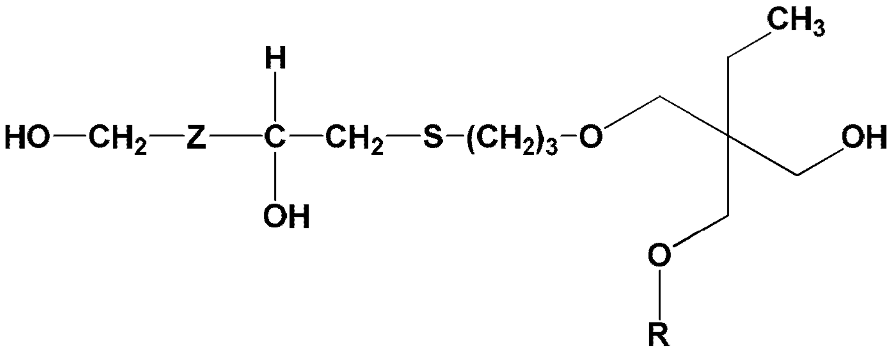
In conclusion, the sulphur-containing polyol compounds of the invention make it possible to synthesize polyurethanes which are characterized by a high glass transition temperature, a high thermal and chemical stability and excellent adhesion to glass or metal.

By virtue of these compounds of the invention, these polyurethanes, used as adhesion primer on metal in metal/rubber composites, make it possible very advantageously to subsequently adhesively bond the metal to the rubber matrices, for example using simple textile adhesives, such as "RFL" (resorcinol-formaldehyde-latex) adhesives or other equivalent adhesive compositions, or else directly (that is to say, without use of such adhesives) to these rubber matrices, for example when these rubber matrices comprise, in particular, appropriate functionalized unsaturated elastomers, such as epoxidized elastomers.

Thus, cobalt salts (or other metal salts) can especially be dispensed with in the rubber compositions intended to be attached to brass-coated metal reinforcers.

CLAIMS

1. A sulfur-containing polyol compound, said compound corresponding to the formula (I):



in which:

- Z represents an optional, at least divalent, bonding group selected from the group consisting of aliphatic groups comprising 1 to 20 carbon atoms, aliphatic groups comprising 1 to 20 carbon atoms and a heteroatom, cycloaliphatic groups comprising from 3 to 20 carbon atoms, and cycloaliphatic groups comprising for 3 to 20 carbon atoms and a heteroatom; and
- R represents a hydrogen atom, a saturated hydrocarbon group, a saturated hydrocarbon group comprising a heteroatom, an unsaturated hydrocarbon group, or an unsaturated hydrocarbon group comprising a heteroatom.

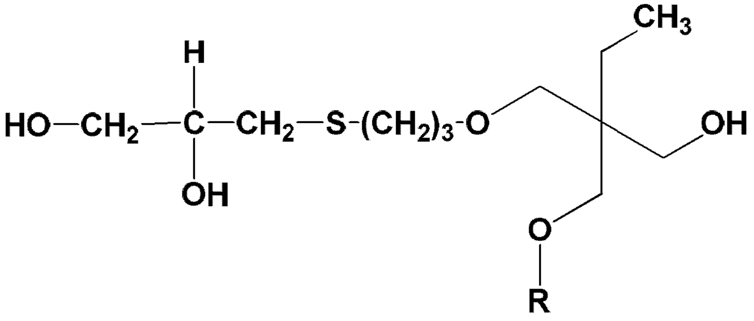
2. The compound according to claim 1, wherein Z represents an aliphatic group comprising from 1 to 12 carbon atoms.

3. The compound according to claim 1, wherein Z represents a cycloaliphatic group comprising from 3 to 12, carbon atoms.

4. The compound according to claim 1, wherein Z represents a C_1-C_{10} alkylene group.

5. The compound according to claim 1, wherein Z represents a C_1-C_5 alkylene group.

6. The compound according to claim 1, wherein said compound corresponds to the formula (II):

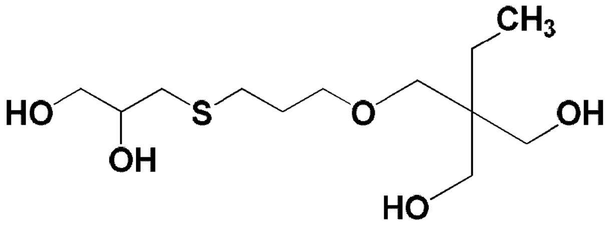


wherein R is as defined in claim 1.

7. The compound according to any one of claims 1 to 6, wherein R is selected from the group consisting of hydrogen, C_1-C_{18} alkyls, C_5-C_{18} cycloalkyls and C_6-C_{18} aryls.

8. The compound according to claim 7, wherein R is selected from the group consisting of C_1-C_6 alkyls, cyclohexyl and phenyl.

9. The compound according to claim 6, wherein said compound corresponds to the formula:



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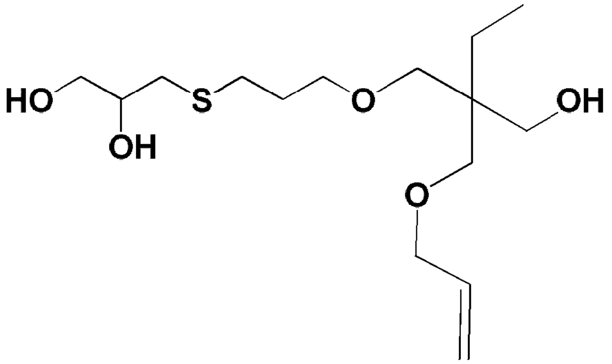
10. The compound according to claim 6, wherein said compound corresponds to the formula:



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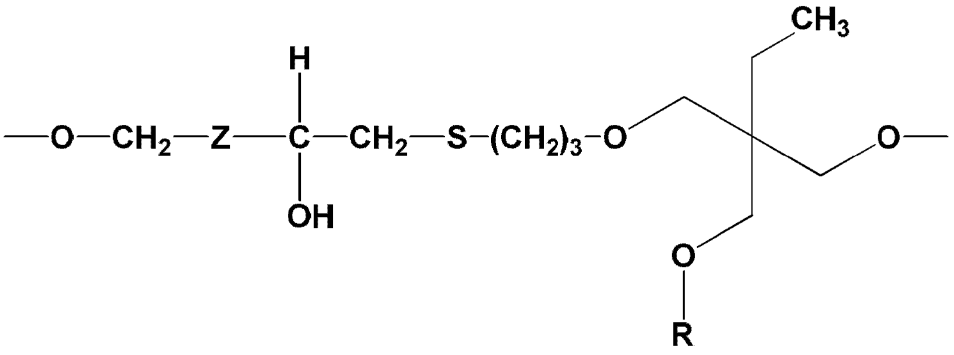
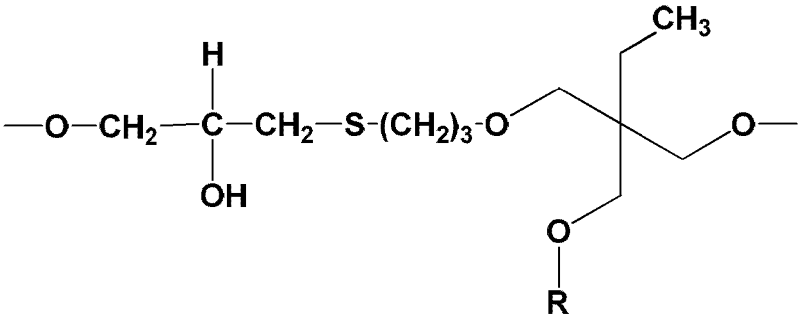
11. The compound according to any one of claims 1 to 10, said compound being useful for the synthesis of a polyurethane by polycondensation with a polyisocyanate.

12. A polymer having urethane units, resulting from at least one sulphur-containing polyol compound as defined in any one of claims 1 to 11, wherein said polymer comprises at least repeat units comprising at least one unit of formula:



wherein Z and R are as defined in any one of claims 1 to 11.

13. The polymer according to claim 12, resulting from at least one sulphur-containing polyol compound as defined in claim 6, wherein the at least repeat units comprises at least one unit the formula:

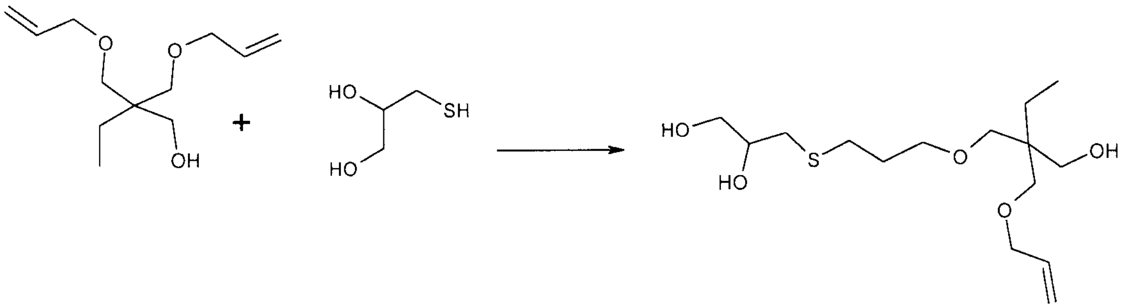


wherein R is as defined in claim 6.

14. A process for the synthesis of a polymer having urethane units by polycondensation of at least one sulphur-containing polyol compound as defined in any one of claims 1 to 11 with a polyisocyanate compound.

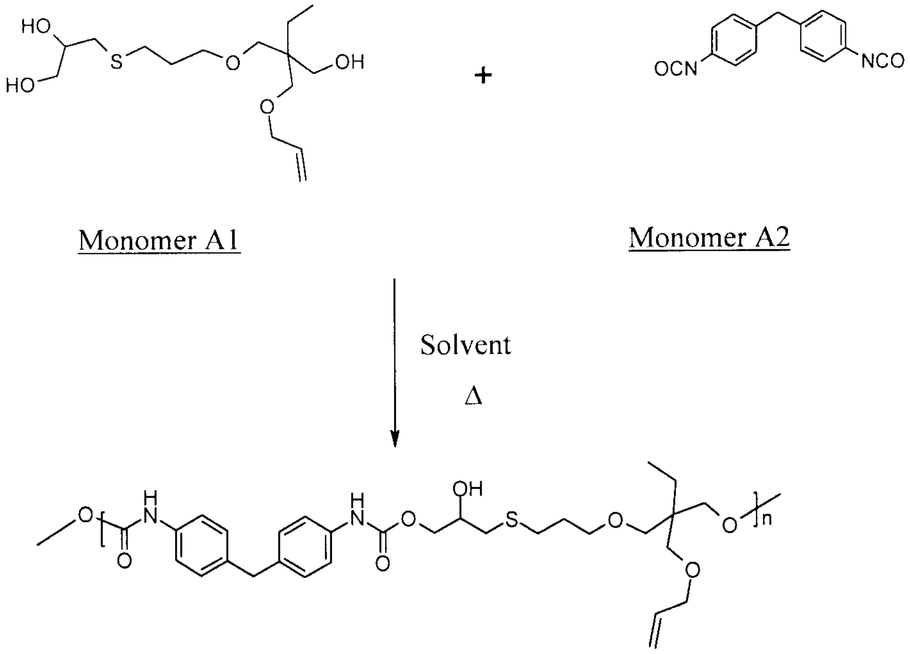
15. Use of the sulphur-containing polyol compound as defined in any one of claims 1 to 11 in the manufacture of a polymer having urethane units.

Fig. 1



Compound 1 Compound 2 Monomer A1 (or M1)

Fig. 2



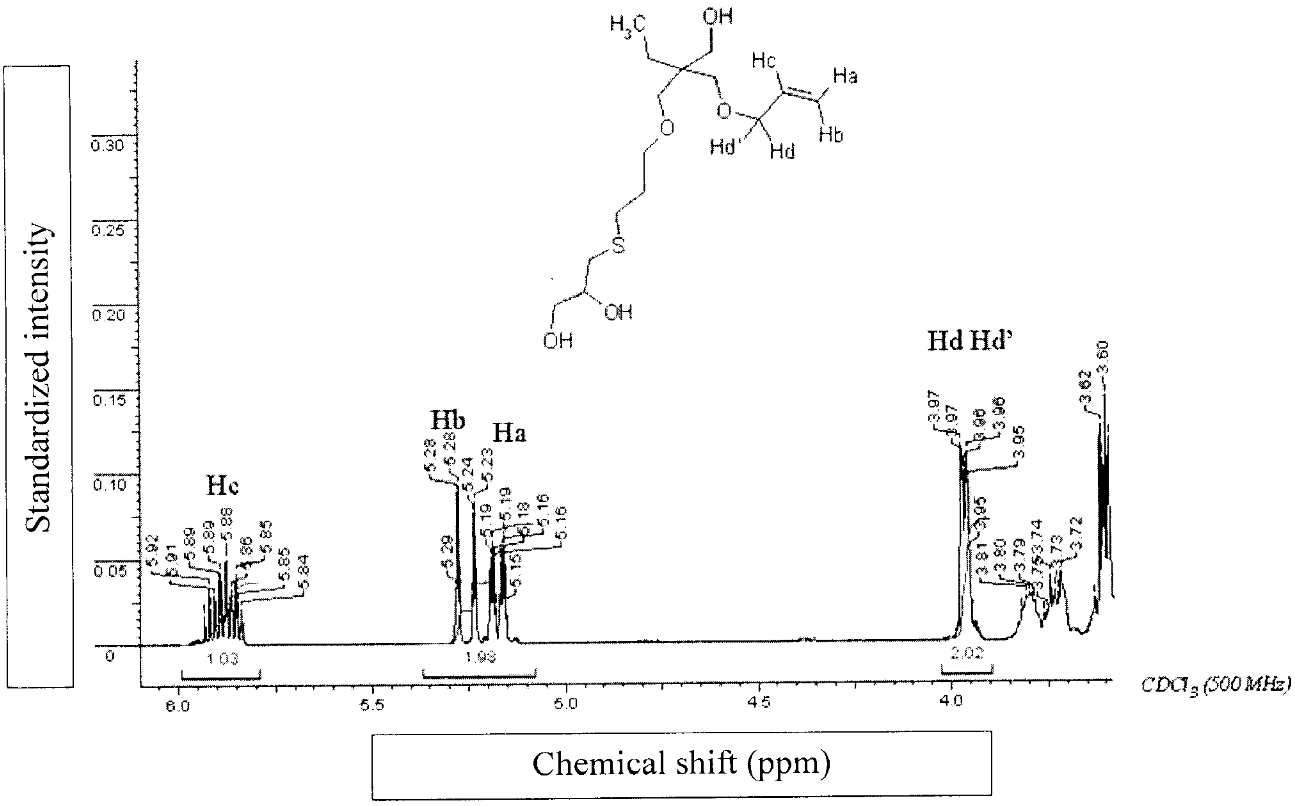
Monomer A1 Monomer A2

Solvent

Δ

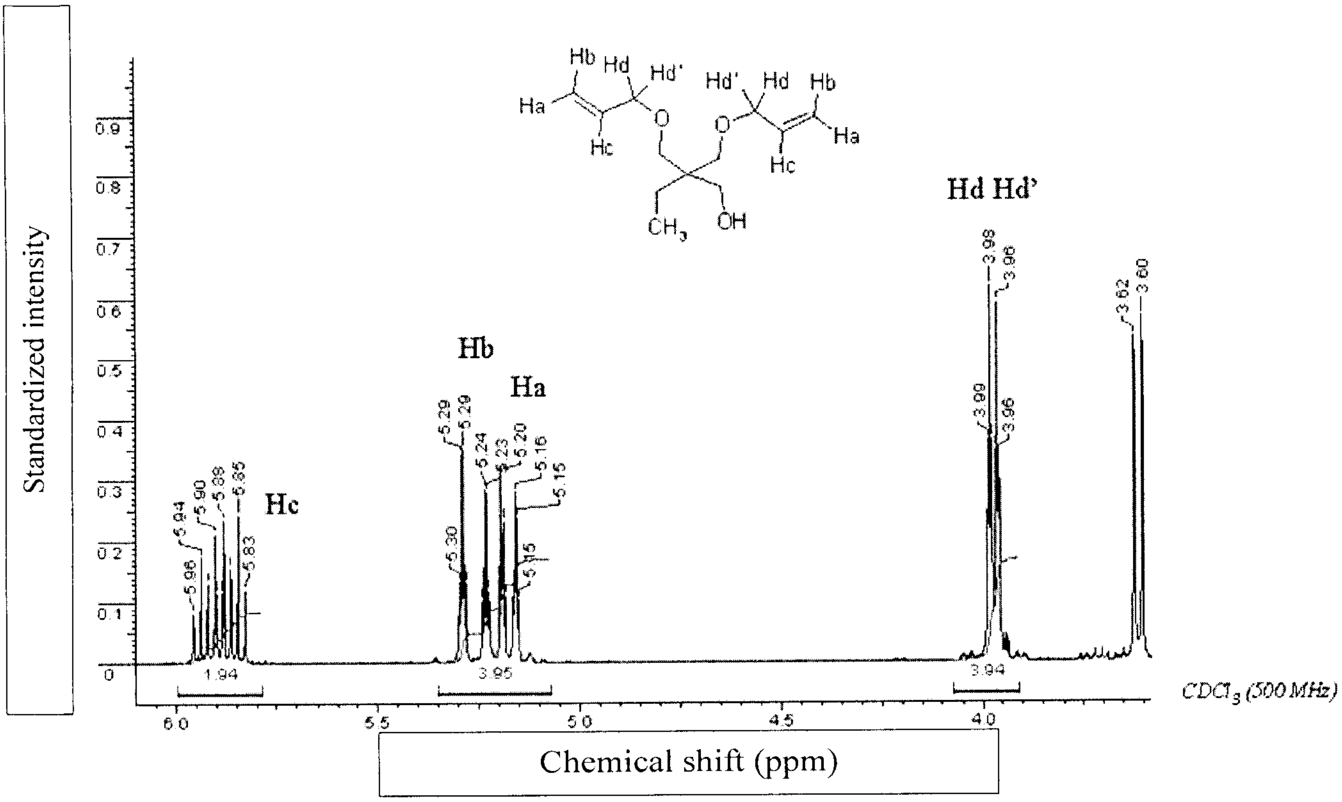
Polymer P1

Fig. 3.1



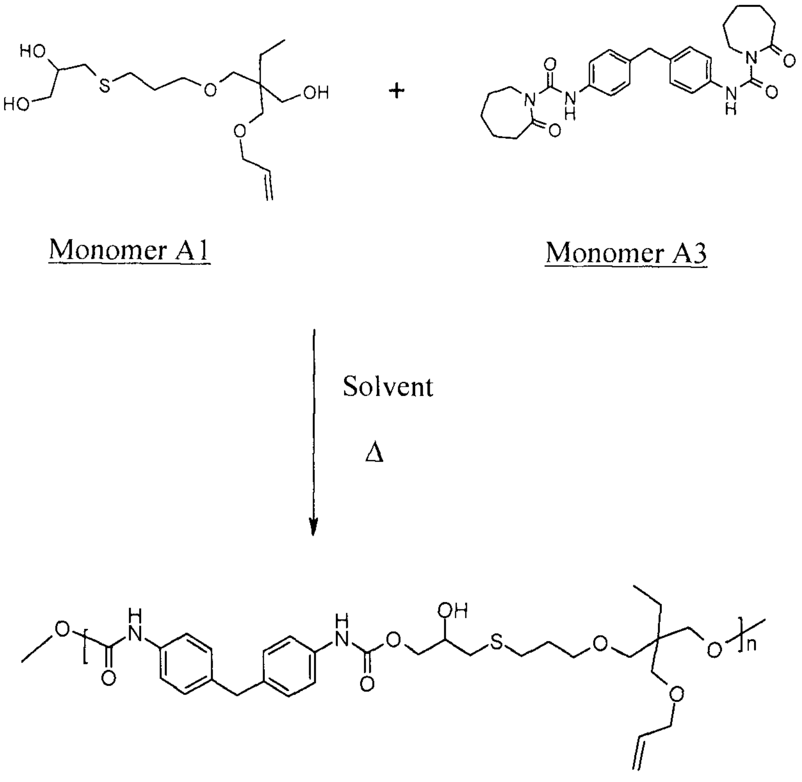
NMR spectrum of Monomer A1

Fig. 3.2



NMR spectrum of compound 1

Fig. 4

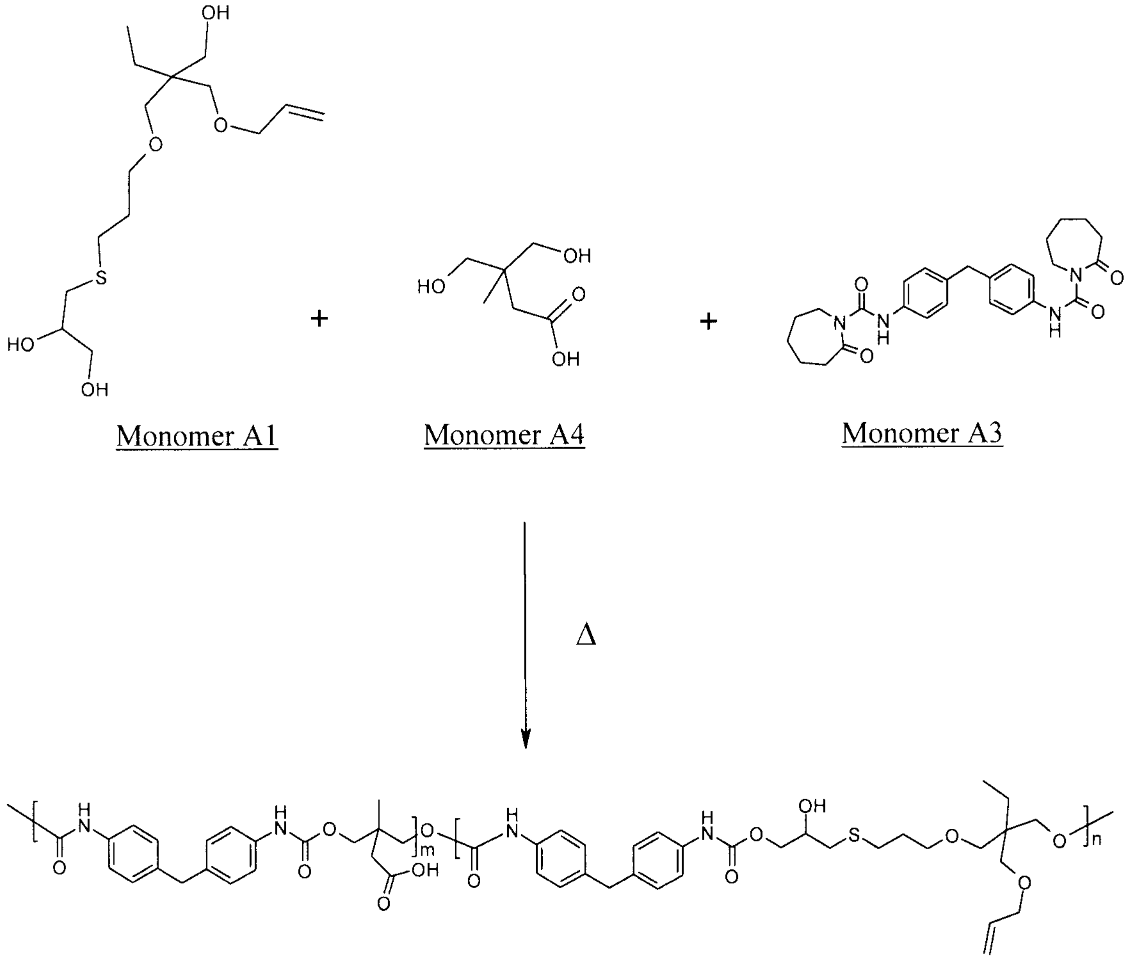


Monomer A1

Monomer A3

Polymer P1

Fig. 5

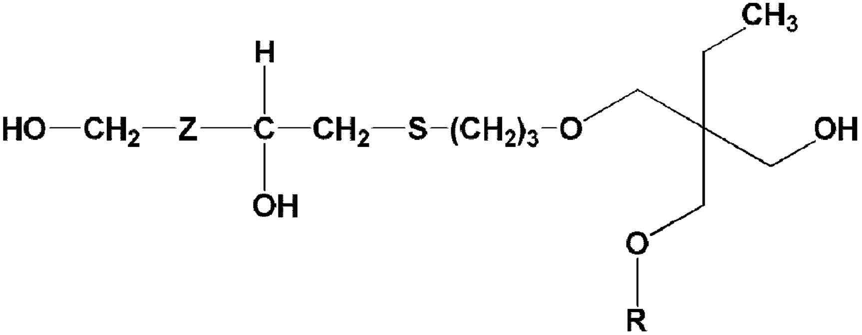


Monomer A1

Monomer A4

Monomer A3

Polymer P2



(I)