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(54) Titre : ESTERS D'ACIDE CARBOXYLIQUE α -HALOGENE AVEC DES ALCOOLS POLYVALENTS UTILISES
COMME INITIATEURS POUR POLYMERISATION RADICALE A TRANSFERT D'ATOME
(54) Title: α -HALOGENATED ACID ESTERS WITH POLYVALENT ALCOHOLS AS ATOM TRANSFER RADICAL
POLYMERIZATION INITIATORS

(57) **Abrégé/Abstract:**

The invention relates to α -halogenated acid esters of polyvalent, but at least trivalent, alcohols which can be used as atom transfer radical polymerization initiators. Using said initiators block copolymers having branched structures can be produced.



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α -Halogenated acid esters with polyvalent alcohols as ATRP initiators

Abstract

The invention relates to α -halocarboxylic acid esters of polyhydric, at least trihydric, alcohols, which can be used as initiators for ATRP. Using those initiators it is possible to prepare block copolymers having branched structures.

α -Halogenated acid esters with polyvalent alcohols as atom transfer radical polymerization initiators

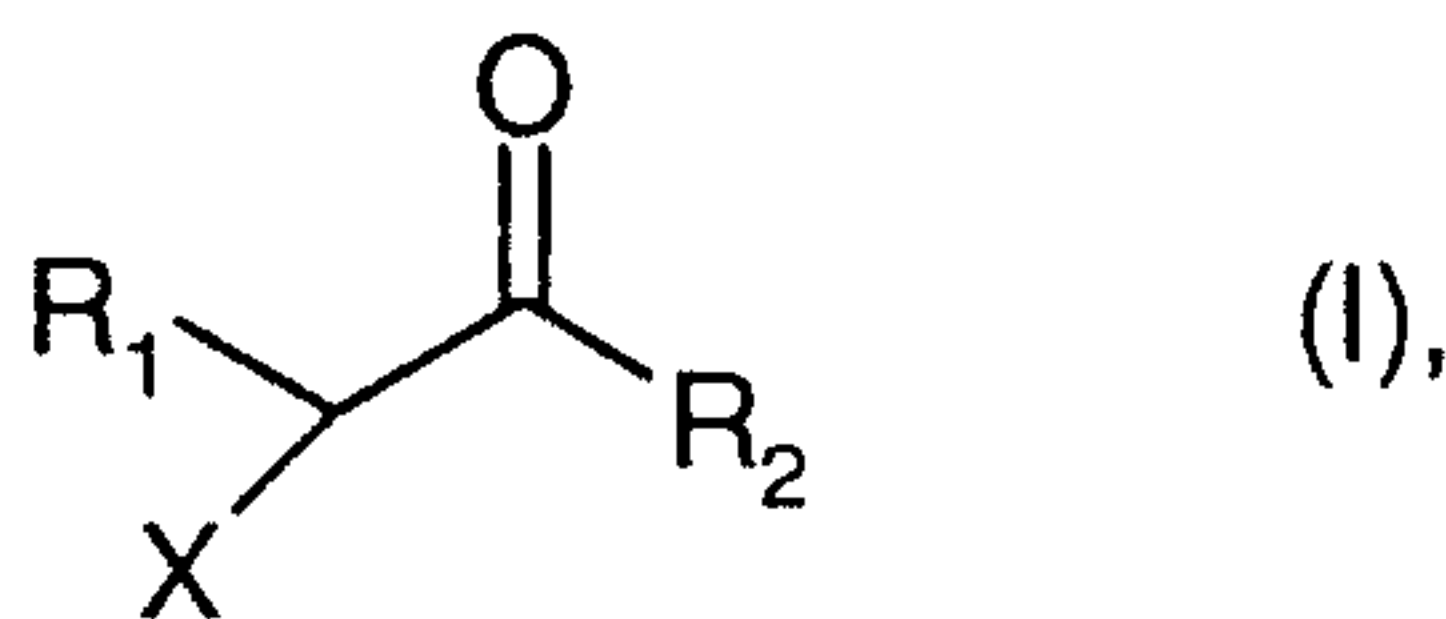
The present invention relates to α -halocarboxylic acid esters with polyhydric alcohols, which can be used as initiators for ATRP, to processes for the preparation of such initiators, to polymers or copolymers that can be prepared using those initiators, to compositions comprising such polymers or copolymers, to processes for the preparation thereof and to the use thereof in the preparation of polymers or block copolymers wherein the terminal group $\bullet X$ is replaced by an open-chain or cyclic group $R'R''N-O\bullet$.

Atom Transfer Radical Polymerisation (ATRP) is a polymerisation process that has been known for a long time and is especially suitable for the preparation of "living" polymers, block copolymers, graft copolymers, etc. having low polydispersity and largely predeterminable molecular weights.

Despite their obvious advantages, such polymerisation processes have a disadvantage in that there is only a small selection of initiators suitable for the preparation of branched polymer structures. The known polymerisation initiators, which are described, for example, in WO 96/30421, e.g. 2-chloro- or 2-bromo-acetic acid or 2-chloro- or 2-bromo-isobutyric acid, result in linear, but not branched, structures of the polymer chain and therefore allow only a small structural variation in the polymers that can be obtained.

The problem underlying the present invention is to prepare polymerisation initiators suitable for the synthesis of branched polymer structures, e.g. star polymers, dendrimers, comb-shaped polymers, etc.. The problem is solved by the present invention, which relates to α -halocarboxylic acid esters with polyhydric alcohols that can be prepared by simple acylation processes.

The invention relates to α -halocarboxylic acid esters of formula



wherein

R_1 is hydrogen, C_1 - C_4 alkyl, cyano, phenyl or C_1 - C_4 alkylphenyl;

X is chlorine, bromine or iodine; and

R_2 is the radical of an acylated, branched, trihydric alcohol, the radical of a fully or partially acylated, linear or branched, tetrahydric alcohol, the radical of a fully or partially acylated,

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linear, penta- or hexa-hydric alcohol, the radical of a fully or partially acylated, linear or cyclic C₄-C₆aldose or C₄-C₆ketose or the radical of a fully or partially acylated disaccharide,

and to isomers of such compounds.

The terms and nomenclature used in the description of the present invention are preferably defined as follows:

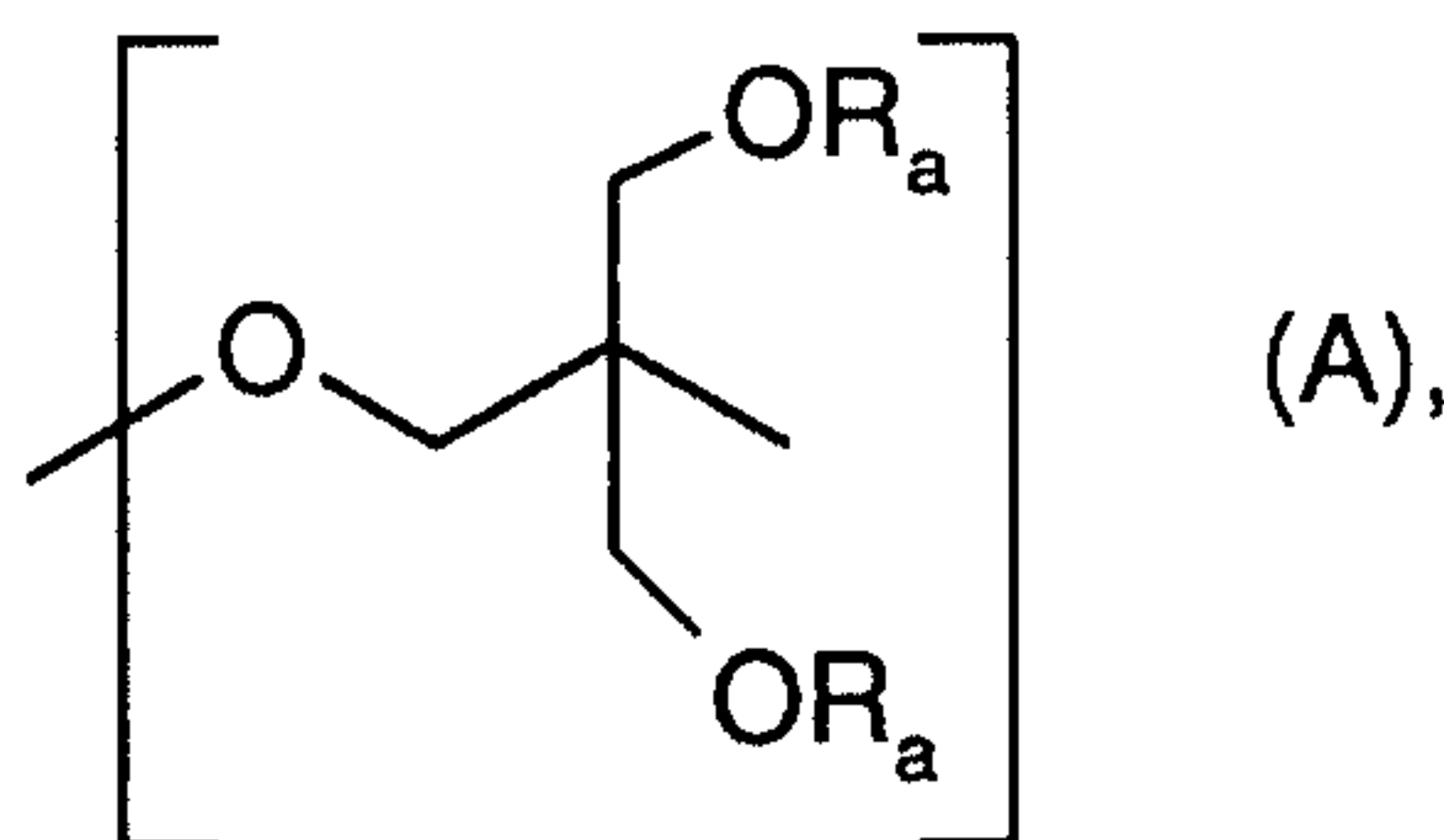
C₁-C₄Alkyl is methyl, ethyl, n-propyl or isopropyl or n-, sec- or tert-butyl.

C₁-C₄Alkylphenyl is preferably p-methylphenyl.

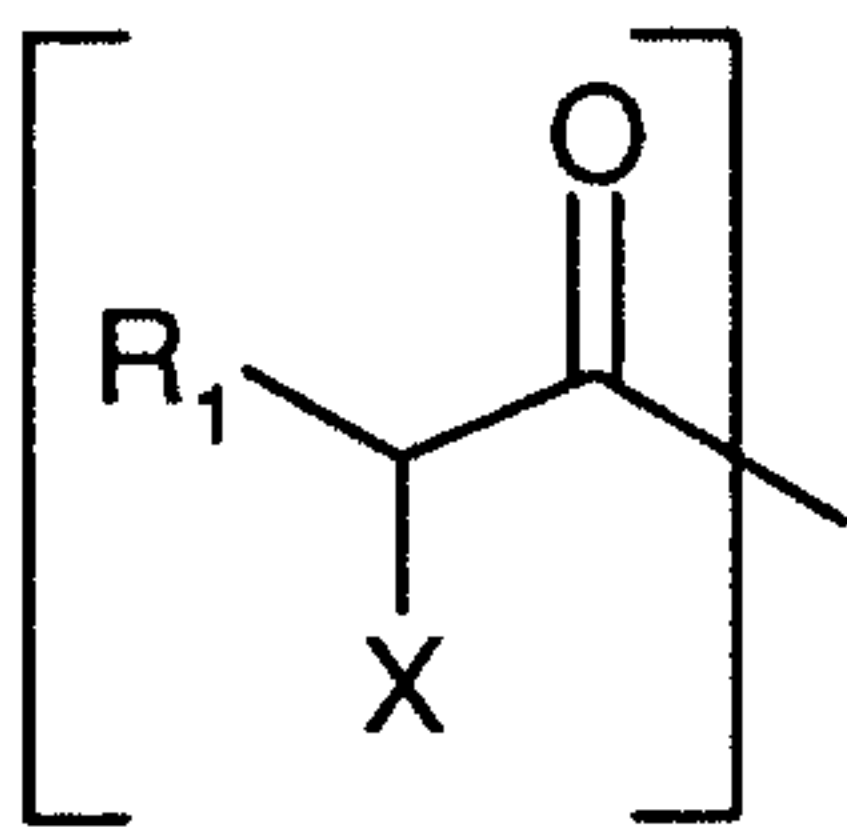
X is preferably chlorine or bromine.

R₁ preferably forms with the α-carbon atom a 2-haloacyl group, e.g. 2-halo-C₃-C₄alkanoyl, e.g. 2-halopropionyl, 2-halo-n-butyryl or 2-halo-isobutyryl, e.g. 2-chloro- or 2-bromo-propionyl or α-chloro- or α-bromo-isobutyryl, or an α-halophenylacetyl group, e.g. α-chloro- or α-bromo-phenyl acetate.

The radical R₂ of an acylated, branched, trihydric alcohol is preferably derived from 1,3,5-trihydroxybenzene or trimethylolethane and is, for example, a group of the partial formula



wherein R_a is α-haloacyl. R_a having the meaning α-haloacyl preferably denotes identical

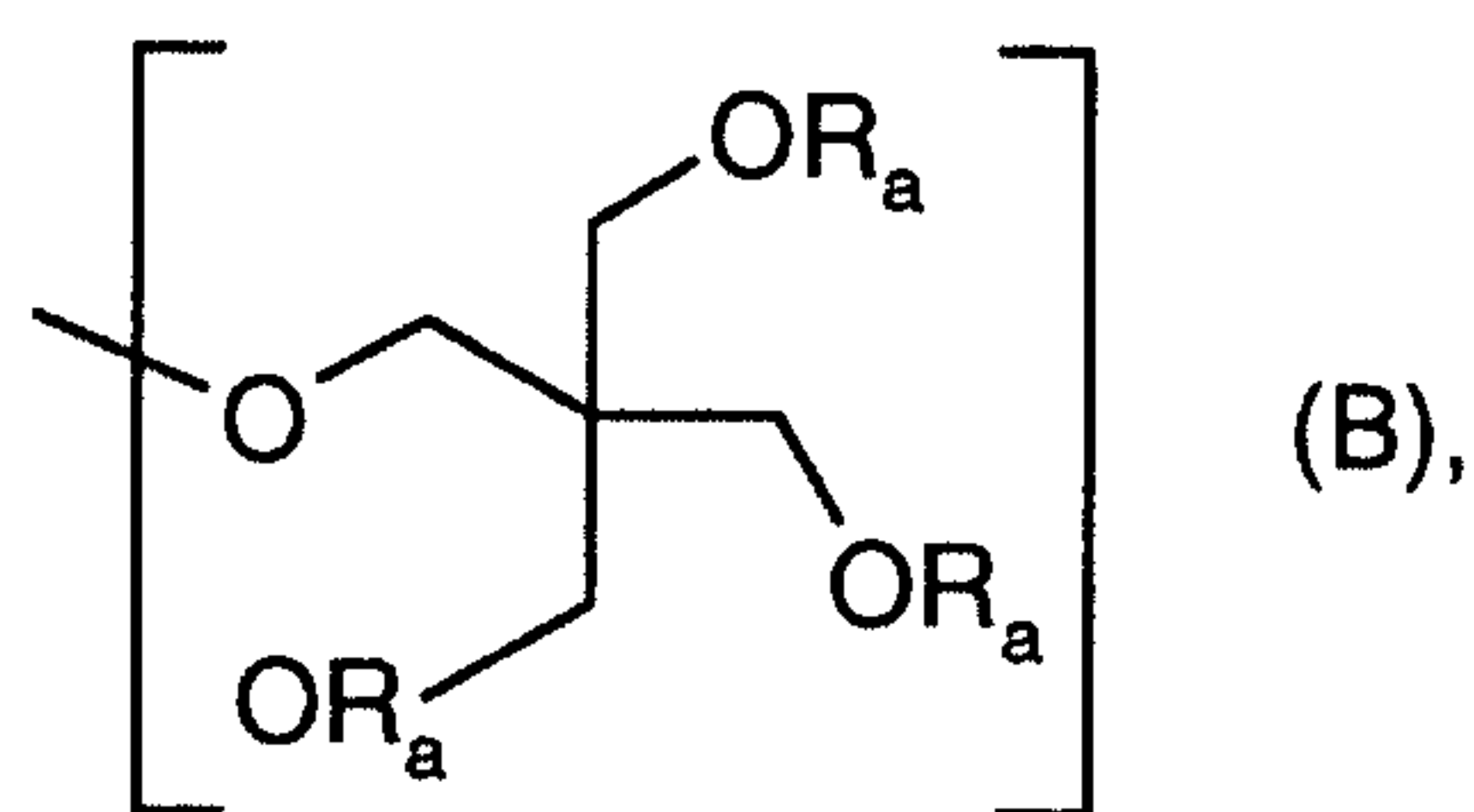


groups of the partial formula , e.g. α-halo-C₃-C₄alkanoyl or α-halophenylacetyl, e.g. α-chloropropionyl, α-bromopropionyl or α-chlorophenylacetyl.

The radical R₂ of a fully or partially acylated, linear tetrahydric alcohol is derived, for example, from erythritol and its 3 isomeric forms, e.g. D-, L- and meso-erythritol.

The radical R₂ is preferably derived from a fully or partially acylated, branched tetrahydric alcohol, e.g. from pentaerythritol, and is, for example, a group of the partial formula

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wherein R_a is α -haloacyl having the meanings mentioned.

The radical of a fully or partially acylated, linear, penta- or hexa-hydric alcohol is derived, for example, from linear pentitols, such as D(+)- and L(-)-arabitol, adonitol or xylitol, or from linear hexitols, such as D-sorbitol, D-mannitol or dulcitol, all or some of the hydroxy groups of which are substituted by R_a (= α -haloacyl).

The radical of a fully or partially acylated, linear or cyclic C_4 - C_6 aldose or C_5 - C_6 ketose is derived, for example, from C_4 aldoses, such as D(-)- and L(+)-erythrose or D(-)- and L(+)-threose, C_5 aldoses, such as D(-)- and L(+)-arabinose, D(-)-ribose or D(+)-xylose, C_6 aldoses, such as D(+)-glucose, D(+)-mannose or D(+)-galactose, or from a C_6 ketose, such as fructose or L(-)-sorbose, and epimeric forms thereof, wherein all or some of the hydroxy groups are likewise substituted by R_a (= α -haloacyl).

The radical of a fully or partially acylated disaccharide is derived, for example, from saccharose, lactose or maltose, all or some of the hydroxy groups of which are likewise substituted by R_a (= α -haloacyl).

The term "isomeric forms" encompasses the forms of isomerism known in the chemistry of sugar alcohols and carbohydrates, e.g. the optically pure stereoisomers (antipodes), diastereoisomers or epimers or racemic mixtures.

A preferred embodiment of the invention relates to α -halocarboxylic acid esters (I) wherein

R_1 is C_1 - C_3 alkyl or phenyl;

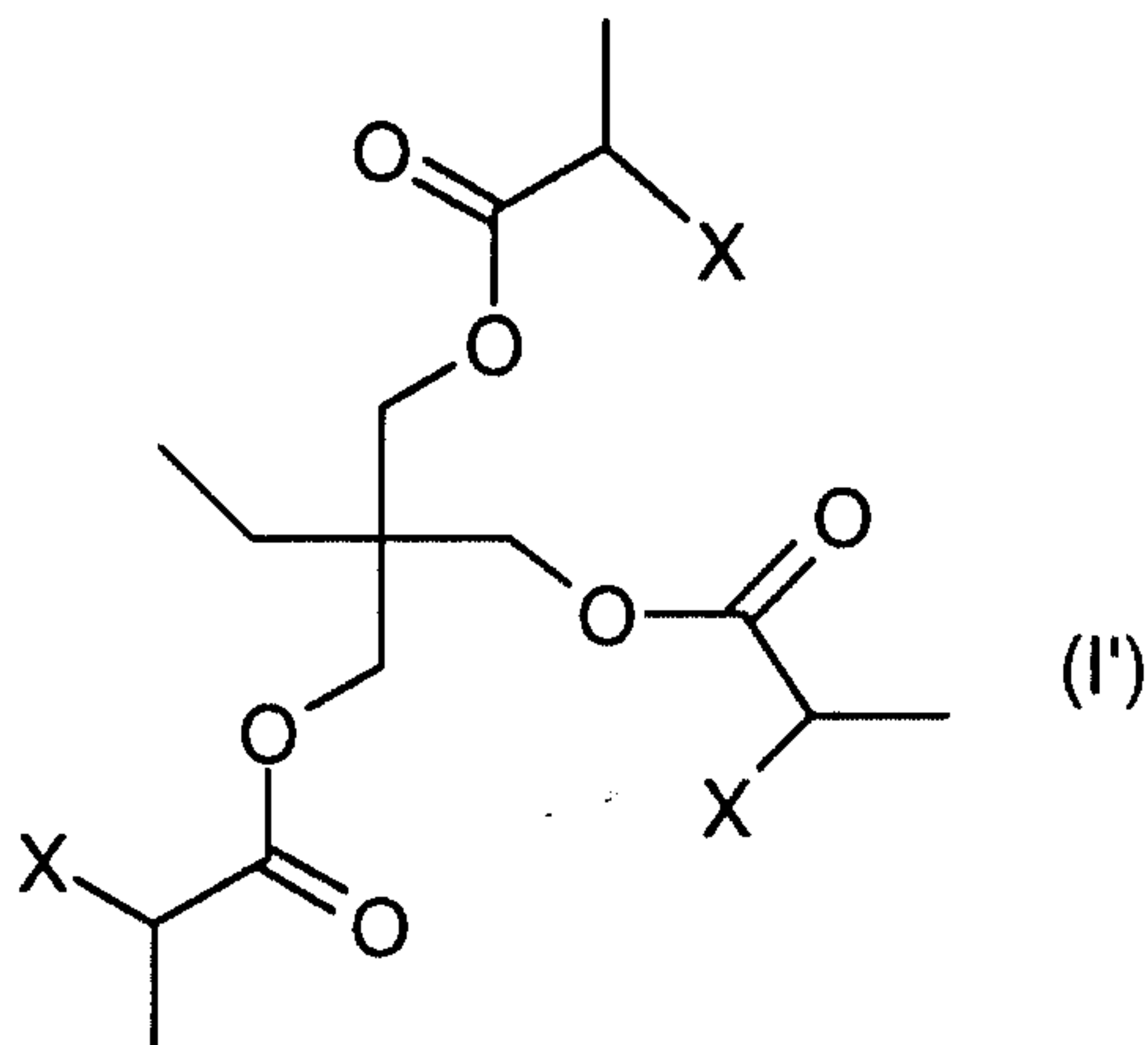
X is chlorine or bromine and

R_2 is the radical of an acylated, branched, trihydric alcohol, e.g. the R_a -acylated radical of 1,3,5-trihydroxybenzene or trimethylolethane, the radical of a fully or partially acylated, linear or branched, tetrahydric alcohol, e.g. the radical of pentaerythritol fully acylated by R_a , or the radical of a fully or partially acylated, linear, penta- or hexa-hydric alcohol, and to isomers of such compounds.

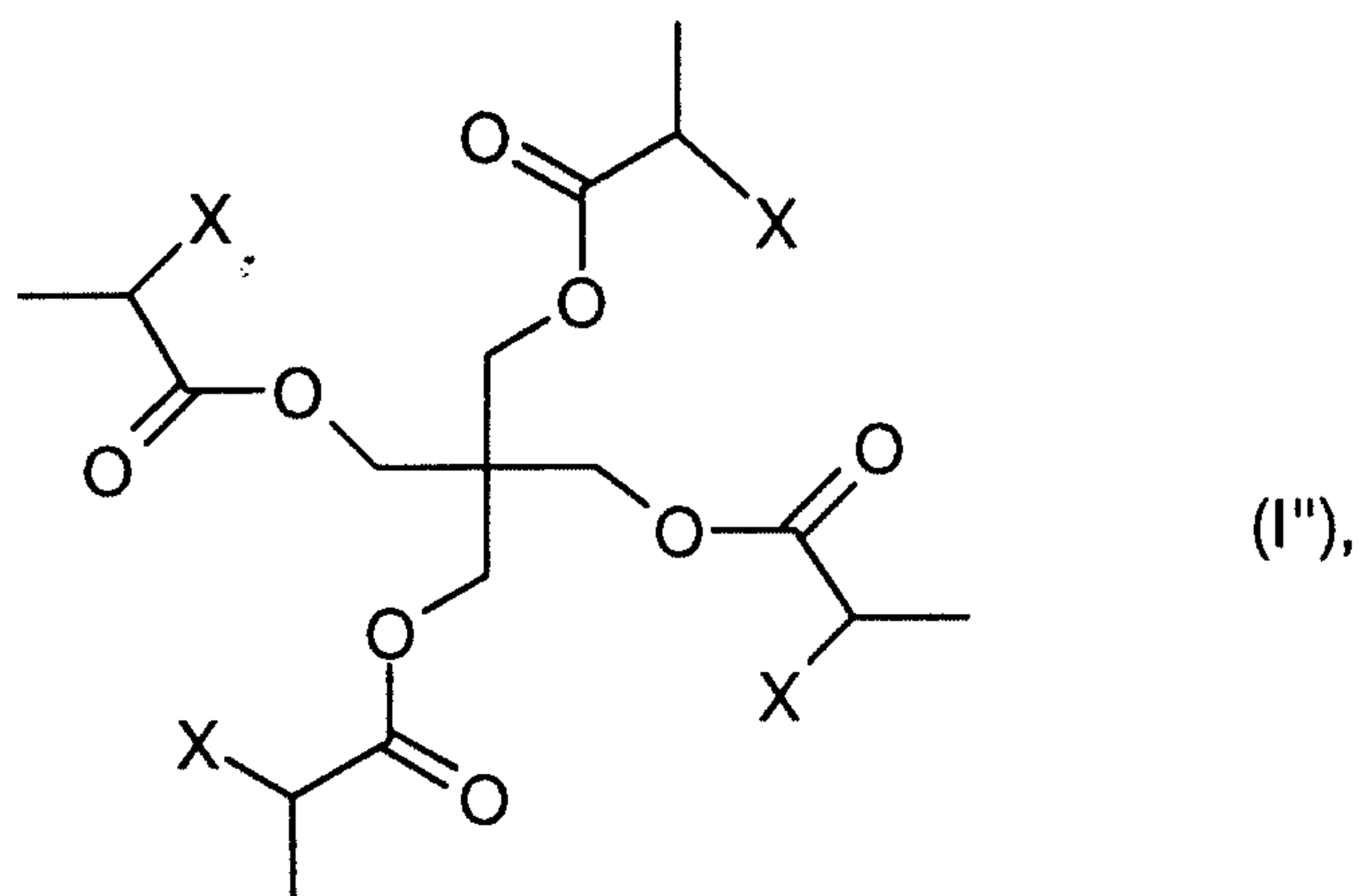
In those preferred embodiments, R_a has the meaning α -haloacyl, especially the meaning α -chloropropionyl or α -bromopropionyl.

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An especially preferred embodiment relates to α -halocarboxylic acid esters of formula

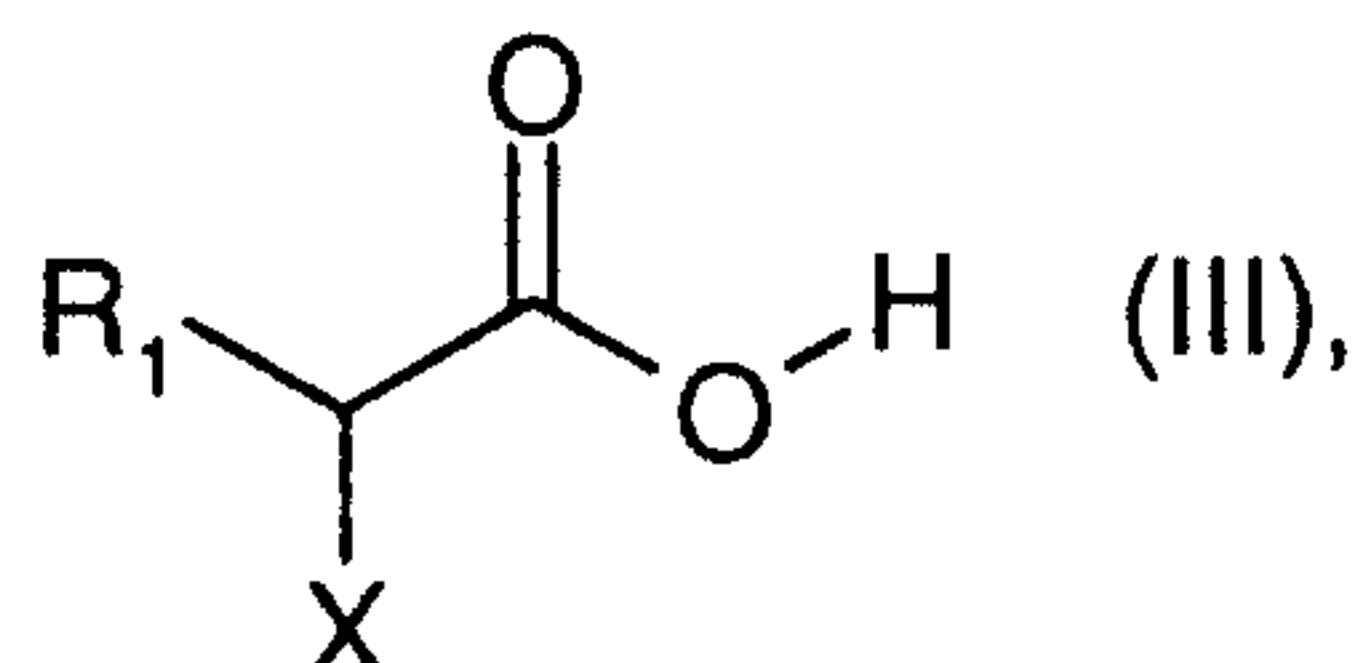


or of formula



wherein X is bromine or iodine.

The invention relates also to a process for the preparation of the α -halocarboxylic acid ester (I), wherein R_1 , R_2 and X are as defined above, in which process an α -halocarboxylic acid of formula



or a reactive, functional acid derivative thereof, is reacted with an alcohol



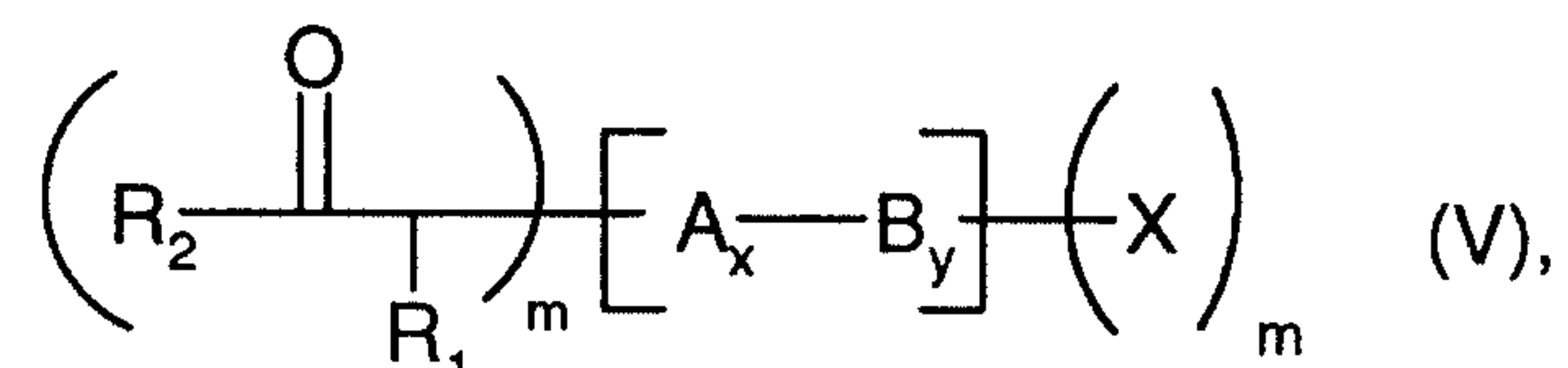
or with a reactive alcohol derivative, wherein R_2' together with the OH group forms a branched, trihydric alcohol, a linear or branched, tetrahydric alcohol, a linear, penta- or

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hexa-hydric alcohol, a linear or cyclic C₄-C₆aldose or C₄-C₆ketose or a disaccharide, and isomers of such compounds.

For the preparation of the α -halocarboxylic acid ester (I) there are used the customary methods of esterification, in which, for example, the equivalents of a reactive functional acid derivative of the α -halocarboxylic acid (II), for example an acid halide, e.g. the acid chloride, which correspond to the valence of the alcohol (III), are reacted with that alcohol, or the α -halocarboxylic acid (II) is reacted with the equivalents of a reactive functional derivative of the alcohol (III), for example with an ester of that alcohol, e.g. a halide, e.g. chloride, or with a sulfonic acid ester of the alcohol, e.g. with the p-toluenesulfonic acid ester.

The invention relates also to a polymer or block copolymer of formula:



wherein

R₁ is hydrogen, C₁-C₄alkyl, cyano, phenyl or C₁-C₄alkylphenyl;

R₂ is the radical of an acylated, branched, trihydric alcohol, the radical of a fully or partially acylated, linear or branched, tetrahydric alcohol, the radical of a fully or partially acylated, linear, penta- or hexa-hydric alcohol, the radical of a fully or partially acylated, linear or cyclic C₄-C₆aldose or C₄-C₆ketose or the radical of a fully or partially acylated disaccharide;

A and B are polymer blocks of ethylenically unsaturated monomer units;

x and y denote the number of monomer units in the blocks A and B, one value of x and y being zero and the other value being an integer greater than zero, or both values x and y being integers greater than zero;

X is chlorine, bromine or iodine; and

m denotes an integer from three to six.

The invention relates also to a process for the preparation of the polymer or block copolymer (V), wherein R₁, R₂, A, B, X, x, y and m are as defined above, in which process ethylene-group-containing aliphatic monomers that form the basis of the polymer blocks A and B are subjected to a polymerisation reaction by atom transfer radical polymerisation (ATRP) in the presence of the α -halocarboxylic acid ester (I) as polymerisation initiator,

wherein R_1 , R_2 and X are as defined above, and in the presence of an oxidisable transition metal complex catalyst.

The term "polymer" encompasses oligomers, co-oligomers, polymers and copolymers, for example block copolymers, multiblock copolymers, star, gradient, random, branched and dendritic copolymers and graft copolymers. The copolymer blocks A and B comprise at least two structural repeating units of polymerisable, aliphatic monomers having at least one or more olefinic double bonds.

Such polymerisable, aliphatic monomers having an olefinic double bond are selected, for example, from the group comprising styrenes, acrolein, acrylic acid or methacrylic acid or salts thereof, acrylic acid or methacrylic acid anhydrides, acrylic acid or methacrylic acid C_1 - C_{24} alkyl esters, acrylic acid or methacrylic acid mono- or di- C_1 - C_4 alkylamino- C_2 - C_4 alkyl esters, acrylic acid or methacrylic acid hydroxy- C_2 - C_4 alkyl esters, acrylic acid or methacrylic acid (C_1 - C_4 alkyl) $_3$ silyloxy- C_2 - C_4 alkyl esters, acrylic acid or methacrylic acid (C_1 - C_4 alkyl) $_3$ silyl- C_2 - C_4 alkyl esters, acrylic acid or methacrylic acid heterocyclyl- C_2 - C_4 alkyl esters, acrylic or methacrylic acid esters containing poly- C_2 - C_4 alkylene glycol ester groups, which may themselves be esterified by substituted C_1 - C_{24} alkoxy groups, acrylic acid or methacrylic acid amides, acrylic acid or methacrylic acid mono- or di- C_1 - C_4 alkylamides, acrylic acid or methacrylic acid amino- C_2 - C_4 alkylamides and acrylonitrile.

Suitable styrenes can be substituted on the phenyl group by from one to three substituents from the group comprising hydroxy, C_1 - C_4 alkoxy, e.g. methoxy or ethoxy, halogen, e.g. chlorine, amino and C_1 - C_4 alkyl, e.g. methyl or ethyl.

Suitable salts of acrylic acid or methacrylic acid are, for example, (C_1 - C_4 alkyl) $_4$ ammonium or (C_1 - C_4 alkyl) $_3$ NH salts, e.g. the tetramethyl-, tetraethyl-, trimethyl-ammonium or triethyl-ammonium salt, the trimethyl-2-hydroxyethylammonium or triethyl-2-hydroxyethyl-ammonium salt, the dimethyl-2-hydroxyethylammonium or diethyl-2-hydroxyethylammonium salt.

Suitable acrylic acid or methacrylic acid C_1 - C_{24} alkyl esters are esterified, for example, by methyl, ethyl, n-butyl, isobutyl, tert-butyl, 2-ethylhexyl, isobornyl, isodecyl, lauryl, myristyl, stearyl or behenyl.

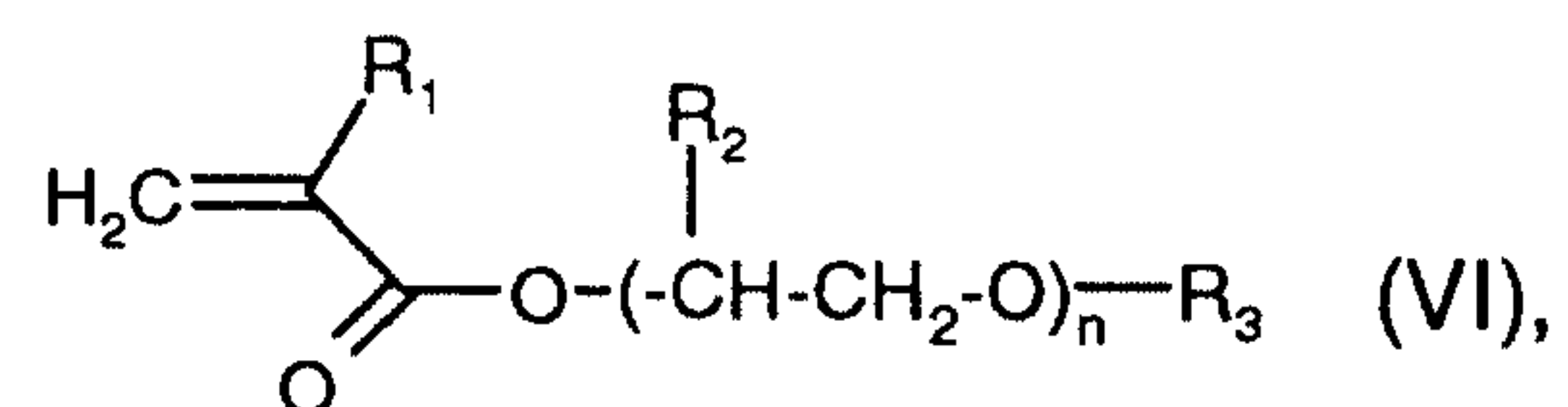
Examples of acrylic acid and methacrylic acid mono- or di- C_1 - C_4 alkylamino- C_2 - C_4 alkyl esters are acrylic acid or methacrylic acid 2-monomethylaminoethyl ester, acrylic acid or methacrylic acid 2-dimethylaminoethyl ester or the corresponding 2-monoethylaminoethyl ester or 2-diethylaminoethyl ester and the acrylic acid or methacrylic acid 2-tert-butyl-aminoethyl ester.

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Examples of acrylic acid and methacrylic acid hydroxy-C₂-C₄alkyl esters are acrylic acid or methacrylic acid 2-hydroxyethyl ester (HEA, HEMA) or acrylic acid or methacrylic acid 2-hydroxypropyl ester (HPA, HPMA).

Examples of acrylic acid and methacrylic acid silyloxy-C₂-C₄alkyl esters are acrylic acid or methacrylic acid 2-trimethylsilyloxyethyl ester (TMS-HEA, TMS-HEMA). Examples of acrylic acid or methacrylic acid (C₁-C₄alkyl)₃silyl-C₂-C₄alkyl esters are acrylic acid or methacrylic acid 2-trimethylsilylethyl ester or acrylic acid or methacrylic acid 3-trimethylsilyl-n-propyl ester.

Acrylic or methacrylic acid esters containing poly-C₂-C₄alkylene glycol ester groups, which may themselves be esterified by substituted C₁-C₂₄alkoxy groups, correspond to the formula:



wherein R₁ and R₂ are each independently of the other hydrogen or methyl and R₃ is C₁-C₂₄-alkyl, e.g. methyl, ethyl, n- or iso-propyl, n-, iso-, or tert-butyl, n- or neo-pentyl, lauryl, myristyl or stearyl, or aryl-C₁-C₂₄alkyl, e.g. benzyl or phenyl-n-nonyl, and C₁-C₂₄alkylaryl or C₁-C₂₄alkylaryl-C₁-C₂₄alkyl.

Examples of acrylic acid and methacrylic acid heterocyclyl-C₂-C₄alkyl esters are acrylic acid or methacrylic acid 2-(N-morpholinyl, 2-pyridyl, 1-imidazolyl, 2-oxo-1-pyrrolidinyl, 4-methyl-piperidin-1-yl or 2-oxoimidazolidin-1-yl)-ethyl esters.

Examples of the mentioned acrylic acid or methacrylic acid mono- or di-C₁-C₄alkylamides, acrylic acid or methacrylic di-C₁-C₄alkylamino-C₂-C₄alkylamides and acrylic acid or methacrylic acid amino-C₂-C₄alkylamides are N,N-dimethylacrylamide, N,N-dimethyl-(meth)acrylamide, 2-(N,N-dimethylaminoethyl)acrylamide, 2-(N,N-dimethylamino-ethyl)methacrylamide, 2-aminoethylacrylamide and 2-aminoethylmethacrylamide.

The indices x and y define the number of monomer units in the blocks A and B, one value of x and y being zero and the other value being an integer greater than zero, or both values x and y being integers greater than zero. For x and y, a number range of from 2 to 1000 is preferred.

In a block copolymer (V) the preferred molecular weight range of the blocks A and B is about from 1000 to 100 000, especially about from 1000 to 50 000. An especially preferred molecular weight range is about from 2000 to 15 000.

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An especially preferred embodiment of the invention relates to a block copolymer (V) wherein

R_1 is C_1 - C_3 alkyl or phenyl;

X is chlorine or bromine and

R_2 is the radical of an acylated, branched, trihydric alcohol, the radical of an acylated, linear or branched, tetrahydric alcohol or the radical of a fully or partially acylated, linear, penta- or hexa-hydric alcohol;

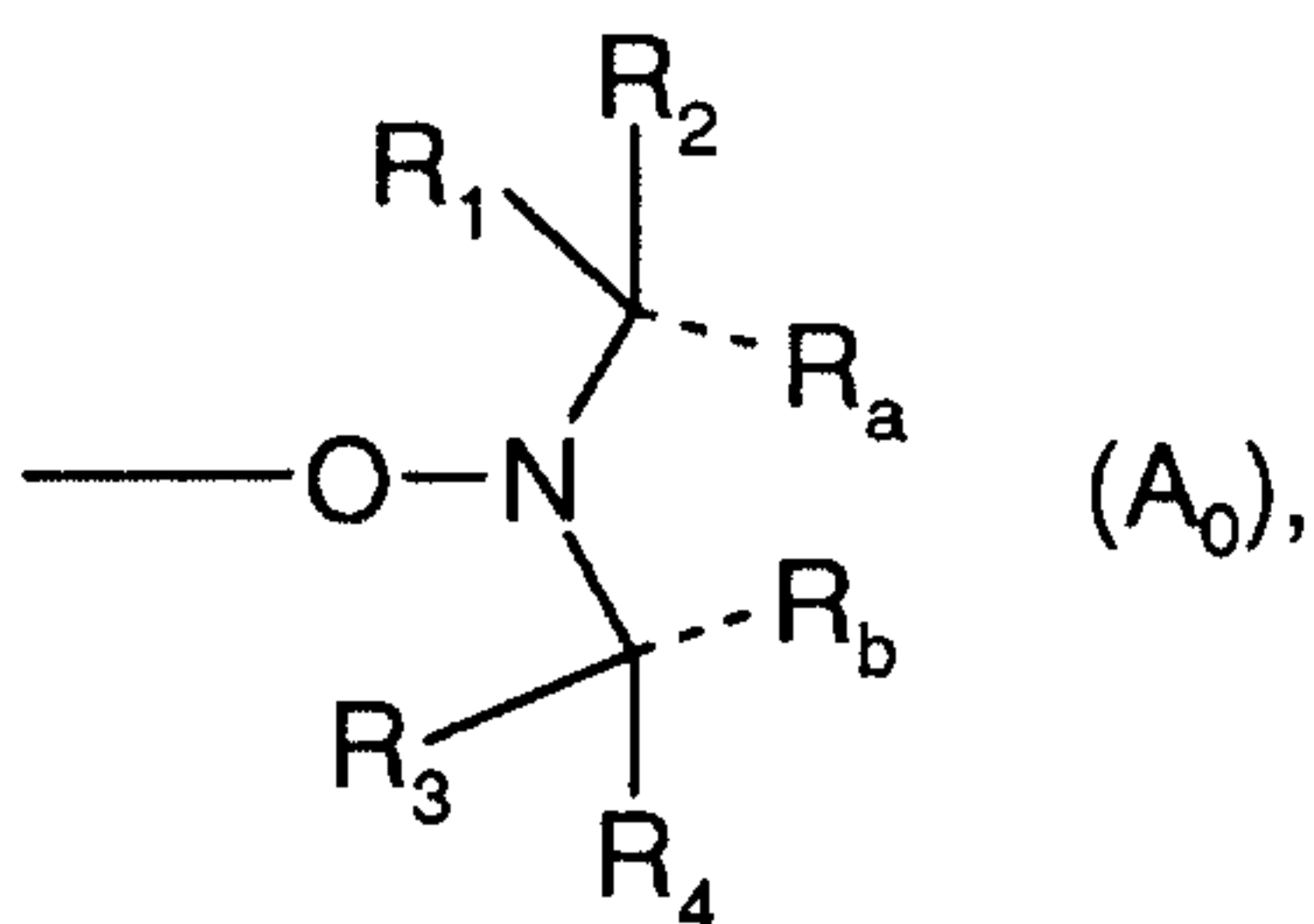
A and B are polymer blocks of ethylenically unsaturated monomer units;

x and y denote integers greater than zero and represent the number of monomer units in the blocks A and B; and

m is three or four.

The invention relates also to all the polymers or block copolymers that can be prepared using α -halocarboxylic acid esters (I) and the ATRP method. The invention relates to all the products-by-process, even where they do not come under the definitions of formula V above or where formula V does not correctly define the structure of the products-by-process.

In a block copolymer (V), X is chlorine, bromine or iodine in the terminal position of the polymer chain. Those terminal groups are obtained using initiators according to the ATRP method. Halogen as the terminal group of a polymer chain can be disadvantageous. It is therefore possible, in a subsequent step, to replace halogen by other suitable terminal groups that are derived from TEMPO (= 2,2,6,6-tetramethylpiperidyl-1-oxides) and derivatives thereof and have a structure of the following partial formula:



wherein

one of R_1 and R_2 is C_1 - C_7 alkyl and the other is C_1 - C_4 alkyl or C_1 - C_4 alkyl substituted by C_1 - C_4 -alkoxycarbonyl or by C_1 - C_4 alkoxy; or

R_1 and R_2 together with the adjacent carbon atom are C_3 - C_7 cycloalkyl;

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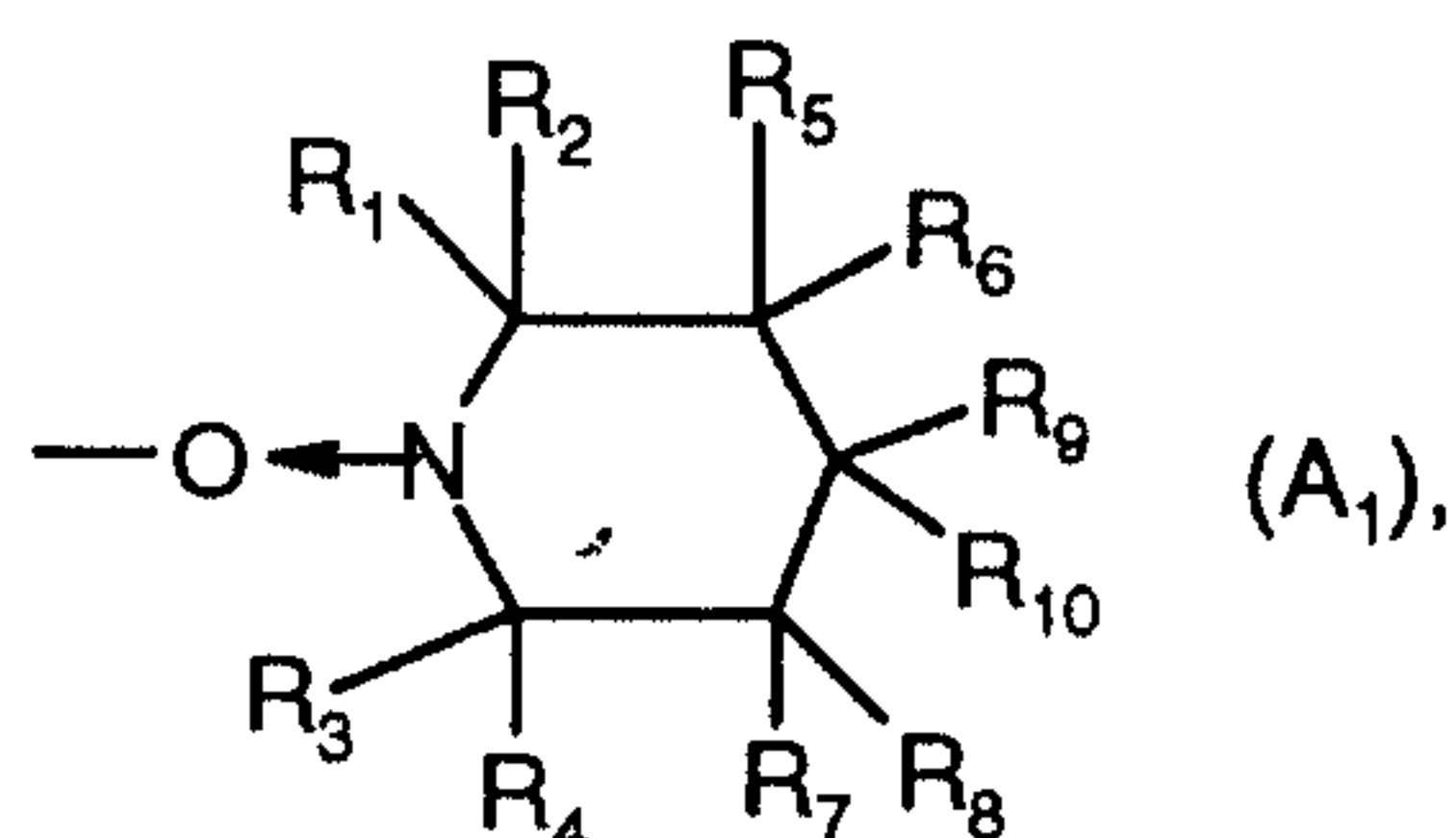
R_3 and R_4 have the meanings of R_1 and R_2 ;

R_a is C_1 - C_4 alkyl, cyano, C_1 - C_4 alkoxycarbonyl, C_1 - C_4 alkanoyloxy, C_1 - C_4 alkanoyloxy- C_1 - C_4 -alkyl, carbamoyl, mono- or di- C_1 - C_4 alkylcarbamoyl, mono- or di-2-hydroxyethylcarbamoyl, amidino, 2-imidazolyl, 1-hydroxy-2-hydroxymethyl-2-propylcarbamoyl or 1,1-dihydroxymethyl-2-hydroxycarbamoyl; and

R_b has the meanings of R_a ; or

R_a and R_b together form a bivalent group and an aliphatic or aromatic heterocyclic group having 5, 6, 7 or 8 ring members, which can contain from 1 to 3 additional hetero atoms from the group nitrogen, oxygen and sulfur.

A preferred embodiment includes a group of the partial formula:



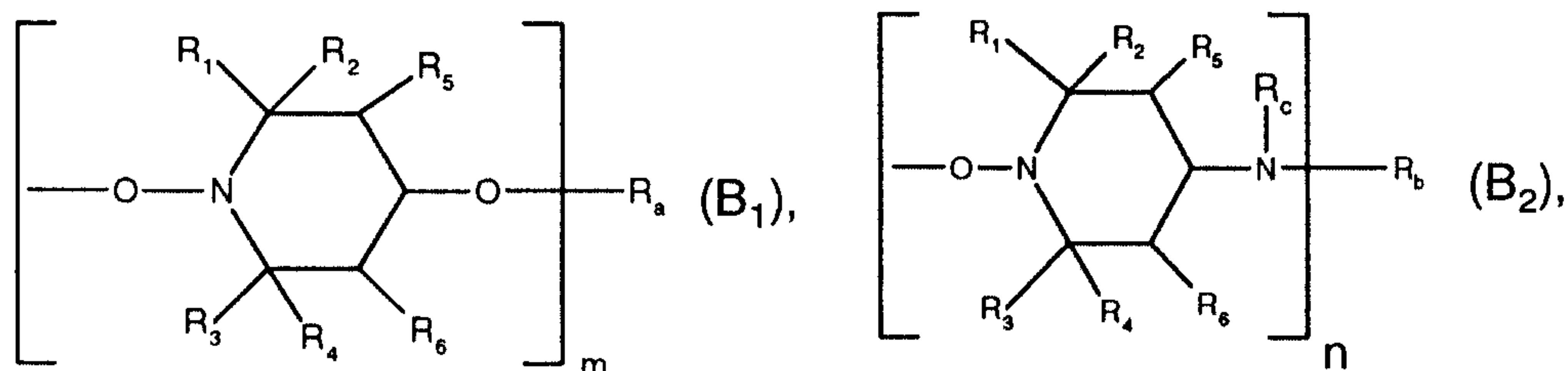
which can be substituted in the 4-position by one or two substituents. In the partial formula A_1

R_1 , R_2 , R_3 and R_4 are C_1 - C_4 alkyl;

R_5 , R_6 , R_7 and R_8 are hydrogen; and

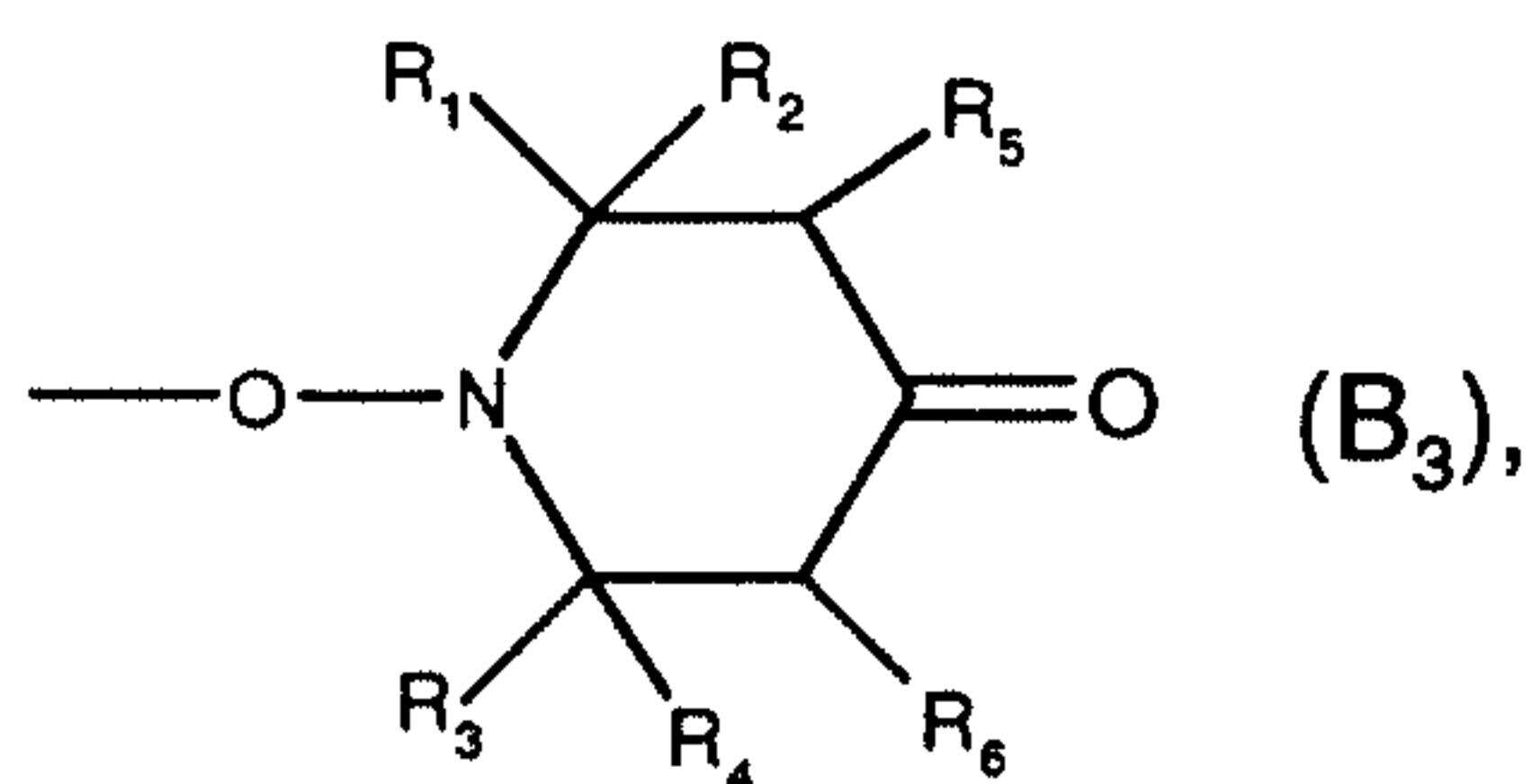
one of the radicals R_9 and R_{10} each independently of the other denotes hydrogen or further substituents.

Representative examples of groups of the partial formula A_1 are the groups



and

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wherein

m is 1;

R_a is hydrogen, C₁-C₁₈alkyl, which can be interrupted by one or more oxygen atoms, 2-cyanoethyl, benzoyl, glycidyl, or the acyl group of an aliphatic C₂-C₁₂carboxylic acid, of a cycloaliphatic C₇-C₁₅carboxylic acid, of an α,β-unsaturated C₃-C₅carboxylic acid or of an aromatic C₇-C₁₅carboxylic acid;

m is 2;

R_a is the bivalent acyl group of an aliphatic C₂-C₃₆dicarboxylic acid;

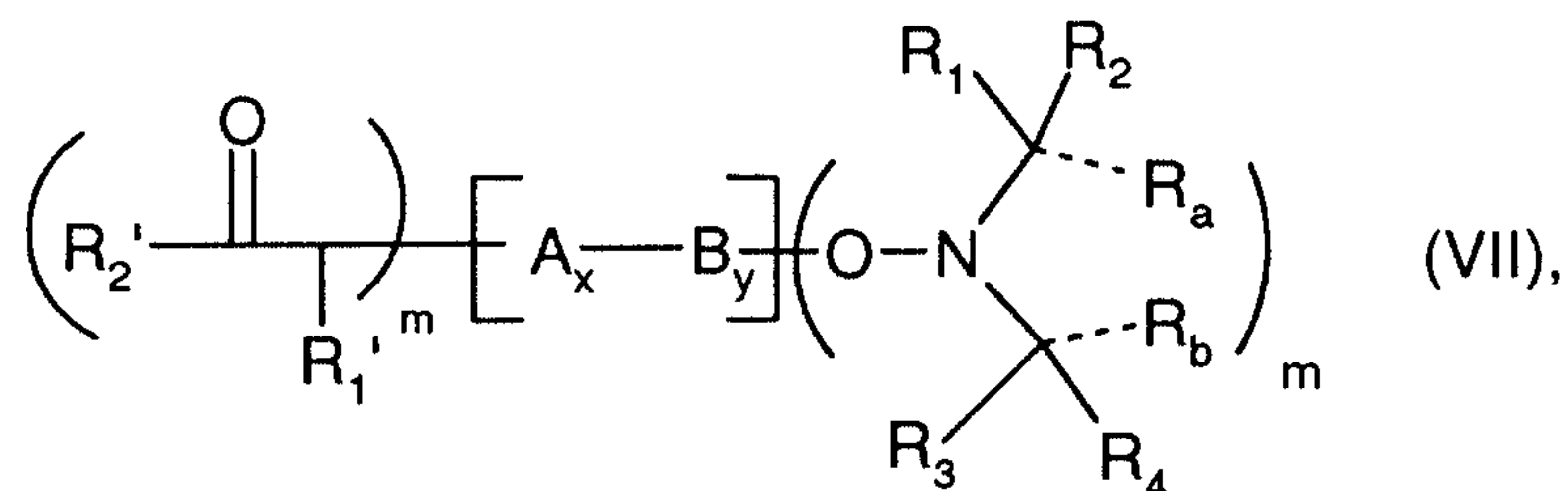
n is 1;

R_b is C₁-C₁₂alkyl, C₅-C₇cycloalkyl, C₇-C₈aralkyl, C₂-C₁₈alkanoyl, C₃-C₅alkenoyl or benzoyl; and

R_c is C₁-C₁₈alkyl, C₅-C₇cycloalkyl, C₂-C₈alkenyl, which can be substituted by cyano, carbonyl or by a carbamide group, glycidyl, or a group of the partial formula -CH₂CH(OH)-Z, -CO-Z or -CONH-Z, wherein Z is hydrogen, methyl or phenyl.

A further preferred embodiment relates to a group of partial formula A₁ wherein one of the groups R₉ and R₁₀ is hydrogen and the other is C₁-C₄alkanoyl or C₁-C₄alkanoylamino.

The invention relates also to an N → O-substituted polymer or block copolymer of formula:



wherein

R₁' is hydrogen, C₁-C₄alkyl, cyano, phenyl or C₁-C₄alkylphenyl;

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R_2 is the radical of an acylated, branched, trihydric alcohol, the radical of a fully or partially acylated, linear or branched tetrahydric alcohol, the radical of a fully or partially acylated, linear, branched or cyclic, penta- or hexa-hydric alcohol, the radical of a fully or partially acylated, linear or cyclic C_4 - C_6 aldose or C_4 - C_6 ketose or the radical of a fully or partially acylated disaccharide;

A and B are polymer blocks of ethylenically unsaturated monomer units;

x and y denote the number of monomer units in the blocks A and B, one value of x and y being zero and the other value being an integer greater than zero, or both values x and y being integers greater than zero;

X is chlorine, bromine or iodine;

m denotes an integer from three to six;

one of R_1 and R_2 is C_1 - C_7 alkyl and the other is C_1 - C_4 alkyl or C_1 - C_4 alkyl substituted by C_1 - C_4 -alkoxycarbonyl or by C_1 - C_4 alkoxy; or

R_1 and R_2 together with the adjacent carbon atom are C_3 - C_7 cycloalkyl;

R_3 and R_4 have the meanings of R_1 and R_2 ;

R_a is C_1 - C_4 alkyl, cyano, C_1 - C_4 alkoxycarbonyl, C_1 - C_4 alkanoyloxy, C_1 - C_4 alkanoyloxy- C_1 - C_4 -alkyl, carbamoyl, mono- or di- C_1 - C_4 alkylcarbamoyl, mono- or di-2-hydroxyethylcarbamoyl, amidino, 2-imidazolyl, 1-hydroxy-2-hydroxymethyl-2-propylcarbamoyl or 1,1-dihydroxy-methyl-2-hydroxycarbamoyl; and

R_b has the meanings of R_a ; or

R_a and R_b together form a bivalent group and an aliphatic or aromatic heterocyclic group having 5, 6, 7 or 8 ring members, which can contain from 1 to 3 additional hetero atoms from the group nitrogen, oxygen and sulfur.

The polymerisation process can be carried out in the presence of water or an organic solvent or mixtures thereof. Additional co-solvents or surfactants, for example glycols or ammonium salts of carboxylic acids, may be added to the reaction mixture. The amount of solvent should be kept as small as possible. The reaction mixture can contain the above-mentioned monomers or oligomers in a concentration of from 1.0 to 99.9 % by weight, preferably from 5.0 to 99.9 % by weight, especially from 50.0 to 99.9 % by weight, based on the monomer content in the polymerisate.

Suitable organic solvents include alkanes (hexane, heptane, octane, isooctane), hydrocarbons (benzene, toluene, xylene), halogenated hydrocarbons (chlorobenzene),

alkanols (methanol, ethanol, ethylene glycol, ethylene glycol monomethyl ether), esters (ethyl acetate) or ethers (diethyl ether, dibutyl ether, ethylene glycol dimethyl ether, tetrahydrofuran) or mixtures thereof.

When using water as solvent, it is possible to add to the reaction mixture a water-miscible or hydrophilic solvent. In doing so, care should be taken to ensure that during the polymerisation reaction the reaction mixture remains in a single homogeneous phase and no precipitation or phase separation occurs. Suitable co-solvents are selected from the group of aliphatic alcohols, glycols, ethers, glycol ethers, pyrrolidines, N-alkylpyrrolidinones, polyethylene glycols, polypropylene glycols, amides, carboxylic acids and salts thereof, esters, organosulfides, sulfoxides, sulfones, alcohol derivatives, hydroxyether derivatives, e.g. butylcarbitol or Cellosolve, amino-alcohols, ketones, derivatives and mixtures thereof, e.g. methanol, ethanol, propanol, dioxane, ethylene glycol, propylene glycol, diethylene glycol, glycerol, dipropylene glycol, tetrahydrofuran and other water-soluble or water-miscible solvents or mixtures thereof.

Hydrophilic monomers, polymers and copolymers can be separated from the reaction mixture using customary processes, for example by distillation, precipitation, extraction, alteration of the pH range or other customary methods of separation. The temperature range for the polymerisation reaction is from about 50°C to about 180°C, preferably about from 80°C to 150°C.

The oxidisable transition metal complex catalyst that can be used in the ATRP process is in the form of an oxidisable complex ion in the lower state of a redox system. Preferred examples of such redox systems are composed of elements of groups V(B), VI(B), VII(B), VIII, IB and IIB of the Periodic Table, e.g. redox systems of $\text{Cu}^+/\text{Cu}^{2+}$, Cu^0/Cu^+ , $\text{Fe}^0/\text{Fe}^{2+}$, $\text{Fe}^{2+}/\text{Fe}^{3+}$, $\text{Cr}^{2+}/\text{Cr}^{3+}$, $\text{Co}^+/\text{Co}^{2+}$, $\text{Co}^{2+}/\text{Co}^{3+}$, Ni^0/Ni^+ , $\text{Ni}^+/\text{Ni}^{2+}$, $\text{Ni}^{2+}/\text{Ni}^{3+}$, $\text{Mn}^0/\text{Mn}^{2+}$, $\text{Mn}^{2+}/\text{Mn}^{3+}$, $\text{Mn}^{3+}/\text{Mn}^{4+}$ or $\text{Zn}^+/\text{Zn}^{2+}$. The transition metal or transition metal cation in the oxidisable transition metal complex catalyst is converted from the lower state of oxidation to a higher state of oxidation. In a preferred embodiment of the process, a Cu(I) complex catalyst salt is converted to the corresponding Cu(II) state of oxidation.

The oxidisable transition metal complex catalyst that can be used in the ATRP process can be prepared in a separate preliminary step or preferably *in situ* from the ligands and a metal salt, e.g. Cu(I)Cl, which is then converted to the complex compound by the addition of the ligand-former, e.g. ethylenediamine, EDTA, Me₆TREN or PMDETA.

The ionic charges are balanced by anionic ligands known from transition metal complex chemistry, e.g. hydride ions (H^-) or anions of inorganic or organic acids, e.g. F^- , Cl^- , Br^- or

I^- , fluorine complexes of the type BF_4^- , PF_6^- , SbF_6^- or AsF_6^- , anions of oxygen acids, alcoholates or acetylides or anions of the cyclopentadiene anion type.

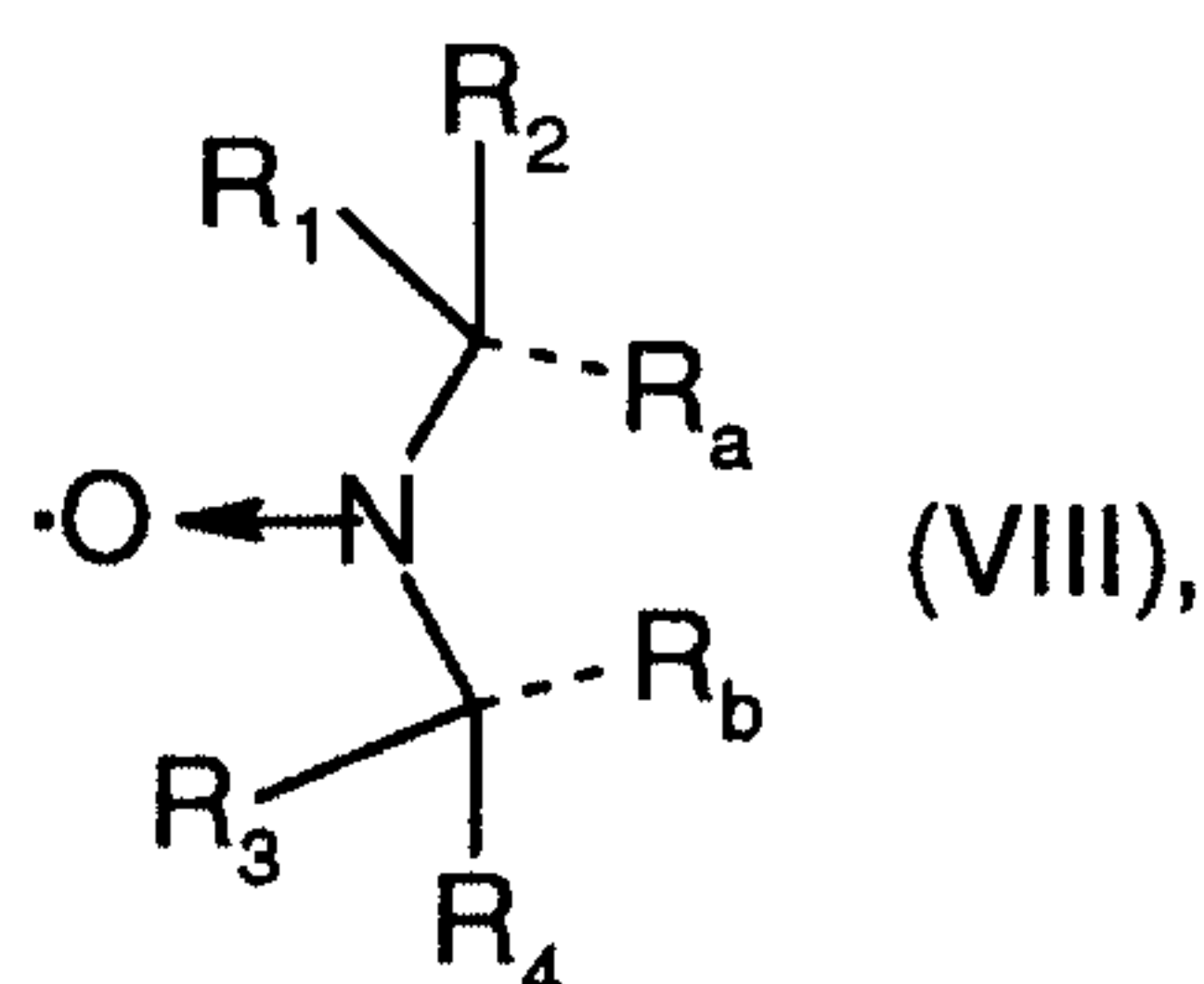
Anions of oxygen acids include, for example, sulfate, phosphate, perchlorate, perbromate, periodate, antimonate, arsenate, nitrate, carbonate, anions of C_1 - C_8 carboxylic acids, e.g. formate, acetate, propionate, butyrate, benzoate, phenylacetate, mono-, di- or tri-chloro-acetate or -fluoroacetate, sulfonates, e.g. mesylate, ethanesulfonate, propanesulfonate or n-butanesulfonate, trifluoromethanesulfonate (triflate) or benzenesulfonate or benzyl-sulfonate, which can be substituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy or by halogen, especially by fluorine, chlorine or by bromine, e.g. tosylate, brosylate, p-methoxy- or p-ethoxy-benzenesulfonate, pentafluorobenzenesulfonate or 2,4,6-triisopropylbenzenesulfonate, phosphonates, e.g. methyl-, ethyl-, n-propyl- or n-butyl-phosphonate, phenylphosphonate, p-methylphenylphosphonate or benzylphosphonate, and C_1 - C_{12} alcoholates, e.g. methanolate or ethanolate.

Neutral and anionic ligands can be present up to the preferred coordination number, especially four, five or six. Negative total charges are balanced by cations, for example monovalent cations, e.g. Na^+ , K^+ , NH_4^+ or $(C_1$ - C_4 alkyl) $_4N^+$.

Suitable neutral ligands are known from transition metal complex chemistry. They are coordinated with the coordination centre with emphasis on different types of bond, e.g. σ , π , μ , η bonds or combinations thereof up to the preferred coordination number of the complex cation. Suitable ligands are selected from the group comprising aqua (H_2O), amino, nitrogen, carbon monoxide, nitrosyl, phosphines, e.g. $(C_6H_5)_3P$, $(iso-C_3H_7)_3P$, $(C_5H_9)_3P$ or $(C_6H_{11})_3P$, amines, e.g. ethylenediamine, ethylenediaminetetraacetate (EDTA), N,N-dimethyl-N',N'-bis(2-dimethylaminoethyl)ethylenediamine (Me_6TREN), catechol, N,N'-dimethyl-1,2-phenyldiamine, 2-(methylamino)phenol, 3-(methylamino)-2-butanol, N,N'-bis(1,1-dimethylethyl)-1,2-ethanediamine or N,N,N',N'',N''-pentamethyldiethyltri-amine (PMDETA), C_1 - C_8 glycols or glycerides, e.g. ethylene glycol or propylene glycol or derivatives thereof, e.g. di-, tri- or tetra-glymes, and monodentate or bidentate heterocyclic e^- donor ligands.

Heterocyclic e^- donor ligands are derived, for example, from unsubstituted or substituted hetero-arenes from the group comprising furan, thiophene, pyrrole, pyridine, bis-pyridine, picolyimine, γ -pyran, γ -thiopyran, phenanthroline, pyrimidine, bis-pyrimidine, pyrazine, indole, coumarin, thionaphthene, carbazoles, dibenzofuran, dibenzothiophene, pyrazole, imidazole, benzimidazole, oxazole, thiazole, bis-thiazole, isoxazole, isothiazole, quinoline, bisquinoline, isoquinoline, bisisoquinoline, acridine, chroman, phenazines, phenoxazines, phenothiazines, triazines, thianthrene, purine, bis-imidazole and bisoxazole.

Following the polymerisation reaction, the polymerisate (V) can be isolated or reacted, preferably *in situ*, with an N → O compound of formula



which corresponds to the group of partial formula A₀ and wherein R₁ - R₄ and R_a and R_b are as defined above, and the N → O-substituted polymer or block copolymer (VII) prepared. Isolation of the polymerisate can be carried out, for example, according to known methods, for example distillation and removal of unreacted monomers by filtration.

The invention relates also to the use of a polymer or block copolymer (V) in the preparation of polymers or block copolymers (VII) wherein •X is replaced by an open-chain or cyclic group R'R''N-O•.

After the substitution of the polymerisate by the N→O compound (VIII), the transition metal complex catalyst is separated off, the solvent is removed by evaporation or the N→O-group-substituted polymer (VII) is precipitated from a suitable liquid phase, and the polymer is filtered off and washed and then dried.

The elimination of the leaving group -X, e.g. halogen, and the substitution of the polymerisate by the N → O compound (VIII) are carried out, for example, by dissolving the polymerisate (V) in a solvent and adding the N→O compound (VIII). The reaction can be carried out in a temperature range of from room temperature to the boiling temperature of the reaction mixture, preferably from room temperature to 100°C.

Since the polymerisation and subsequent derivatisation with an N→O compound (VIII) according to the ATRP method have the characteristics of a "living" polymerisation reaction, it is possible to start and end the polymerisation reaction as desired. The block copolymers (V) and (VII) obtainable according to the process have low polydispersity. It is preferable to obtain a polydispersity of from 1.01 to 2.2, preferably from 1.01 to 1.9, especially from 1.01 to 1.5.

N → O compounds (VIII) are known. They are commercially available or can be prepared according to the processes mentioned in U.S. Patent Specifications 5 204 473 and 4 581 429 and the publications cited therein.

The ATRP process and its various advantages are described, for example, in the publication by K. Matyjaszewski in ACS Symp. Ser. Vol. 685 (1998), pp. 2-30. The polymers and copolymers can be processed further according to customary processes and in most cases can be used without further purification steps. This is advantageous if the batches are to be scaled-up with a view to industrial application.

The invention relates also to all N \rightarrow O-substituted polymers or block copolymers that can be prepared using α -halocarboxylic acid esters (I), an N \rightarrow O compound of formula VIII and the ATRP method. The invention relates to all products-by-process, even where they do not come under the definitions of formula VII above or where formula VII does not correctly define the structure of the products-by-process.

The invention relates also to a polymer composition comprising a polymer or block copolymer (V), wherein R₁, R₂, A, B, x, y and m are as defined, and additives customarily present in polymer compositions.

The invention relates also to polymer compositions comprising a polymer or block copolymer (V) in admixture with an N \rightarrow O-substituted polymer or block copolymer (VII) and additives customarily present in polymer compositions.

Such additives can be added in small amounts, e.g. UV absorbers or light stabilisers, for example from the series of hydroxyphenylbenzotriazoles, hydroxyphenylbenzophenones, oxalamides and hydroxyphenyl-s-triazines. Especially suitable are light stabilisers from the group of so-called sterically hindered amines (HALS), e.g. of the 2-(2-hydroxyphenyl)-1,3,5-triazine or 2-hydroxyphenyl-2H-benzotriazole type. Examples of light stabilisers of the 2-(2-hydroxyphenyl)-1,3,5-triazine type are known from the patent literature, e.g. US-A-4 619 956, EP-A-434 608, US-A-5 198 498, US-A-5 322 868, US-A-5 369 140, US-A-5 298 067, WO-94/18278, EP-A-704 437, GB-A-2 297 091 or WO-96/28431.

The compositions may comprise further customary additives, for example fillers, e.g. calcium carbonate, silicates, glass or glass fibre material, talcum, kaolin, mica, barium sulfate, metal oxides and hydroxides, carbon black, graphite, powdered wood and powdered or fibrous material of other natural products, synthetic fibres, plasticisers, lubricants, emulsifiers, pigments, flow auxiliaries, catalysts, optical brighteners, flame-retardants, antistatics and blowing agents.

The composition can contain the mentioned polymers in concentrations of about from 0.01 to 99.0 % by weight, preferably from 0.1 to 95 % by weight, especially from 1.0 to 90.0 % by

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weight, more especially from 5.0 to 80.0 % by weight, based on the monomer content of the composition.

The invention relates also to a polymer composition comprising

- a) a polymer or block copolymer (V),
wherein R_1 , R_2 , A, B, x, y and m are as defined above; and
- b) a further polymer or oligomer of formula



wherein

A and B are polymer blocks of ethylenically unsaturated monomer units and x and y denote the number of monomer units in the blocks A and B, one value of x and y being zero and the other value being an integer greater than zero, or both values x and y being integers greater than zero.

The invention relates also to a polymer composition comprising

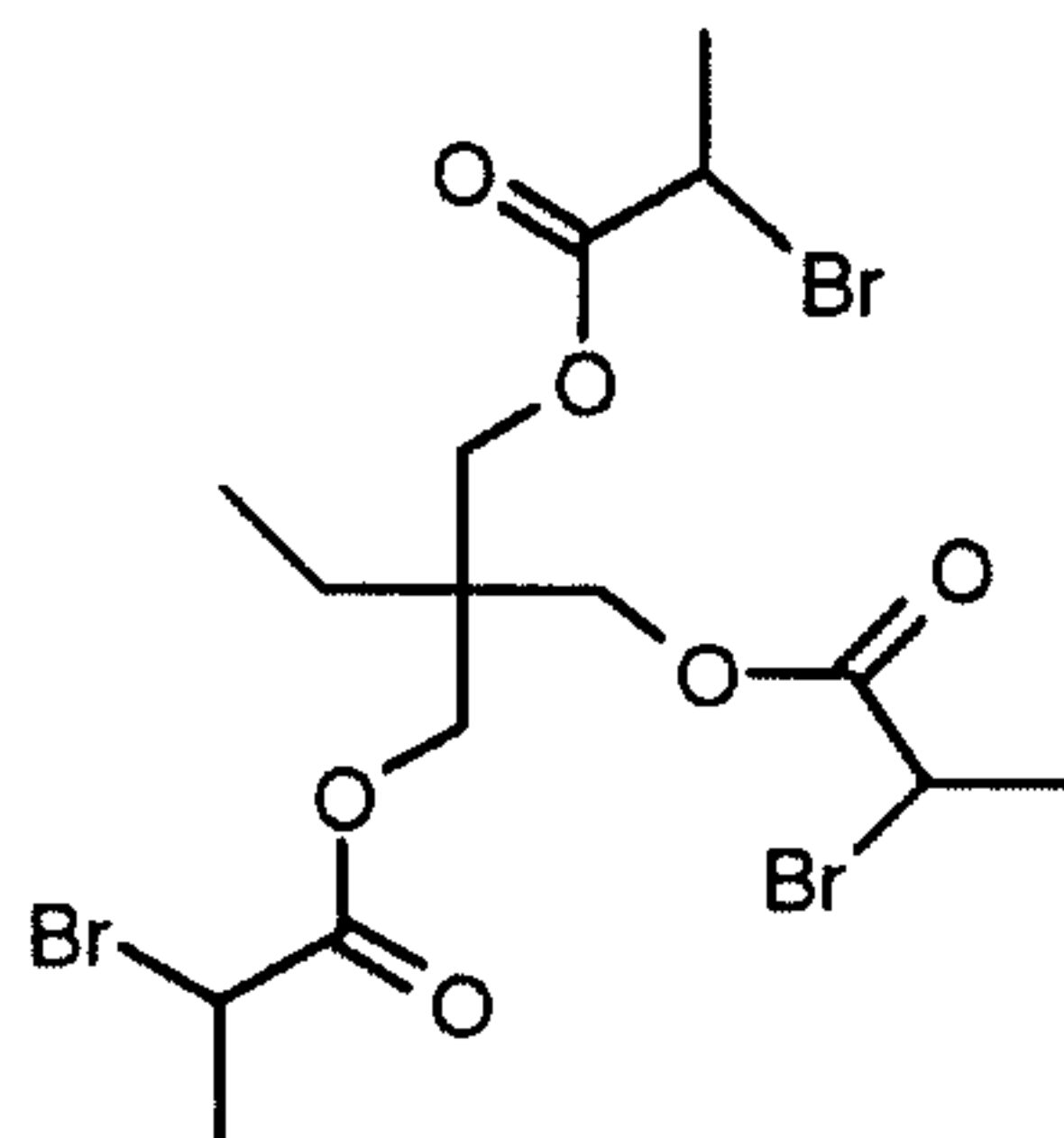
- a') an N \rightarrow O-substituted polymer or block copolymer (VII) and
- b') a further polymer or oligomer (IX).

The compositions can contain the mentioned customary additives and the polymer or oligomer components a) and b), or a') and b'), in concentrations of about from 0.01 to 99.0 % by weight, preferably from 0.1 to 95 % by weight, especially from 1.0 to 90.0 % by weight, more especially from 5.0 to 80.0 % by weight, based on the monomer content of the composition.

The polymers and the compositions according to the present invention can be used for a very wide variety of technical applications, for example as adhesives, detergent adjuvants, detergents, dispersants, emulsifiers, surfactants, antifoams, tackifiers, corrosion inhibitors, viscosity improvers, lubricants, flow improvers, thickeners, crosslinking agents, as additives for water treatment, electronic materials, paints and lacquers, coatings, inks, photo developers, superabsorbents, cosmetics, preservatives, or as biocides or modifiers and adjuvants for asphalt, textiles, ceramics and wood.

ExamplesExample 1

Preparation of the compound:



Starting materials:

26.84 g (0.2 mol) of 1,1,1-(tris-hydroxymethyl)-propane (Fluka, purum); 136.4 g (0.6 mol) of 2-bromopropanoyl bromide (Fluka, pract. 95%); 47.5 g (0.6 mol) of pyridine (Fluka, puriss. p.a.); 500 ml of THF (Fluka, puriss. p.a.); 1500 ml sulfonating flask having a reflux condenser and mechanical stirring apparatus.

A solution of 2-bromopropanoyl bromide in 180 ml of THF is added dropwise over the course of 45 minutes, with cooling to 10-15°C, to a solution of 1,1,1-(tris-hydroxymethyl)-propane and pyridine in 320 ml of THF (slightly exothermic reaction). The reaction mixture is then heated at 60°C for 3 hours and then cooled and filtered. Dilution is carried out with 500 ml of tert-butyl methyl ether and extraction is carried out twice with 150 ml of water each time until the reaction becomes neutral. The organic phase is dried over Na₂SO₄, filtered and concentrated completely in a rotary evaporator. Crude yield: 116.95 g. The crude product is purified by column chromatography (silica gel, toluene as eluant): Yield of pure product: 70.48 g (65 %).

Elemental analysis:

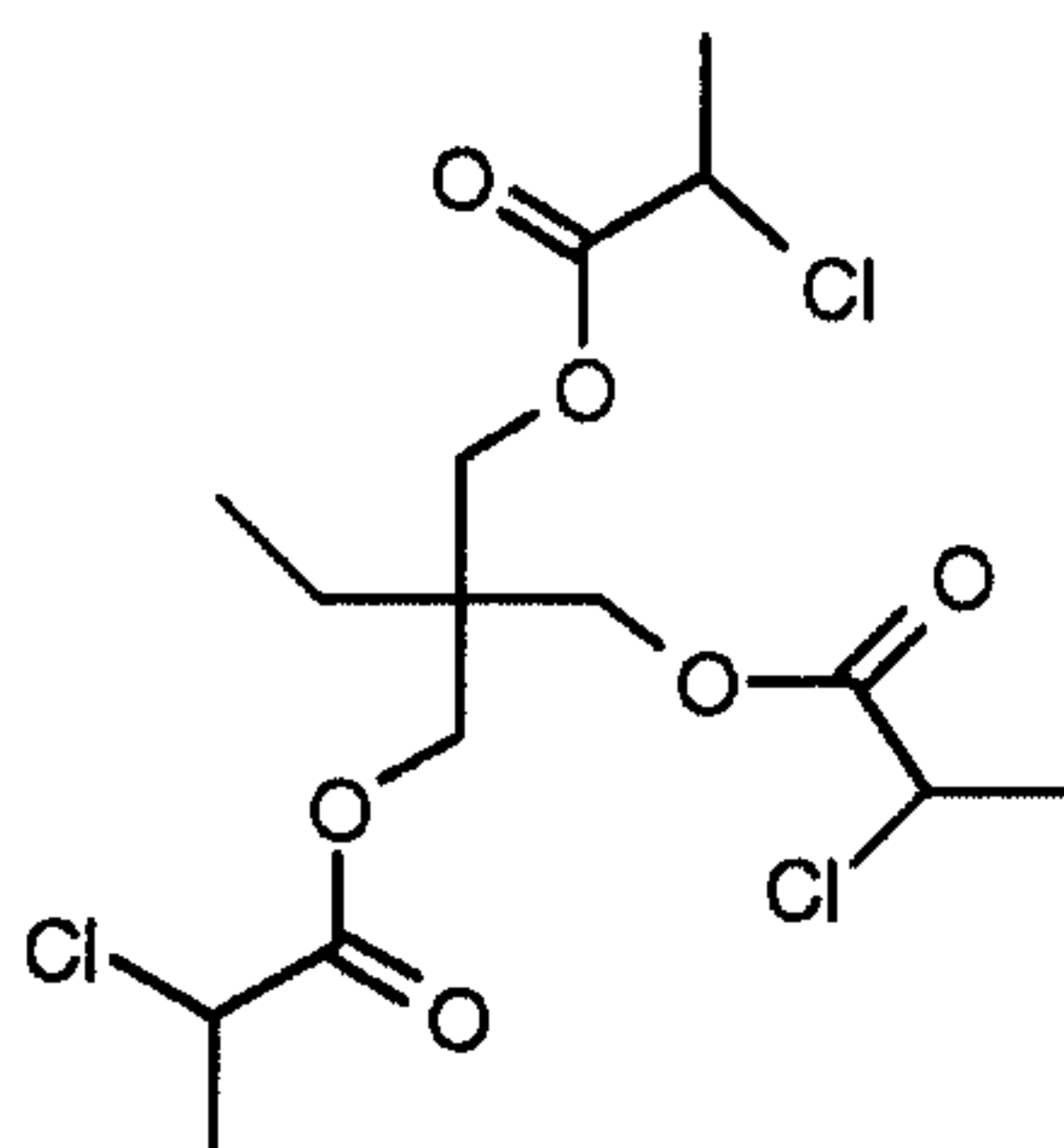
C	H	Br
33.69 ¹	4.30 ¹	44.47 ¹
33.63 ²	4.22 ²	44.60 ²

¹)calculated; ²)found

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Example 2

Preparation of the compound



Starting materials:

26.84 g (0.2 mol) of 1,1,1-(tris-hydroxymethyl)-propane (Fluka, purum); 76.18 g (0.6 mol) of 2-chloropropanoyl chloride (Fluka, pract. 97 %); 47.5 g (0.6 mol) of pyridine (Fluka, puriss. p.a.); 500 ml of THF (Fluka, puriss. p.a.); 1500 ml sulfonating flask having a reflux condenser and mechanical stirring apparatus.

Analogously to Example 1, 66.32 g (82 %) of pure product are obtained.

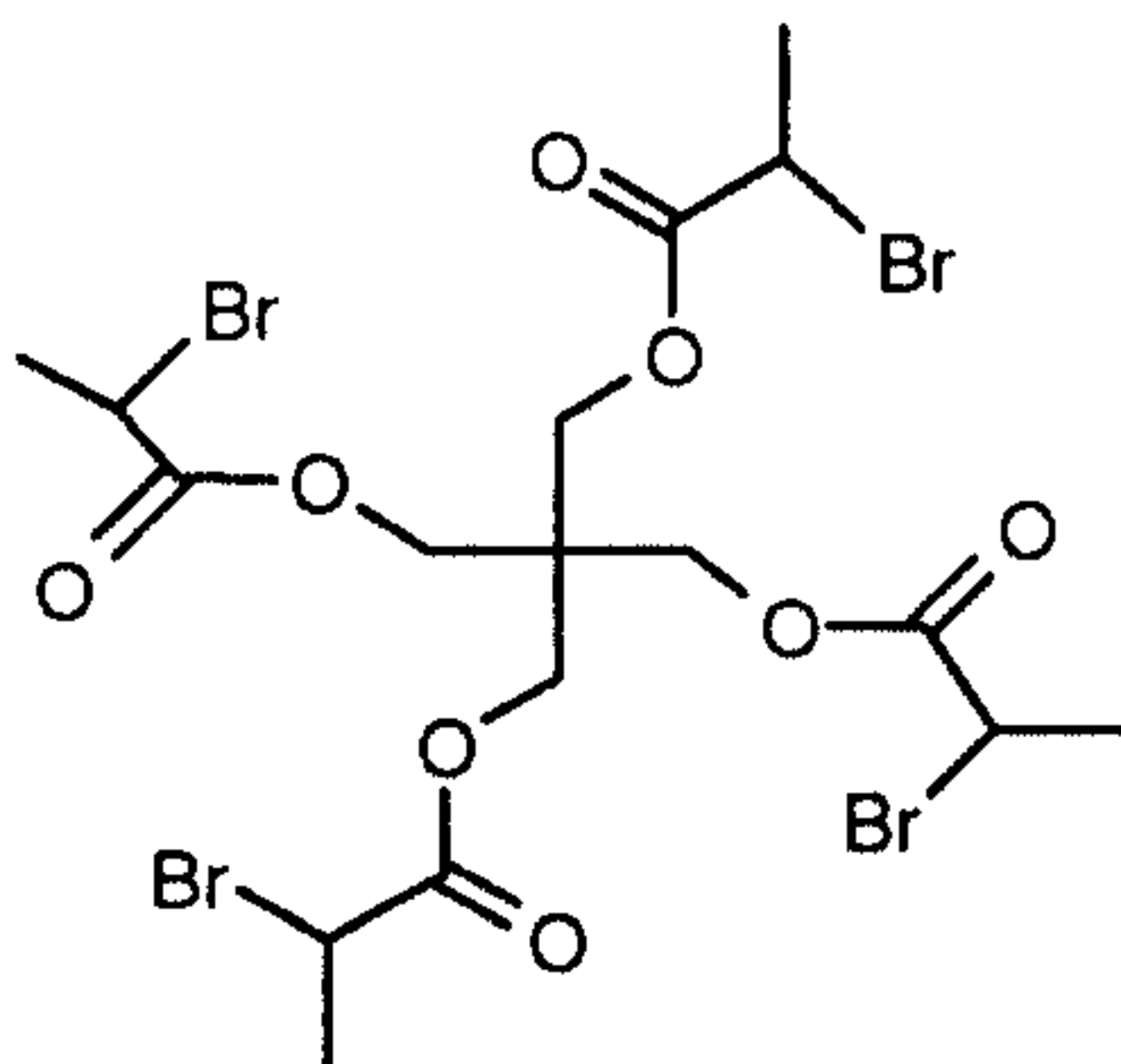
Elemental analysis:

C	H	Cl
44.41 ¹	5.71 ¹	26.21 ¹
44.09 ²	5.34 ²	26.45 ²

¹)calculated; ²)found

Example 3

Preparation of the compound



Starting materials:

27.20 g (0.2 mol) of pentaerythritol (Fluka, purum); 181.7 g (0.8 mol) of 2-bromopropanoyl

bromide (Fluka, pract. 97 %); 63.2 g (0.8 mol) of pyridine (Fluka, puriss. p.a.); 500 ml of THF (Fluka, puriss. p.a.); 1500 ml sulfonating flask having a reflux condenser and mechanical stirring apparatus.

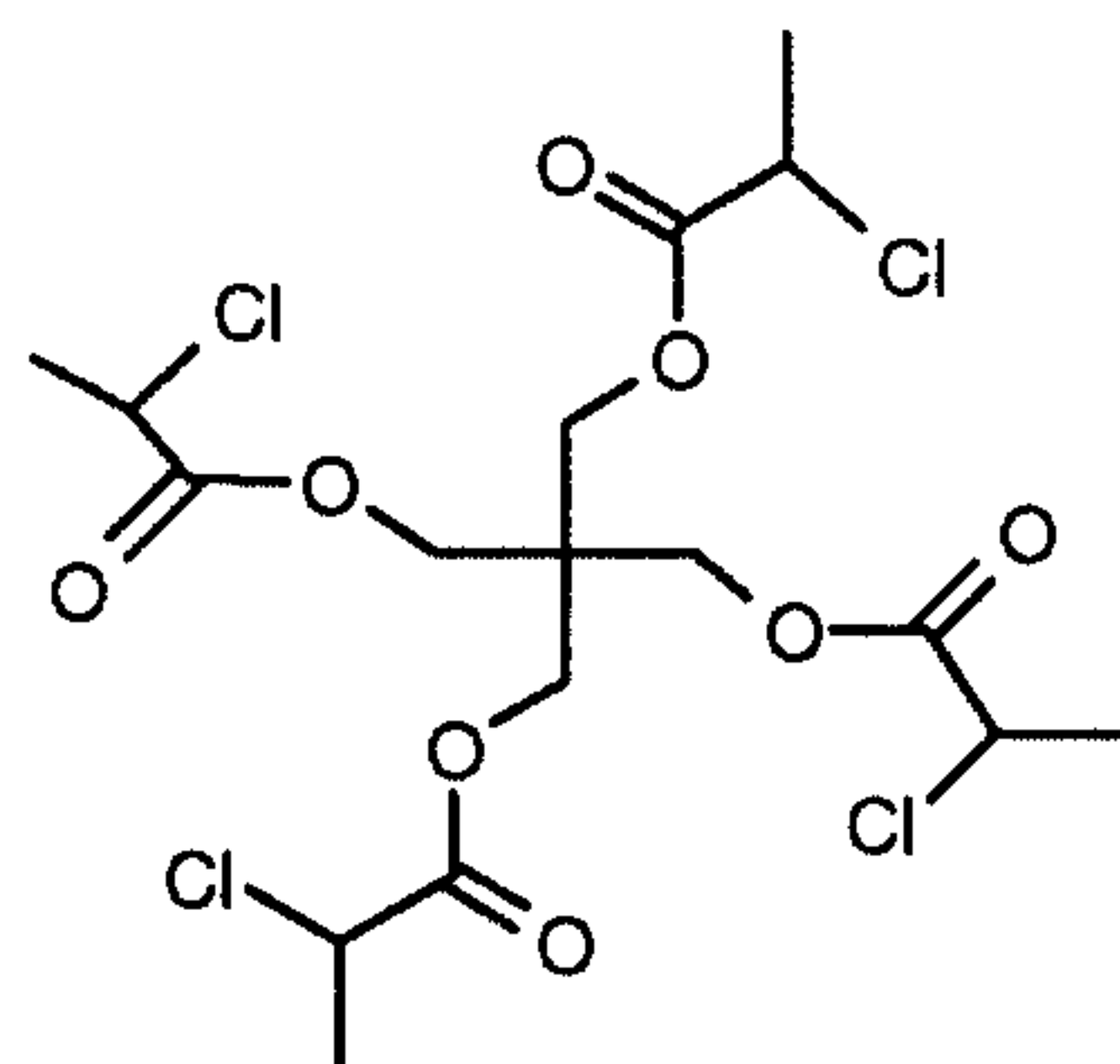
The procedure is analogous to Example 1. The crude product (150 mg) is purified by recrystallisation from isopropanol. 35.48 g (26 %) of pure product are obtained. Melting point: 95°C;

Elemental analysis:

C	H	Br
30.21 ¹	3.58 ¹	47.30 ¹
30.70 ²	3.61 ²	45.28 ²
¹ calculated; ² found		

Example 4

Preparation of the compound



Starting materials:

2.72 g (0.02 mol) of pentaerythritol (Fluka, purum); 10.15 g (0.08 mol) of 2-chloropropanoyl chloride (Fluka, pract. 97 %); 6.32 g (0.08 mol) of pyridine (Fluka, puriss. p.a.); 50 ml of THF (Fluka, puriss. p.a.); 100 ml sulfonating flask having a reflux condenser and mechanical stirring apparatus.

Analogously to Example 3 (1/10 batch), 6.10 g (48 %) of pure product are obtained; melting point: 84°C.

Elemental analysis:

C	H	Cl
40.72 ¹	4.82 ¹	28.28 ¹
40.98 ²	4.60 ²	28.45 ²

¹)calculated; ²)found

Example 5:

a) Preparation of a "3-star" polymerisate having a low molecular weight

Starting materials:

30.76 g (0.24 mol) of n-butyl acrylate (Fluka, purum); 0.57 g (4.0 mmol) of Cu(I)Br (Fluka, purum washed with acetic acid and dried); 0.52 g (3.0 mmol) of N,N,N',N'',N''-penta-methyldiethylenetriamine (Fluka, purum); 10.78 g (20.0 mmol) of 1-(2-bromopropionyl-oxy)-2-bis(2-bromopropionyloxymethyl)butane (initiator Example 1); 30.76 g of dioxane (Fluka, puriss. p.a.); 150 ml sulfonating flask having a reflux condenser, mechanical stirrer and dropping funnel; connections for vacuum and N₂.

Cu(I)Br and the monomer n-butyl acrylate are weighed into the reaction vessel, 20 g of dioxane are added and the vessel is degassed several times by evacuation and flushing with N₂. The ligand former PMDETA (N,N,N',N'',N''-pentamethyldiethylenetriamine) is added, and evacuation and flushing with N₂ are effected again. By immersion in an oil bath (85°C), the mixture is heated to 50°C, at which temperature the initiator (Example 1), dissolved in 10.76 g of dioxane, is added rapidly from the dropping funnel. The strongly exothermic polymerisation reaction commences at about 85°C with the temperature rising rapidly. By cooling using an ice bath, the temperature is maintained at 95-100°C. A conversion of 100% is achieved after 20 minutes' polymerisation time (¹H-NMR monitoring), and the reaction mixture is cooled and diluted with 50 ml of dioxane. 30 g of Al₂O₃ (Alox®) are added, and the mixture is stirred for 1 hour and filtered. The polymer solution is concentrated completely *in vacuo* at 80°C in a rotary evaporator. Yield: 39.5 g (95 %).

GPC (THF, PS standards): M_n=1700 (calculated: 2080), M_w=2160, PDI=1.27; MALDI-TOF MS: M_n=2030, M_w=2300, PDI=1.17;

Elemental analysis:

C	H	Br
57.27 ¹	8.07 ¹	11.54 ¹
57.26 ²	8.26 ²	11.44 ²

¹)calculated; ²)found

b) Replacement of the Br terminal groups by 4-benzoyloxy-TEMPO

Starting materials:

5.0 g (12.0 mmol Br terminal groups) of Br-substituted polymer Example 5 a); 3.31 g (12.0 mmol) of 4-benzoyloxy-TEMPO; 0.86 g (6.0 mmol) of CuBr; 2.07 g (12.0 mmol) of PMDETA; 7.5 ml of dioxane

In a 25 ml three-necked flask having a magnetic stirrer, the mentioned reagents (without the ligand former PMDETA) are mixed under N₂, and the oxygen is expelled by evacuation and flushing with N₂ three times. The ligand former PMDETA is then added at room temperature and the mixture is heated in an oil bath to 65°C, during which the mixture rapidly changes colour from orange via black to green. The mixture is left to react for a further 4 hours at 65°C and filtered. 10 ml of dioxane and four 5 g portions of aluminium oxide are then added (to adsorb the residual copper complex), with stirring each time and filtration through a suction filter each time. The solution is concentrated at 60°C for 2 hours in a rotary evaporator, to yield 6.6 g (90 %) of product.

GPC: M_n= 2172 (calculated: 2290); M_w= 2600; PDI= 1.20; N content: 2.48 %; Br content: <0.3%, which works out as a degree of replacement of more than 97.4 %.

c) Preparation of a "3-star" polymerisate having a relatively high molecular weight

Starting materials:

17.96 g (0.14 mol) of n-butyl acrylate (Fluka, purum); 0.111 g (0.8 mmol) of Cu(I)Br (Fluka, purum washed with acetic acid and dried); 0.139 g (0.8 mmol) of N,N,N',N'',N''-pentamethyldiethylenetriamine (Fluka, purum); 2.10 g (3.9 mmol) of 1-(2-bromopropionyl-oxy)-2-bis(2-bromopropionyloxymethyl)butane (initiator Example 1); 30.76 g of dioxane

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(Fluka, puriss. p.a.); 150 ml sulfonating flask having a reflux condenser, mechanical stirrer and dropping funnel; connections for vacuum and N₂.

Cu(I)Br and 14.0 g of the monomer n-butyl acrylate are weighed into the reaction vessel and the vessel is degassed several times by evacuation and flushing with N₂. The ligand former (N,N,N',N'',N''-pentamethyldiethylenetriamine) is added, and evacuation and flushing with N₂ are effected again. By immersion in an oil bath (85°C), the mixture is heated to 50°C, at which temperature the initiator, dissolved in 3.96 g of residual monomer, is added rapidly from the dropping funnel. The strongly exothermic polymerisation reaction commences at about 85°C, with the temperature rising rapidly. By cooling using an ice bath, the temperature is maintained at a maximum of 105°C. A conversion of 100 % is achieved after 45 minutes' polymerisation time (¹H-NMR monitoring), and the reaction mixture is cooled and diluted with 50 ml of dioxane. 30 g of Alox® are added, and the mixture is stirred for 1 hour and filtered. The polymer solution is concentrated completely *in vacuo* at 80°C in a rotary evaporator. Yield: 18.5 g (92 %).

GPC (THF, PS standards): M_n=4890 (calculated: M_n=5150), M_w=6520, PDI=1.33;

Elemental analysis:

C	H	Br
62.23 ¹	8.90 ¹	4.65 ¹
62.25 ²	8.84 ²	4.43 ²

¹)calculated; ²)found

- d) Preparation of a "3-star" copolymerisate comprising 1st block poly(n-BA) and 2nd block poly-DMAEA

Starting materials:

5.15 g of "3-star" polymerisate having a low molecular weight, Example 5 a); 0.71 g (5 mmol) of 2-dimethylaminoethyl acrylate (DMAEA, BASF, techn.); 72.0 mg (0.5 mmol) of Cu(I)Br (Fluka, purum washed with acetic acid and dried); 87.0 mg (0.5 mmol) of N,N,N',N'',N''-pentamethyldiethylenetriamine (Fluka, purum); 25 ml round-bottomed flask having a magnetic stirrer and septum.

Cu(I)Br, the "3-star" polymerisate having a low molecular weight, Example 5 a), and DMAEA are weighed into the reaction vessel and the vessel is degassed several times

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by evacuation and flushing with N₂. The ligand former PMDETA is added, and evacuation and flushing with N₂ are effected again. By immersion in an oil bath, the mixture is heated to 50°C and is left to react for 30 minutes, conversion of about 100 % (¹H-NMR monitoring) being achieved. The mixture is cooled and diluted with 20 ml of ethyl acetate, 5 g of Al₂O₃ (Alox®) are added, and the mixture is stirred for 30 minutes and filtered. The polymer solution is concentrated completely (1 hour) at 80°C in a rotary evaporator, to yield 5.0 g (85 %) of product.

GPC (THF, PS standards): M_n=5590 (calculated: M_n=5870), M_w=7520, PDI=1.35

Elemental analysis:

C	H	N	Br
61.80 ¹	8.93 ¹	1.19 ¹	4.08 ¹
62.24 ²	8.80 ²	0.87 ²	3.44

¹)calculated; ²)found

- e) Preparation of a "3-star" copolymerisate comprising 1st block poly(n-BA) and 2nd block poly-HEA

Starting materials:

5.15 g of "3-star" polymerisate having a low molecular weight, Example 5 a); 0.58 g (5 mmol) of 2-hydroxyethyl acrylate (DMAEA, BASF, techn.); 72.0 mg (0.5 mmol) of Cu(I)Br (Fluka, purum washed with acetic acid and dried); 87.0 mg (0.5 mmol) of N,N,N',N'',N''-pentamethyldiethylenetriamine (Fluka, purum); 25 ml round-bottomed flask having a magnetic stirrer and septum.

Analogously to Example 5 d), 5.0 g (85 %) of product are obtained.

GPC (THF, PS standards): M_n=6530 (calculated: M_n=5730), M_w=9690, PDI=1.48;

Elemental analysis:

C	H	Br
61.17 ¹	8.70 ¹	4.18 ¹
61.67 ²	8.83 ²	3.42 ²

¹)calculated; ²)found

Example 6:

a) Preparation of a "4-star" polymerisate having a low molecular weight

Starting materials:

15.38 g (0.12 mol) of n-butyl acrylate (Fluka, purum); 0.28 g (2.0 mmol) of Cu(I)Br (Fluka, purum washed with acetic acid and dried); 0.35 g (2.0 mmol) of N,N,N',N'',N''-penta-methyldiethylenetriamine (Fluka, purum); 6.76 g (20.0 mmol) of 1,2,2,3-tetrakis(2-bromopropionyloxymethyl)propane (initiator Example 3); 15.38 g of dioxane (Fluka, puriss. p.a.); 50 ml sulfonating flask having a reflux condenser, mechanical stirrer and dropping funnel; connections for vacuum and N₂.

Analogously to Example 5 a), the reactants are left to react at 90°C, a conversion of about 100 % being obtained after 90 minutes' polymerisation time (¹H-NMR monitoring). 19.9 g (90 %) of pure product are isolated.

GPC (THF, PS standards): M_n= 1770, M_w= 2080, PDI= 1.17 (calculated: M_n= 2210);
MALDI-TOF MS: M_n= 1920, M_w= 2020, PDI= 1.09;

Elemental analysis:

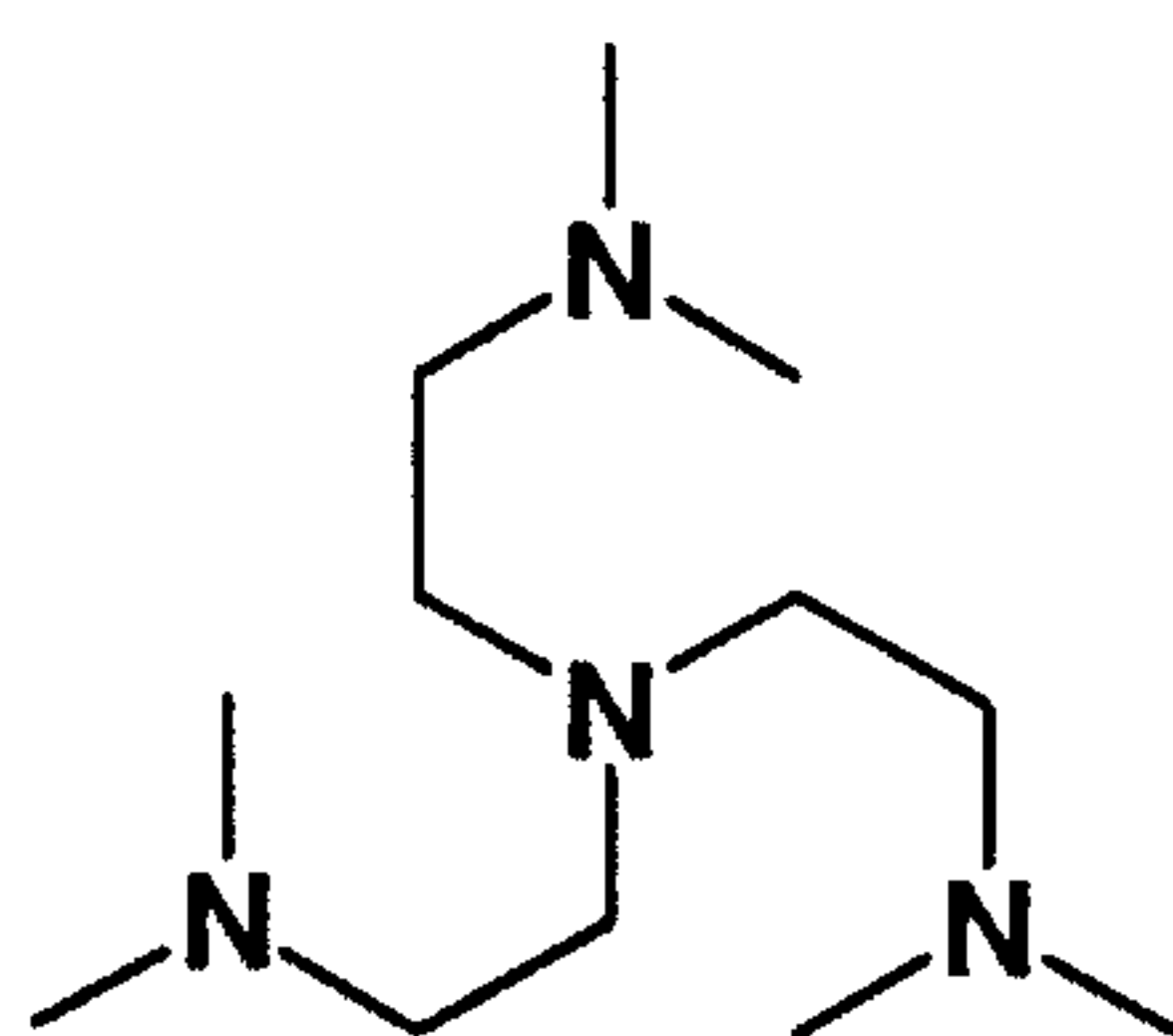
C	H	Br
54.79 ¹	7.65 ¹	14.44 ¹
55.29 ²	7.58 ²	13.26 ²
¹ calculated; ² found		

b) Replacement of the Br terminal groups by 4-hydroxy-TEMPO

Starting materials:

5.0 g (8.3 mmol of Br terminal groups) of Br-substituted polymer Example 6 a); 1.43 g (8.3 mmol) of 4-hydroxy-TEMPO; 1.20 g (8.3 mmol) of CuBr; 1.91 g (8.3 mmol) of Me₆TREN of formula

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(Me₆TREN); 7.0 ml of dioxane

In a 25 ml three-necked flask having a magnetic stirrer, the mentioned reagents (without the ligand former Me₆TREN) are mixed under N₂, and the oxygen is expelled by evacuation and flushing with N₂ three times. The ligand former Me₆TREN is then added at room temperature, during which the mixture changes colour rapidly from orange via black to green and the temperature rises to 50°C. The reagents are left to react for a further 1 hour at room temperature and then filtration is carried out. 10 ml of dioxane and two 5.0 g portions of aluminium oxide are then added (to adsorb the residual copper complex), and the mixture is stirred and filtered through a suction filter. The solution is concentrated at 60°C for 2 hours in a rotary evaporator, to yield 5.2 g (90 %) of product.

GPC: M_n = 2280 (calculated: 2140), M_w = 2630, PDI = 1.15

Elemental analysis:

C	H	N	Br
63.70 ¹	9.36 ¹	2.17 ¹	0.00 ¹
62.45 ²	9.21 ²	1.72 ²	1.13

¹)calculated; ²)found

From the bromine content it is possible to calculate a degree of replacement of 91.5 %.

c) Preparation of a "4-star" polymerisate having a relatively high molecular weight

Starting materials:

269.4 g (2.1 mol) of n-butyl acrylate (Fluka, purum); 1.67 g (12.0 mmol) of Cu(I)Br (Fluka, purum washed with acetic acid and dried); 2.09 g (3.0 mmol) of N,N,N',N'',N''-penta-methyldiethylenetriamine (Fluka, purum); 39.54 g (20.0 mmol) of 1,2,2,3-tetrakis(2-bromopropionyloxymethyl)propane (initiator Example 3); 1000 ml sulfonating flask having a reflux condenser, mechanical stirring apparatus and a dropping funnel; connections for

vacuum and N₂.

Analogously to Example 5 c), a conversion of about 100 % is obtained after 45 minutes' polymerisation time (¹H-NMR monitoring) and, after treatment with Al₂O₃ in ethyl acetate, 297.0 g (96 %) of pure product are isolated.

GPC (THF, PS standards): M_n=5080 (calculated: M_n= 5290), M_w= 6190, PDI= 1.22

Elemental analysis:

C	H	Br
61.07 ¹	8.68 ¹	6.04 ¹
61.10 ²	8.63 ²	5.56 ²
¹)calculated; ²)found		

d) Preparation of a "4-star" copolymerisate comprising 1st block poly(n-BA) and 2nd block poly-DMAEA

Starting materials:

80.0 g of "4-star" polymerisate having a low molecular weight, Example 6 a); 10.74 g (75 mmol) of 2-dimethylaminoethyl acrylate (DMAEA, BASF, techn.); 1.08 g (7.5 mmol) of Cu(I)Br (Fluka, purum washed with acetic acid and dried); 1.23 g (7.5 mmol) of N,N,N',N'',N''-pentamethyldiethylenetriamine (Fluka, purum); 750 ml sulfonating flask having mechanical stirring apparatus and septum.

Cu(I)Br, the "4-star" polymerisate having a low molecular weight, Example 6 a), and DMAEA are weighed into the reaction vessel and the vessel is degassed several times by evacuation and flushing with N₂. The ligand former (N,N,N',N'',N''-pentamethyl-diethylenetriamine) is then added, and evacuation and flushing with N₂ are effected again. By immersion in an oil bath, the mixture is heated to 90°C and left to react for 60 minutes, a conversion of about 100 % being obtained (¹H-NMR monitoring). The mixture is cooled and diluted with 150 ml of ethyl acetate, 80.0 g of Al₂O₃ (Alox®) are added, and the mixture is stirred for 60 minutes and filtered. The polymer solution is concentrated completely (1 hour) at 80°C in a rotary evaporator, to yield 76.6 g (85 %) of

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product.

GPC (THF, PS standards): $M_n=5820$ (calculated: $M_n=5800$), $M_w=7410$, $PDI=1.27$

Elemental analysis:

C	H	N	Br
60.79 ¹	8.74 ¹	1.17 ¹	5.33 ¹
61.36 ²	8.86 ²	1.04 ²	4.16 ²

¹)calculated; ²)found

e) Preparation of a "4-star" copolymerisate comprising 1st block poly(n-BA) and 2nd block poly-HEA

Starting materials:

80.0 g of "4-star" polymerisate having a low molecular weight, Example 6 a); 8.71 g (75 mmol) of 2-hydroxyethyl acrylate (HEA, BASF, techn.); 1.08 g (7.5 mmol) of Cu(I)Br (Fluka, purum washed with acetic acid and dried); 1.23 g (7.5 mmol) of N,N,N',N'',N''-pentamethyldiethylenetriamine (Fluka, purum); 750 ml sulfonating flask having mechanical stirring apparatus and septum.

Analogously to Example 6 d), 68.4 g (77 %) of product are obtained.

GPC (THF, PS standards): $M_n= 6880$ (calculated: $M_n= 5660$), $M_w= 9730$, $PDI= 1.41$

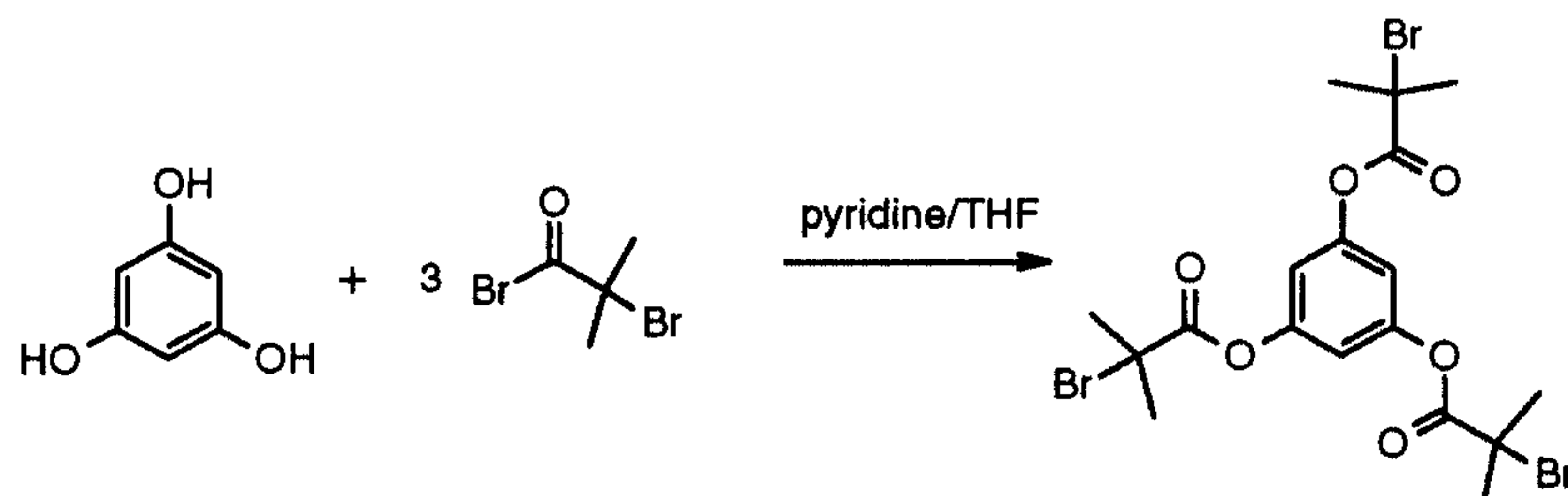
Elemental analysis:

C	H	Br
60.15 ¹	8.51 ¹	5.45 ¹
60.96 ²	8.66 ²	4.27 ²

¹)calculated; ²)found

Example 7

Preparation of 1,3,5-tris(2-bromo-2-methylpropanoyloxy)benzene:



In a 100 ml round-bottomed flask, 5.0 g (39.6 mmol) of 1,3,5-trihydroxybenzene (Fluka, puriss) are dissolved in 40 ml of THF with stirring using a magnetic stirrer, and 9.40 g (118.8 mmol) of pyridine (Fluka, puriss) are added. The solution is cooled to 5°C and 27.34 g (118.8 mmol) of α -bromo-isobutyric acid bromide (Fluka pract) dissolved in 20 ml of THF are added slowly with stirring over the course of 1 hour. After the addition, the mixture is stirred for a further one hour at 60°C, the suspension is left to cool to room temperature and filtered. The solvent is evaporated off using a rotary evaporator, and the residue is washed with water and recrystallised from isopropanol. Yield: 11.04 g (48.2 %) of white crystals. Melting point of the product purified by thin-layer chromatography: 186.4°C.

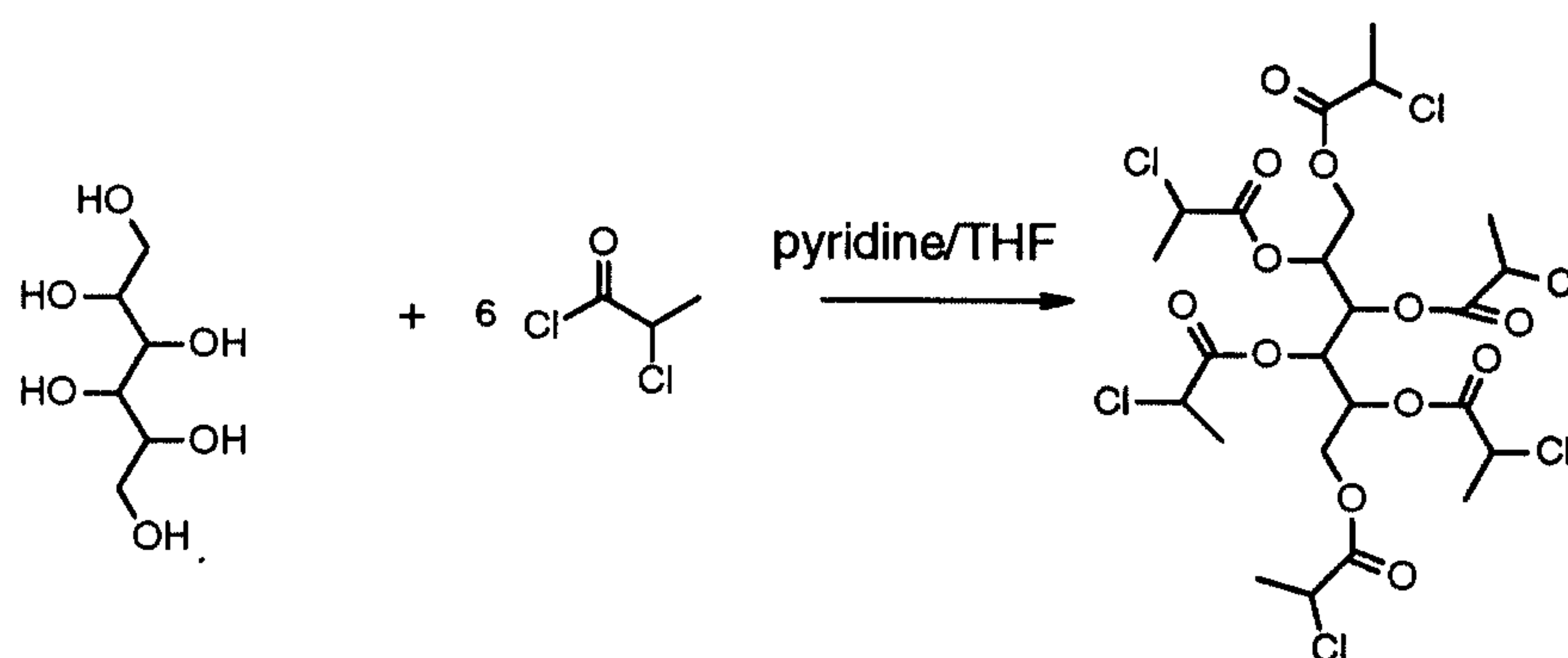
Elemental analysis:

C	H	Br
37.72 ¹	3.69 ¹	41.82 ¹
38.10 ²	3.56 ²	41.51 ²

¹)calculated; ²)found

Example 8

Preparation of 1,2,3,4,5,6-hexakis(2-chloro-propanoyloxy)-n-hexane



In a 100 ml round-bottomed flask, 5.0 g (27.4 mmol) of sorbitol (Fluka, puriss) are dissolved in 10 ml of THF with stirring using a magnetic stirrer, and 13.0 g (164.4 mmol) of pyridine (Fluka, puriss) are added. The solution is cooled to room temperature, and 23.35 g (164.4 mmol) of 2-chloropropanoyl chloride (Fluka, pract.) dissolved in 20 ml of THF are added slowly with stirring over the course of 1 hour. After the addition, the mixture is stirred for a further four hours at 60°C, and the suspension is left to cool to room temperature and then filtered. The solvent is evaporated off using a rotary evaporator, and the residue is dissolved in tert-butyl methyl ether, washed with water and filtered over activated carbon. The solvent is removed *in vacuo* at 0.05 mbar. Yield: 11.85 g (59.6 %) of a yellowish oil. The oil is then purified by column chromatography ("flash" method) over silica gel. Yield of product purified by thin-layer chromatography: 7.02 g (35.3 %).

Elemental analysis:

C	H	Cl
39.73 ¹	4.45 ¹	29.36 ¹
40.32 ²	4.31 ²	29.11 ²

¹)calculated; ²)found

Example 9

Preparation of a "3-star" polymerisate having a relatively high molecular weight

In a 25 ml round-bottomed flask provided with a septum and magnetic stirrer, 4.71 g (47 mmol) of methyl methacrylate (MMA, Fluka puriss) are polymerised under a nitrogen atmosphere as follows: the appropriate amounts of Cu(I)Br catalyst (Fluka, purum), the initiator 1,3,5-tris(2-bromo-2-methylpropanoyloxy)benzene, Example 7, the solvent (if

required) and MMA are placed in the flask, which is sealed securely with a rubber septum. With stirring, the vessel is evacuated and flushed three times with nitrogen. The ligand former PMDETA (N,N,N',N'',N''-pentamethyldiethylenetriamine, Fluka, purum) is then added using a syringe. The vessel is heated in an oilbath to 90°C and the progress of the reaction is monitored by taking regular samples and by NMR monitoring in CDCl₃. The reaction conditions are described in Table 1:

Table 1

No.	Initiator (mg)	Cu(I)Br (mg)	PMDETA (mg)	Solvent	Reaction time (h)	Con- version (%)	M _n (calc.)
1	67	34	41	-	0.33	69	28 100
2	22.3	11.2	13.5	-	3.0	60	72 500
3	13.5	6.7	8.1	3 ml dioxane	5.5	50	101 000

Working up: After being taken up in 20 ml of ethyl acetate and filtered, the polymer is precipitated from 150 ml of ethanol. The polymerisate (poly(MMA)) is obtained in the form of a white powder after filtration and drying *in vacuo* at 50°C. Tab. 2 contains details relating to the yield and characteristic data, such as molecular weight determination by means of GPC (THF, PS standards) and light-scattering (LS, Wyatt Down DSP: "Multi Angle Laser Light Scattering Instrument").

Table 2

No.	Yield (%)	GPC: M _n	GPC: M _w	GPC: PDI	LS: M _w	LS: PDI
1	68.6	50 200	67 000	1.33	82 500	1.29
2	40.3	76 500	95 200	1.24	115 700	1.19
3	36.1	87 700	108 000	1.23	124 400	1.18

The PDI values are low and the higher M_w value for the LS relative to that for the GPC indicates a compact molecular structure of those star-shaped macromolecules.

Example 10

Preparation of a six-fold branched polymerisate having a relatively high molecular weight

In a 25 ml round-bottomed flask provided with a septum and magnetic stirrer, 4.71 g (47 mmol) of n-butyl acrylate (n-BA, Fluka puriss) are polymerised under a nitrogen atmosphere as follows: the appropriate amounts of Cu(I)Br catalyst (Fluka, purum), the initiator 1,2,3,4,5,6-hexakis(2-chloro-propanoyloxy)-n-hexane, Example 8, the solvent (if required) and n-BA are placed in the flask, which is sealed securely with a rubber septum. With stirring, the vessel is evacuated and flushed three times with nitrogen. The ligand former PMDETA (N,N,N',N'',N''-pentamethyldiethylenetriamine, Fluka, purum) is then added using a syringe. The vessel is heated in an oil bath to 90°C and the progress of the reaction is monitored by taking regular samples and by NMR monitoring in CDCl₃. Table 3 describes the reaction conditions:

Table 3

No.	Initiator (mg)	Cu(I)Cl (mg)	PMDETA (mg)	Reaction time (h)	Conversion (%)	M _n (calc.)
1	85	23.2	41	1.25	90	46 800
2	34.1	9.3	16.3	1.5	87	112 000
3	167	22.8	39.9	0.58	90	23 800

Working up: After dilution of the reaction mixture with 25 ml of ethyl acetate and the addition of 1.5 g of Al₂O₃ (adsorption of the catalyst), filtration and drying at 100°C *in vacuo* (1h, < 0.4 mbar), poly(n-BA) is obtained in the form of an oil. Tab. 3 contains details relating to the yield and characteristic data, such as molecular weight determination by means of GPC (THF, PS standards) and light-scattering (LS, Wyatt Down DSP: "Multi Angle Laser Light Scattering Instrument").

Table 4

No.	Yield (%)	GPC: M_n	GPC: M_w	GPC: PDI	LS: M_w	LS: PDI
1	84.7	38 700	47 100	1.22	49 400	1.17
2	87	98 400	135 300	1.32	146 600	1.28
3	90	24 000	33 800	1.41	39 400	1.32

The PDI values are low and the higher M_w value for the LS relative to that for the GPC indicates a compact molecular structure of those star-shaped macromolecules.

Example 11

The initiator 1,2,2,3-tetrakis(2-bromopropionyloxymethyl)propane is prepared analogously to Example 3. n-Butyl acrylate (n-BA) is reacted with the initiator analogously to Example 5a to form the 4-armed star polymer: Characterisation: $M_n=5080$, $M_w=6200$, PDI=1.22, Br (found): 5.56 %.

80.0 g of that 4-armed star-shaped poly-n-butyl acrylate and 1.08 g (7.5 mmol) of CuBr (Fluka, purified by washing with acetic acid) are placed in a 750 ml round-bottomed flask having a mechanical stirrer. The air is expelled by stirring and evacuation and flushing with nitrogen three times. 1.23 g (1.57 ml, 7.5 mmol) of PMDETA (Fluka/purum) are added through a septum using a syringe. The vessel is evacuated and flushed with nitrogen again. When the mixture becomes homogeneous as a result of stirring, the mixture is heated to 60°C on an oil bath. 10.74 g (11.47 ml, 75 mmol) of 2-dimethylaminoethyl acrylate (BASF, technical grade) are added through the septum using a syringe. The temperature is raised to 90°C over the course of one hour (polymerisation time). The conversion is determined by $^1\text{H-NMR}$ analysis in CDCl_3 at about 100 %. After cooling to room temperature, 150 ml of ethyl acetate and 80 g of neutral aluminium oxide (Alox[®] for chromatography) are added. The polymer is obtained after stirring for 1 hour at room temperature, filtration and drying for one hour in a rotary evaporator at 80°C under a high vacuum. Yield: 76.62 g (85 %).

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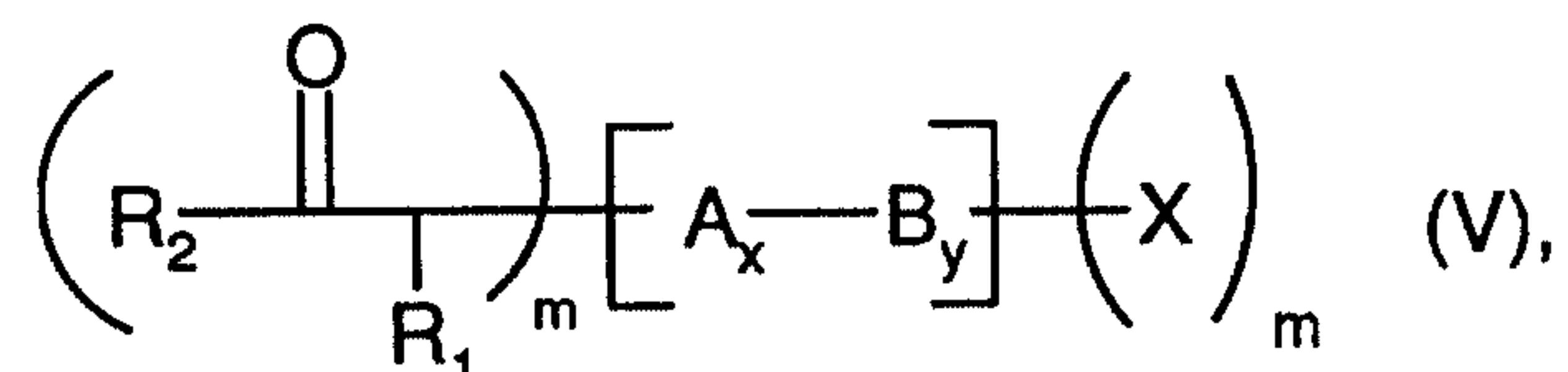
Elemental analysis:

	C	H	N	Br
calculated	60.79	8.74	1.17	5.33
found	61.36	8.86	1.04	4.16

Cu: 166 ppm (X-ray fluorescence); GPC (THF): $M_n = 5800$,
 $M_w = 7370$, PDI = 1.27.

Claims:

1. A polymer or block copolymer of formula:



wherein

R₁ is hydrogen, C₁-C₄alkyl, cyano, phenyl or C₁-C₄alkylphenyl;

R₂ is the radical of an acylated, branched, trihydric alcohol, the radical of a fully or partially acylated, linear or branched, tetrahydric alcohol, the radical of a fully or partially acylated, linear, penta- or hexa-hydric alcohol, the radical of a fully or partially acylated, linear or cyclic C₄-C₆aldose or C₄-C₆ketose or the radical of a fully or partially acylated disaccharide;

A and B are polymer blocks of ethylenically unsaturated monomer units;

x and y denote the number of monomer units in the blocks A and B, one value of x and y being zero and the other value being an integer greater than zero, or both values x and y being integers greater than zero;

X is chlorine, bromine or iodine; and

m denotes an integer from three to six.

2. A block copolymer (V) according to claim 1, wherein

R₁ is C₁-C₃alkyl or phenyl;

X is chlorine or bromine and

R₂ is the radical of an acylated, branched, trihydric alcohol, the radical of an acylated, linear or branched, tetrahydric alcohol or the radical of a fully or partially acylated, linear, penta- or hexa-hydric alcohol,

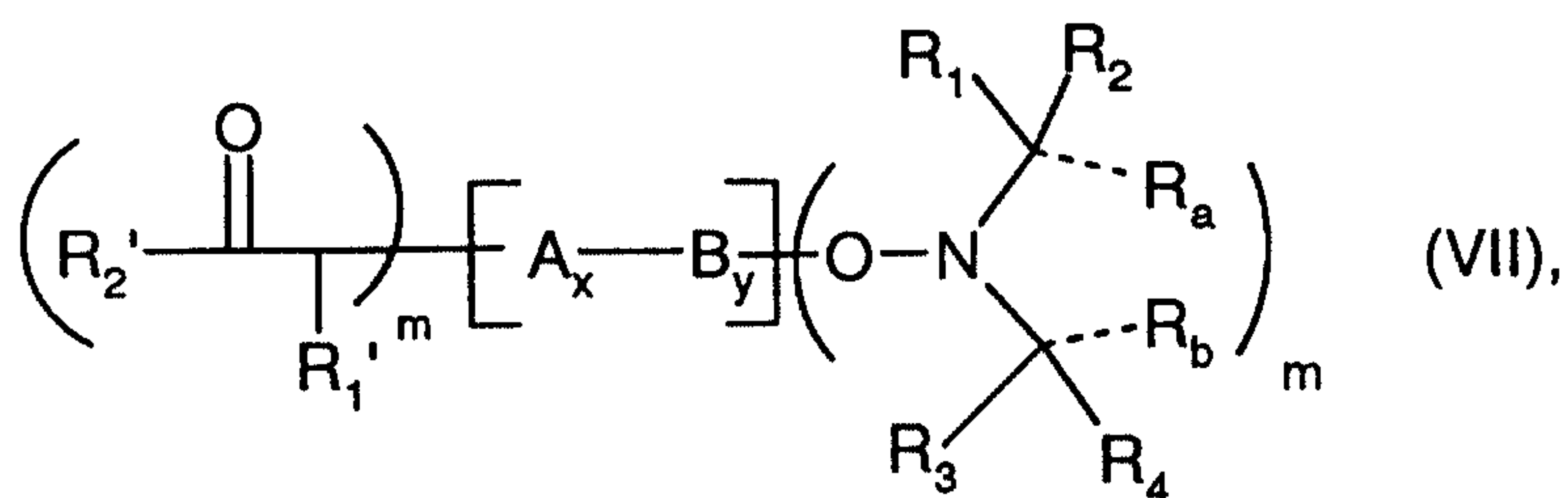
A and B are polymer blocks of ethylenically unsaturated monomer units;

x and y denote integers greater than zero and represent the number of monomer units in the blocks A and B; and

m is three or four.

3. A polymer or block copolymer of formula:

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wherein

R_1' is hydrogen, C_1 - C_4 alkyl, cyano, phenyl or C_1 - C_4 alkylphenyl;

R_2' is the radical of an acylated, branched, trihydric alcohol, the radical of a fully or partially acylated, linear or branched, tetrahydric alcohol, the radical of a fully or partially acylated, linear, penta- or hexa-hydric alcohol, the radical of a fully or partially acylated, linear or cyclic C_4 - C_6 aldose or C_4 - C_6 ketose or the radical of a fully or partially acylated disaccharide;

A and B are polymer blocks of ethylenically unsaturated monomer units;

x and y denote the number of monomer units in the blocks A and B, one value of x and y being zero and the other value being an integer greater than zero, or both values x and y being integers greater than zero;

X is chlorine, bromine or iodine;

m denotes an integer from three to six;

one of R_1 and R_2 is C_1 - C_7 alkyl and the other is C_1 - C_4 alkyl or C_1 - C_4 alkyl substituted by C_1 - C_4 alkoxycarbonyl or by C_1 - C_4 alkoxy; or

R_1 and R_2 together with the adjacent carbon atom are C_3 - C_7 cycloalkyl;

R_3 and R_4 have the meanings of R_1 and R_2 ;

R_a is C_1 - C_4 alkyl, cyano, C_1 - C_4 alkoxycarbonyl, C_1 - C_4 alkanoyloxy, C_1 - C_4 alkanoyloxy- C_1 - C_4 -alkyl, carbamoyl, mono- or di- C_1 - C_4 alkylcarbamoyl, mono- or di-2-hydroxyethyl-carbamoyl, amidino, 2-imidazolyl, 1-hydroxy-2-hydroxymethyl-2-propylcarbamoyl or 1,1-dihydroxymethyl-2-hydroxycarbamoyl; and

R_b has the meanings of R_a ; or

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R_a and R_b together form a bivalent group and an aliphatic or aromatic heterocyclic group having 5, 6, 7 or 8 ring members, which can contain from 1 to 3 additional hetero atoms from the group nitrogen, oxygen and sulfur.

4. A polymer composition comprising a polymer or block copolymer (V) according to claim 8, wherein R_1 , R_2 , A, B, x, y and m are as defined, and additives customary in polymer compositions.
5. A polymer composition comprising
 - a) a polymer or block copolymer (V) according to claim 1, wherein R_1 , R_2 , A, B, x, y and m are as defined; and
 - b) a further polymer or oligomer of formula



wherein

A and B are polymer blocks of ethylenically unsaturated monomer units and x and y denote the number of monomer units in the blocks A and B, one value of x and y being zero and the other value being an integer greater than zero, or both values x and y being integers greater than zero.

6. A process for the preparation of a polymer or block copolymer (V), wherein R_1 , R_2 , A, B, X, x, y and m are as defined in claims 1 and 8, in which process ethylene-group-containing aliphatic monomers that form the basis of the polymer blocks A and B are subjected to a polymerisation reaction by atom transfer radical polymerisation (ATRP) in the presence of the α -halocarboxylic acid ester (I) as polymerisation initiator, wherein R_1 , R_2 and X are as defined above, and in the presence of an oxidisable transition metal complex catalyst.
7. Use of a polymer or block copolymer (V) in the preparation of a polymer or block copolymer wherein $\bullet X$ is replaced by an open-chain or cyclic group $R'R''N-O\bullet$.

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