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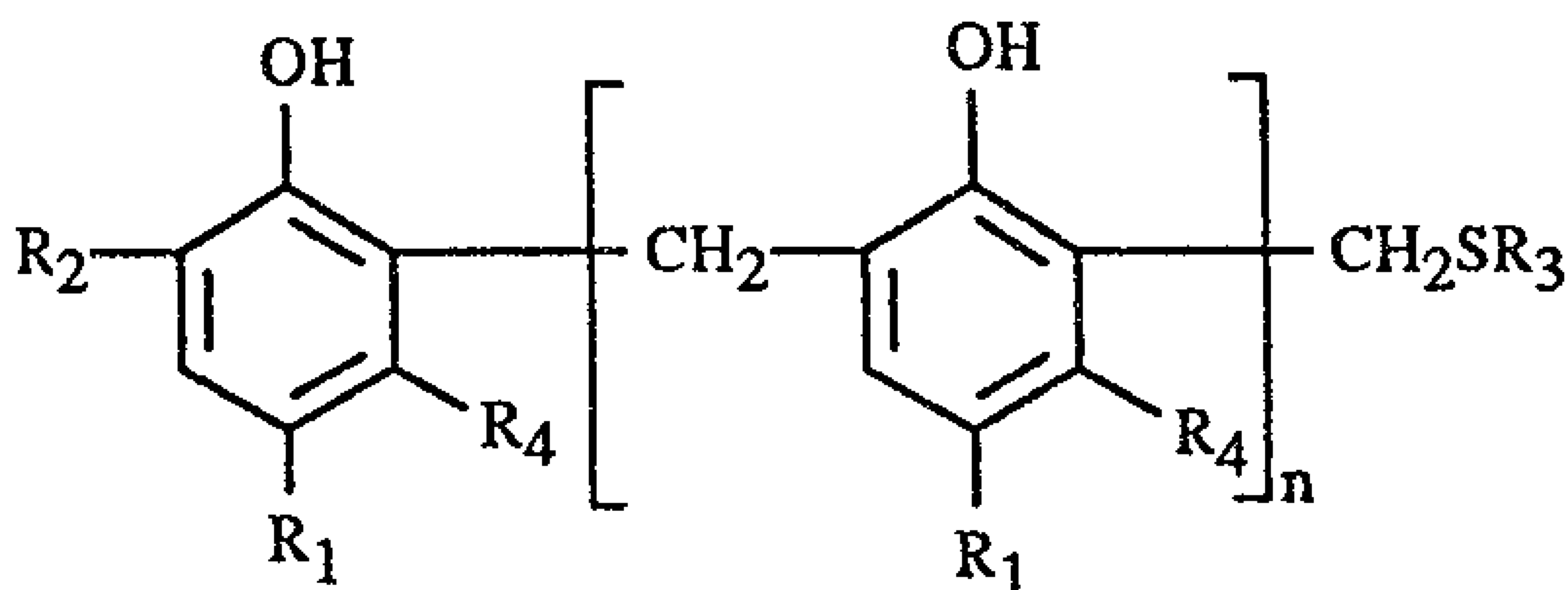
(73) CIBA SPECIALTY CHEMICALS HOLDING INC., CH

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(54) **COMPOSES PHENOLIQUES UTILISES EN BOUT DE CHAINE
POUR LA POLYMERISATION ANIONIQUE EN SOLUTION DE
DIENES**

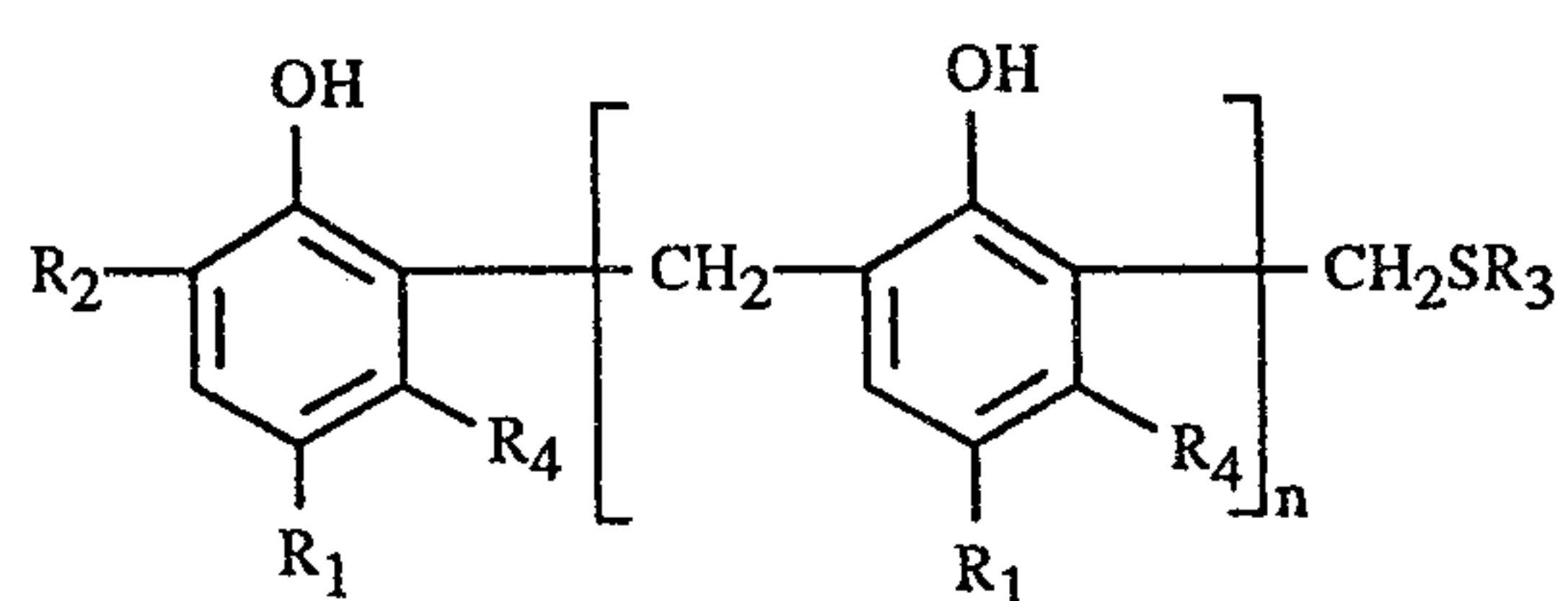
(54) **PHENOLIC COMPOUNDS AS CHAIN-TERMINATORS FOR
THE ANIONIC SOLUTION POLYMERISATION OF DIENES**



(57) Compounds of formula I (see above formula) wherein n is 0 to 3, R₁ and R₂ are C₁-C₁₂alkyl, C₅-C₈cycloalkyl or -CH₂SR₃, R₃ is C₁-C₁₈alkyl, phenyl or benzyl, and R₄ is hydrogen or CH₃, are admirably suitable as chain-terminators in the anionic solution polymerisation of 1,3-dienes.

A-17713/+Phenolic compounds as chain-terminators for the anionic solution polymerisation of dienesAbstract of the Disclosure

Compounds of formula I



wherein n is 0 to 3, R₁ and R₂ are C₁-C₁₂alkyl, C₅-C₈cycloalkyl or -CH₂SR₃, R₃ is C₁-C₁₈alkyl, phenyl or benzyl, and R₄ is hydrogen or CH₃, are admirably suitable as chain-terminators in the anionic solution polymerisation of 1,3-dienes.

A-17713/+Phenolic compounds as chain-terminators for the anionic solution polymerisation of dienes

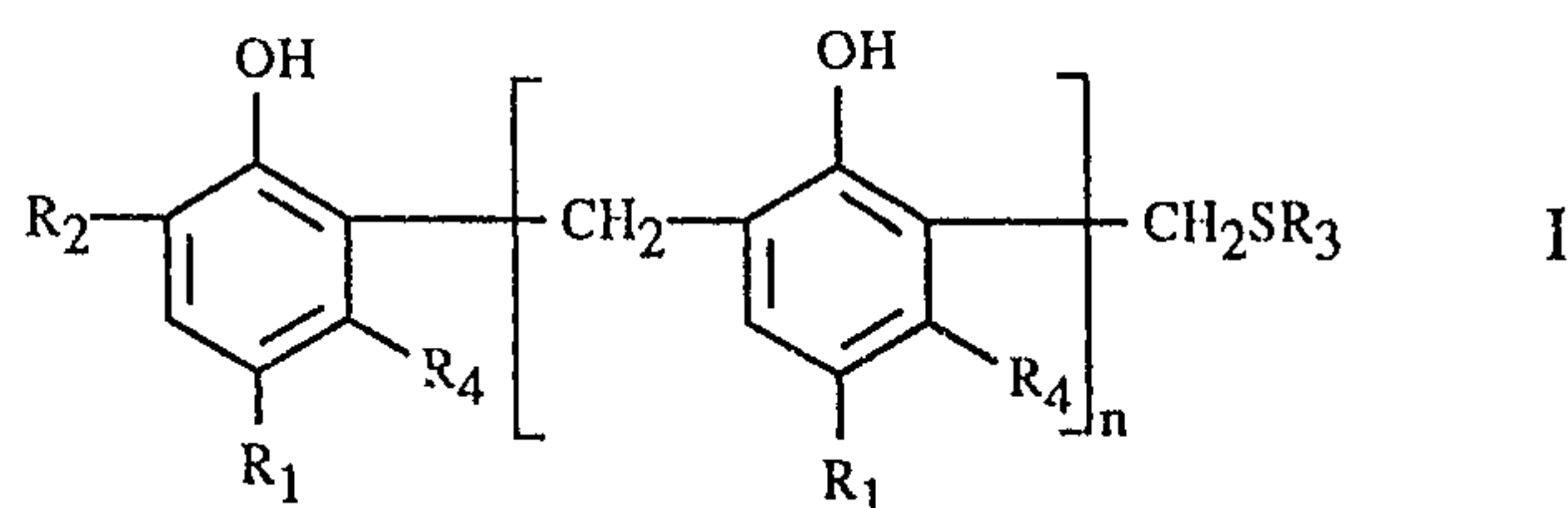
The present invention relates to a process for discontinuing polymerisation during the anionic solution polymerisation of 1,3-dienes.

The anionic solution polymerisation of 1,3-dienes is a process which is used in industrial technology for the preparation of polybutadiene and polyisoprene as well as for the preparation of styrene/butadiene copolymers. The polymerisation initiators used in this process are mainly organolithium compounds, especially alkyl lithium compounds which are soluble in the hydrocarbon solvents employed. A "living polymer" which carries an organolithium group at the chain end is formed. To discontinue the polymerisation it is necessary to destroy this organolithium group. This is accomplished by adding a protic compound such as water or an acid, but preferably an alcohol such as methanol. Further working up is normally effected by addition of an antioxidant and coagulation in an aqueous medium or by distillation of the solvent. The addition of the antioxidant is made before the polymer comes in contact with atmospheric oxygen. Suitable antioxidants are sterically hindered phenols, for example 2,6-di-tert-butyl-p-cresol.

Applicant's own experiments have shown that discolouration and turbidity of the solution occur when phenolic antioxidants such as 2,6-di-tert-butyl-p-cresol are added. The polymers which subsequently precipitate are likewise partially or completely discoloured. However, it has now been found that neither discolouration nor turbidity occur if very specific sulfur-containing phenolic antioxidants are added to the polymerisation solution.

Accordingly, the present invention relates to a process for discontinuing the organolithium-initiated anionic polymerisation of 1,3-dienes and the copolymerisation thereof with styrene compounds by addition of a chain-terminator to the polymerisation solution, which comprises using as chain-terminator at least one phenolic antioxidant of formula I

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wherein n is 0 to 3,

R_1 and R_2 are each independently of the other C_1 - C_{12} alkyl, C_5 - C_8 cycloalkyl or $-CH_2SR_3$,

R_3 is C_1 - C_{18} alkyl, phenyl or benzyl, and

R_4 is hydrogen or methyl.

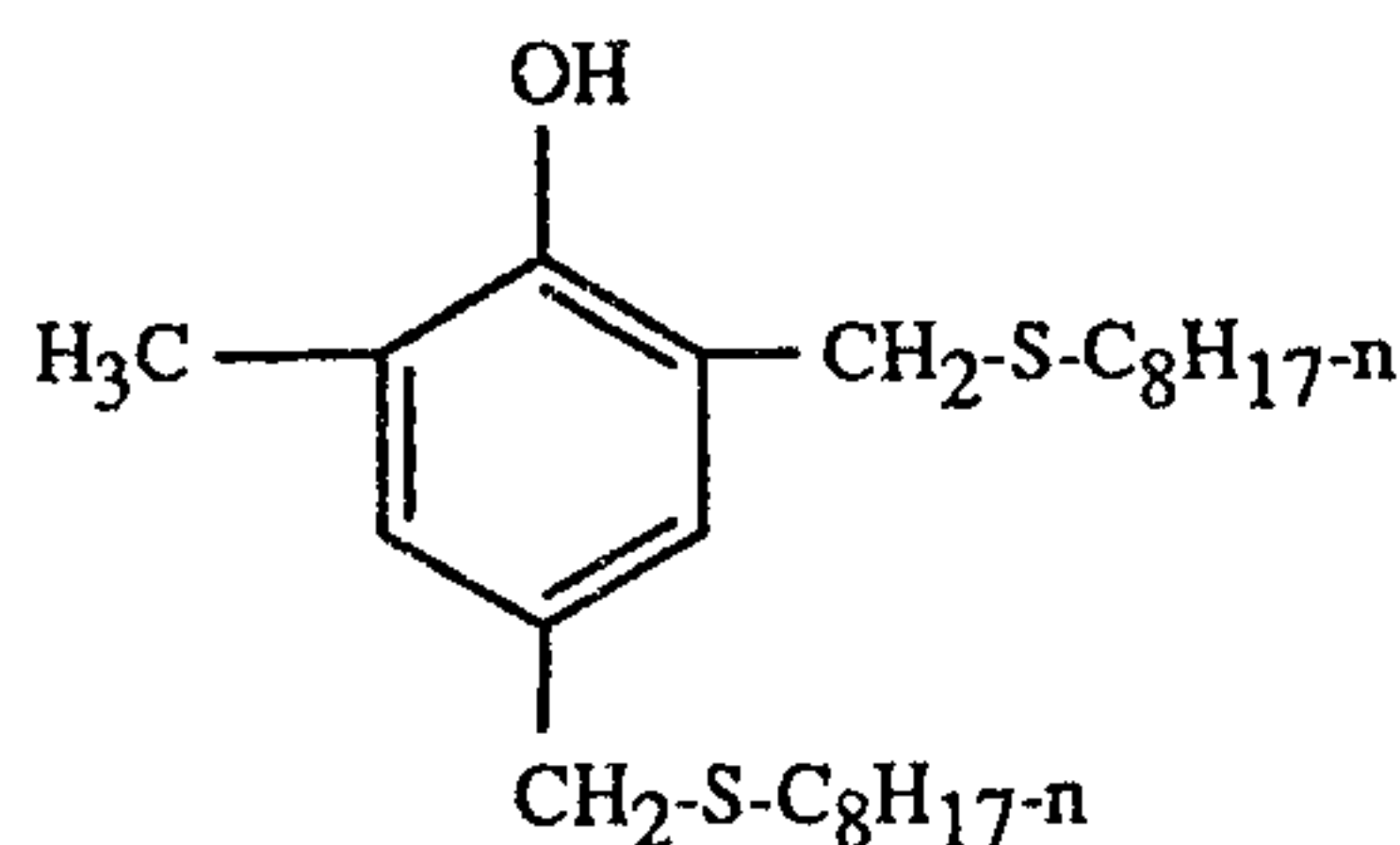
R_1 and R_2 as C_1 - C_8 alkyl may be unbranched or branched alkyl radicals such as methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *sec*-butyl, *tert*-butyl, isopentyl, *tert*-pentyl, *n*-hexyl, *n*-heptyl, *n*-octyl or 2-ethylhexyl. R_3 as C_1 - C_{18} alkyl may additionally be decyl, dodecyl, tetradecyl, hexadecyl or octadecyl.

The preferred chain-terminator used in the process of this invention is a compound of formula I, wherein n is 0 or 1, R_1 and R_2 are each independently of the other C_1 - C_4 alkyl or $-CH_2SR_3$, R_3 is C_4 - C_{18} alkyl, benzyl or phenyl, and R_4 is hydrogen.

It is especially preferred to use a compound of formula I, wherein n is 0.

Mixtures of such compounds may also be used, for example reaction mixtures which contain compounds of formula I, wherein n has different meanings.

The compound of formula



has been found especially suitable.

The chain-terminators used in the practice of this invention are preferably added to the polymerisation solution in such an amount that at least one mole of phenolic hydroxyl group is present per mole of organolithium compound. An excess does not matter and

contributes to the antioxidative stabilisation of the polymer. It is preferred to add the chain-terminator as solution in an inert solvent.

Surprisingly, it has been found that other phenolic antioxidants can also be added simultaneously with the compound of formula I or immediately afterwards, without giving rise to discolouration of the polymers.

Representative examples of suitable phenolic antioxidants are:

1. Alkylated monophenols, for example 2,6-di-tert-butyl-4-methylphenol, 2-tert-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-isobutylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-(α -methylcyclohexyl)-4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, 2,6-di-nonyl-4-methylphenol.
2. Alkylated hydroquinones, for example 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octadecyloxyphenol.
3. Hydroxylated thiodiphenyl ethers, for example 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-2-methylphenol).
4. Alkylidenebisphenols, for example 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis[4-methyl-6-(α -methylcyclohexyl)phenol], 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis(6-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(6-tert-butyl-4-isobutylphenol), 2,2'-methylenebis[6-(α -methylbenzyl)-4-nonylphenol], 2,2'-methylenebis[6-(α,α -dimethylbenzyl)-4-nonylphenol], 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5-methylphenyl)dicyclopentadiene, bis[2-

(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl] terephthalate.

5. Benzyl compounds, for example 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, bis(3,5-di-tert-butyl-4-hydroxybenzyl) sulfide, isooctyl 3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) dithiolterephthalate, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) isocyanurate, dioctadecyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, calcium salt of monoethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl)isocyanurate.

6. Acylaminophenols, for example 4-hydroxylauranilide, 4-hydroxystearanilide, 2,4-bis(octylmercapto)-6-(3,5-di-tert-butyl-4-hydroxyanilino)-s-triazine, octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate.

7. Esters of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, octadecanol, 1,6-hexanediol, neopentyl glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, thiodiethylene glycol, N,N'-bis(hydroxyethyl)oxalodiamide.

8. Esters of β -(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, diethylene glycol, octadecanol, triethylene glycol, 1,6-hexanediol, pentaerythritol, neopentyl glycol, tris(hydroxyethyl) isocyanurate, thiodiethylene glycol, N,N'-bis(hydroxyethyl)oxalodiamide.

9. Esters of β -(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, diethylene glycol, octadecanol, triethylene glycol, 1,6-hexanediol, pentaerythritol, neopentyl glycol, tris(hydroxyethyl) isocyanurate, thiodiethylene glycol, N,N'-bis(hydroxyethyl)oxalodiamide.

10. Amides of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid e.g. N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine.

The process of this invention is susceptible of application to the anionic solution polymerisation of 1,3-dienes, especially of butadiene and isoprene, and the

copolymerisation thereof with styrene compounds, preferably with styrene. Organolithium compounds are used as initiators, preferably alkyl lithium compounds such as n-butyl lithium, tert-butyl lithium or isopropyl lithium. Preferred solvents are hydrocarbons such as hexane, cyclohexane or alkane mixtures. For adjustment of the stereo structure of the polymer, small amounts of a polar solvent such as tetrahydrofuran or diglyme are often added. Further details on carrying out the anionic solution polymerisation of 1,3-dienes will be found in the literature, for example in Encyclopedia of Polymer Science and Engineering, Vol. 2 (1983), 1-43, J. Wiley & Sons.

The following Examples show the effect of different chain-terminators on the appearance of the polymer solution. Parts and percentages are by weight.

Example

A 2 l glass flask is charged, under nitrogen, with 760 g of dry cyclohexane, 0.07 g of tetrahydrofuran and 100 g of 1,3-butadiene. With stirring, 6.4 mmol of n-butyl lithium in the form of a 10% solution in hexane are added. The solution is heated to 70°C and kept for 60 minutes at this temperature. Then 6.3 mmol of a chain-terminator in the form of a ca. 10% solution in cyclohexane are added. The following phenolic antioxidants are used as chain-terminators:

- AO-1 2,6-di-tert-butyl-p-cresol
- AO-2 octadecyl-3,5-di-tert-butyl-4-hydroxyphenylpropionate
- AO-3 2-(3,5-di-tert-butyl-4-hydroxyphenylamino)-4,6-bis(octylthio)-1,3,5-triazine
- AO-4 2,2'-methylen-bis(6-tert-butyl-4-methylphenol)
- AO-5 2,6-di-tert-butyl-4-dodecylthiomethylphenol
- AO-6 2,4-bis(octyloxycarbonylmethylthiomethyl)-6-tert-butylphenol
- AO-7 2-methyl-4,6-bis(n-octylthiomethyl)-phenol (of the invention)
- AO-8 2,4-bis(dodecylthiomethyl)-6-methylphenol (of the invention)
- AO-9 2,4-bis(dodecylthiomethyl)-3,6-dimethylphenol (of the invention)
- AO-10 reaction product of p-nonylphenol, dodecylmercaptan and formaldehyde, containing the compounds of formula I, wherein R_4 is hydrogen, R_1 is nonyl and n is 0 to 3 (of the invention).

After 5 minutes and after 60 minutes the appearance of the solution is assessed visually. The results are reported in the following table.

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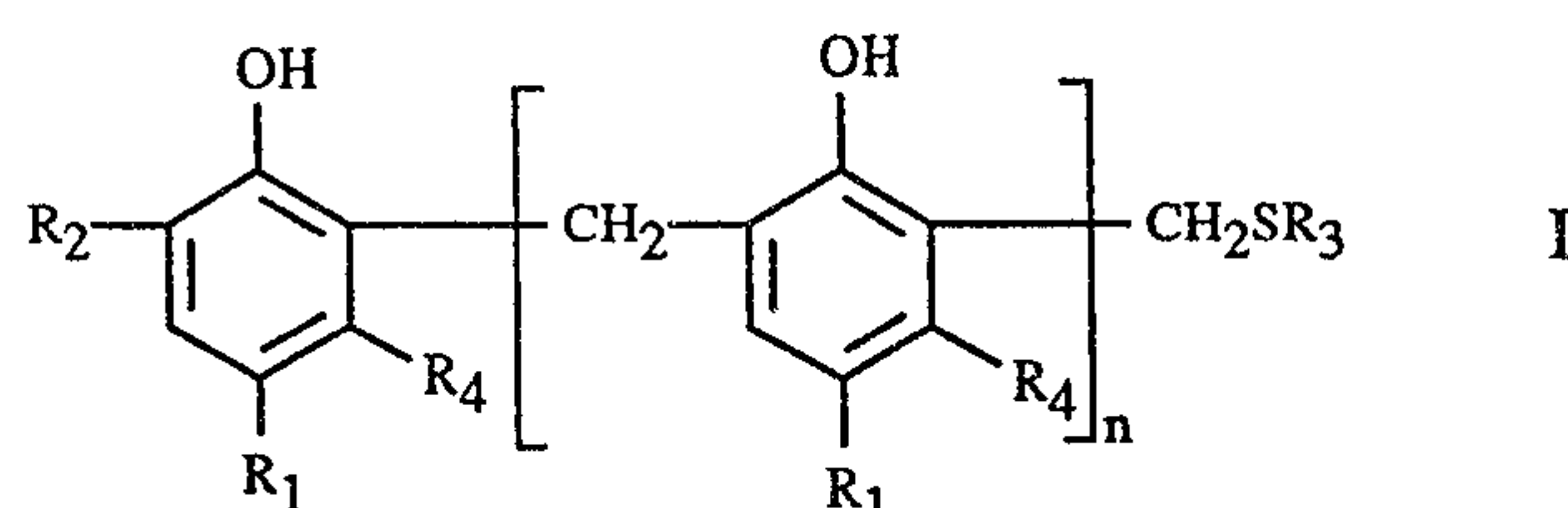
Appearance of the solution after		
Chain-terminator	<u>5 minutes</u>	<u>60 minutes</u>
AO-1	pale yellow, clear	yellowish-brown, turbid
AO-2	white, turbid	yellowish, turbid
AO-3	yellowish-brown, turbid	brown, turbid
AO-4	yellowish-brown, clear	black-brown, clear
AO-5	light brown precipitate	dark brown precipitate
AO-6	yellow precipitate	light brown precipitate
AO-7	colourless, clear	colourless, clear
AO-8	colourless, clear	colourless, clear
AO-9	colourless, clear	colourless, clear

It is evident that the solution remains clear and colourless upon addition of the compounds of this invention, whereas discolouration and turbidity (precipitation) occur when all other chain-terminators are added.

In a further test run, a mixture of 6.5 mmol of AO-7 and 6.4 mmol of AO-1 or AO-2 or AO-3 is used, while otherwise carrying out the polymerisation in the same manner. In all three cases the solution also remains colourless and clear after 3 hours.

What is claimed is:

1. A process for discontinuing the organolithium-initiated anionic polymerisation of 1,3-dienes and the copolymerisation thereof with styrene compounds by addition of a chain-terminator to the polymerisation solution, which process comprises using as chain-terminator at least one phenolic antioxidant of formula I



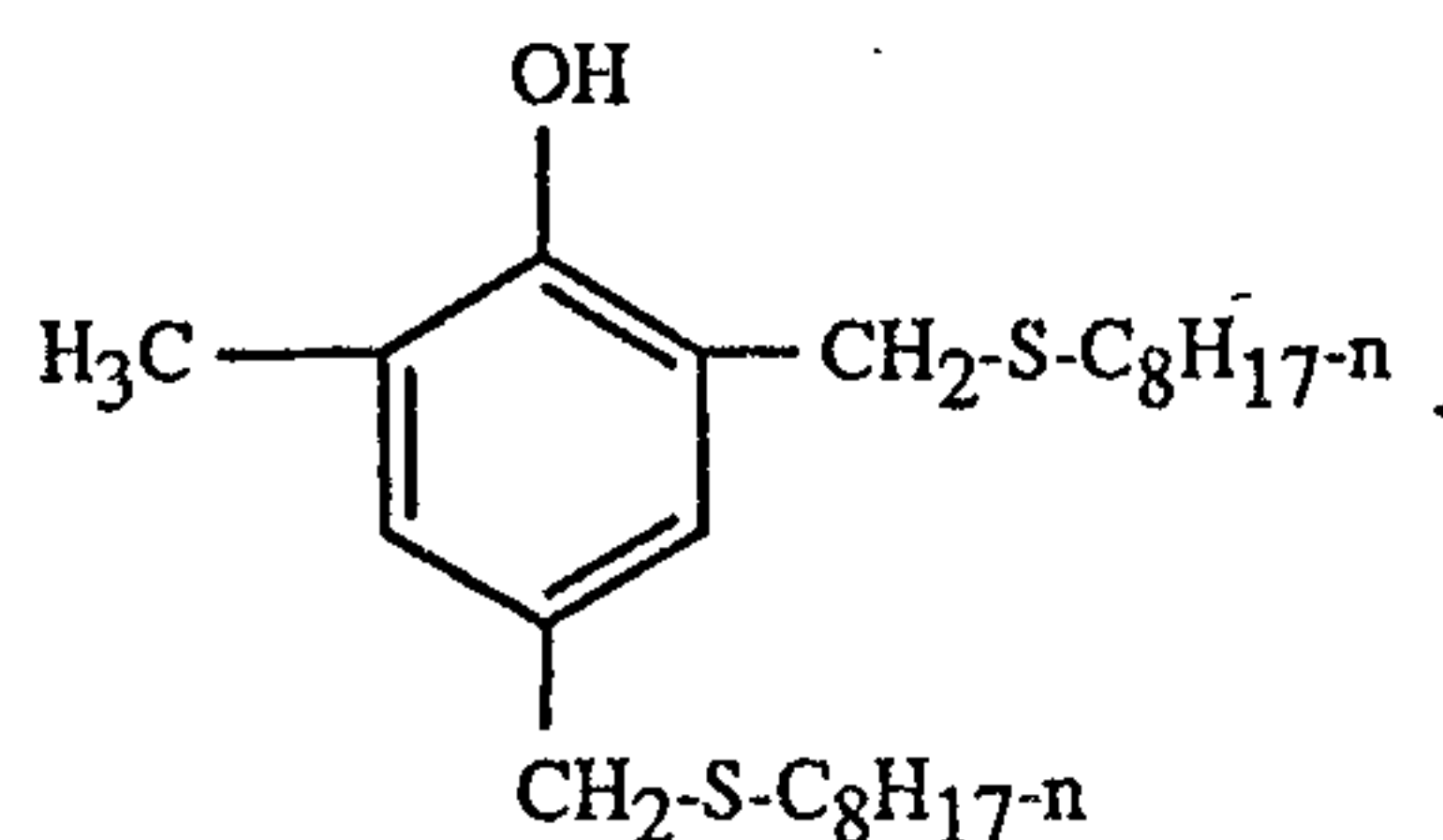
wherein n is 0 to 3,

R_1 and R_2 are each independently of the other C_1 - C_{12} alkyl, C_5 - C_8 cycloalkyl or $-CH_2SR_3$, R_3 is C_1 - C_{18} alkyl, phenyl or benzyl, and R_4 is hydrogen or methyl.

2. A process according to claim 1, wherein the chain-terminator is a phenolic antioxidant of formula I, wherein n is 0 or 1, R_1 and R_2 are each independently of the other C_1 - C_4 alkyl or $-CH_2SR_3$, R_3 is C_4 - C_{18} alkyl, benzyl or phenyl, and R_4 is hydrogen.

3. A process according to claim 2, wherein the chain-terminator is a phenolic antioxidant of formula I, wherein n is 0.

4. A process according to claim 3, wherein the chain-terminator is the compound of formula



5. A process according to claim 1, which comprises adding a second phenolic antioxidant simultaneously with, or immediately after, the addition of the compound of formula I.

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6. A process according to claim 1, wherein the compound of formula I is used in an amount such that one mole of phenolic hydroxylic groups is present per mole of organolithium compound used as initiator.
7. Use of a compound of formula I as defined in claim 1 as chain-terminator in the organolithium-initiated anionic polymerisation of 1,3-dienes and the copolymerisation thereof with styrene compounds.

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