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(54) Titre : POLYMERES POLYRAMIFIES NON RETICULES
(54) Title: NON-CROSSLINKED POLYBRANCHED POLYMERS

(57) Abrégé/Abstract:

This invention discloses non-crosslinked, poly-branched polymers having a comb-burst configuration and a process for preparing such polymers.



ABSTRACT

This invention discloses non-crosslinked, poly-branched polymers having a comb-burst configuration and a process for preparing such polymers.

TO WHOM IT MAY CONCERN:

Be it known that We, David M. Hedstrand and Donald A. Tomalia, both residing in the County of Midland, State of Michigan, both citizens of the United States of America, have invented new and useful improvements in

NON-CROSSLINKED, POLY-BRANCHED POLYMERS

for which the following is a specification and claims.

BACKGROUND OF THE INVENTION

This invention deals with non-crosslinked, poly-branched polymers having a comb-burst configuration and a process for preparing such polymers.

Macromolecular organic compounds having novel structures have been investigated for many years as academic curiosities and very little attention has been paid to their use in industrial applications. Since the early 1980's, there has been a renewed interest in the study and development of such macromolecular materials in order to control their critical molecular design parameters, for example, size, shape, surface chemistry, flexibility and topology, for use in industrial applications. These materials have found such diverse uses as demulsifiers for oil-in-water emulsions, as wet strength agents in the manufacture of paper, as agents for modifying viscosities in aqueous formulations such as paints and as submicron size calibrators. Certain biological uses have also been suggested for these materials.

Structurally, polymers are classified as either linear or branched wherein the term "branched" generally means that the individual molecular units of the branches are discrete from the polymer backbone, yet may have the same chemical constitution as the polymer backbone. Thus, regularly repeating side groups which are inherent in the monomeric structure and are of different chemical constitution than the polymer backbone are not considered as "branches", that is, for example, the methyl groups pendent on a polydimethylsiloxane chain are not considered to be branches of that polymer.

In U.S. Patent 4,507,466, issued March 26, 1985, the patentees therein described the preparation of polymers having "branching" in the following manner:

"To produce a branched polymer, it is necessary to employ an initiator, a monomer, or both that possess at least three moieties that function in the polymerization reaction. Such monomer or initiators are often called polyfunctional. The simplest branched polymers are the chain branched polymers wherein a linear backbone bears one or more essentially linear pendant groups. This simple form of branching, often called comb branching, may be regular wherein the branches are uniformly and regularly distributed on the polymer backbone or irregular wherein the branches are distributed in non-uniform or random fashion on the polymer backbone." "An example of regular comb branching is a comb

branched polystyrene as described by T. Altores et al. in J. Polymer Sci., Part A, Vol. 3 4131-4151 (1965) and an example of irregular comb branching is illustrated by graft copolymers as described by Sorenson et al. in "Preparative Methods of Polymer Chemistry", 2nd Ed., Interscience Publishers, 213-214 (1968).

Another type of branching is exemplified by crosslinked or network polymers wherein the polymer chains are connected via tetravalent compounds, e.g., polystyrene molecules bridged or cross-linked with divinylbenzene. In this type of branching, many of the individual branches are not linear in that each branch may itself contain groups pendant from a linear chain. More importantly in network branching, each polymer macromolecule (backbone) is cross-linked at two or more sites to other polymer macromolecules. Also the chemical constitution of the cross-linkages may vary from that of the polymer macromolecules. In this so-called cross-linked or network branched polymer, the various branches or cross-linkages may be structurally similar (called regular cross-linked) or they may be structurally dissimilar (called irregularly cross-linked). An example of regular cross-linked polymers is a ladder-type poly(phenylsilsesquinone) [sic] {poly(phenylsilsesquioxane)}."

Sogah, et al., in the background of U.S. Patent 4,544,724, issued October 1, 1985, discusses some of these

types of polymers and gives a short review of the many publications and disclosures regarding them.

One of the inventors herein, Donald A. Tomalia, and many of his co-workers have been working in this field for several years and have issued many patents which disclose various
5 non-crosslinked, macromolecular branched assemblies.

For example, U.S. Patent 4,435,548, issued March 6, 1984 discusses branched polyamidoamines; U.S. Patent 4,507,466, issued March 26, 1985, U.S. Patent 4,558,120, issued December 10, 1985, U.S. Patent 4,568,737, issued February 4, 1986,
10 U.S. Patent 4,587,329, issued May 6, 1986, U.S. 4,713,975, issued December 22, 1987, U.S. Patent 4,871,779, issued October 3, 1989, and U.S. Patent 4,631,337, issued December 23, 1986, discuss the preparation and use of dense star polymers, and U.S. Patent 4,737,550, issued April 12, 1988
15 and U.S. Patent 4,857,599, issued August 15, 1989, discuss bridged and other modified dense star polymers.

Also, other structural configurations of macromolecular materials that have been disclosed include star/comb-branched polymers, such disclosure being found in U.S. Patents
20 4,599,400, issued July 8, 1986 and U.S. Patent 4,690,985, issued September 1, 1987, and finally, rod-shaped dendrimer polymers are disclosed in U.S. Patent 4,694,064, issued September 15, 1987.

The polyamidoamines referred to supra are also disclosed
25 in U.S. Patent 4,758,635, issued July 19, 1988 to Wilson et al.

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Hutchins, et al, in U.S. Patents 4,847,328, issued July 11, 1989 and U.S. Patent 4,851,477, issued July 25, 1989, deal with hybrid acrylic-condensation star polymers and Joseph et al in U.S. Patents 4,857,615, issued August 15, 1989, U.S. Patent 4,857,618, issued August 15, 1989, and U.S. Patent 4,906,691, issued March 6, 1990, deal with condensed phase polymers which are linear polymers having regularly, or irregularly, spaced polymeric branches, essentially on the order of a comb structure macromolecule.

10 An excellent presentation of the structures and chemistries of many such macromolecular branched assemblies can be found in Tomalia, D.A., Naylor, A.M., and Goddard, W.A. III, *Angewandte Chemie*, 29/2 (1990), pages 138 to 175.

15 However, none of the disclosures of the prior art deal with the novel polymers of the instant invention which are non-crosslinked, poly-branched polymers. For simplicity sake, the polymers of the instant invention can be generally characterized as multiple polymeric branches on multiple polymeric branches.

20 *BRIEF DESCRIPTION OF THE DRAWINGS*

Fig. 1 is a schematic in two dimensions of the polymer configuration of the polymers of the instant invention wherein

1 is the initiator core (initiator core molecule);

25 2 is first grafting and first branching and generation 0;

3 is second grafting and second branching and
generation 1;

4 is third grafting and third branching and
generation 2;

5 is fourth grafting and fourth branching and
generation 3;

6 is $(i + 1)^{\text{th}}$ grafting and $(i + 1)^{\text{th}}$ branching and
generation i , and

7 is $(i + 2)^{\text{th}}$ and all iterative grafting and
 $(i + 2)^{\text{th}}$ and all iterative branching, and
generation $(i + 1)$ and all subsequent generations.

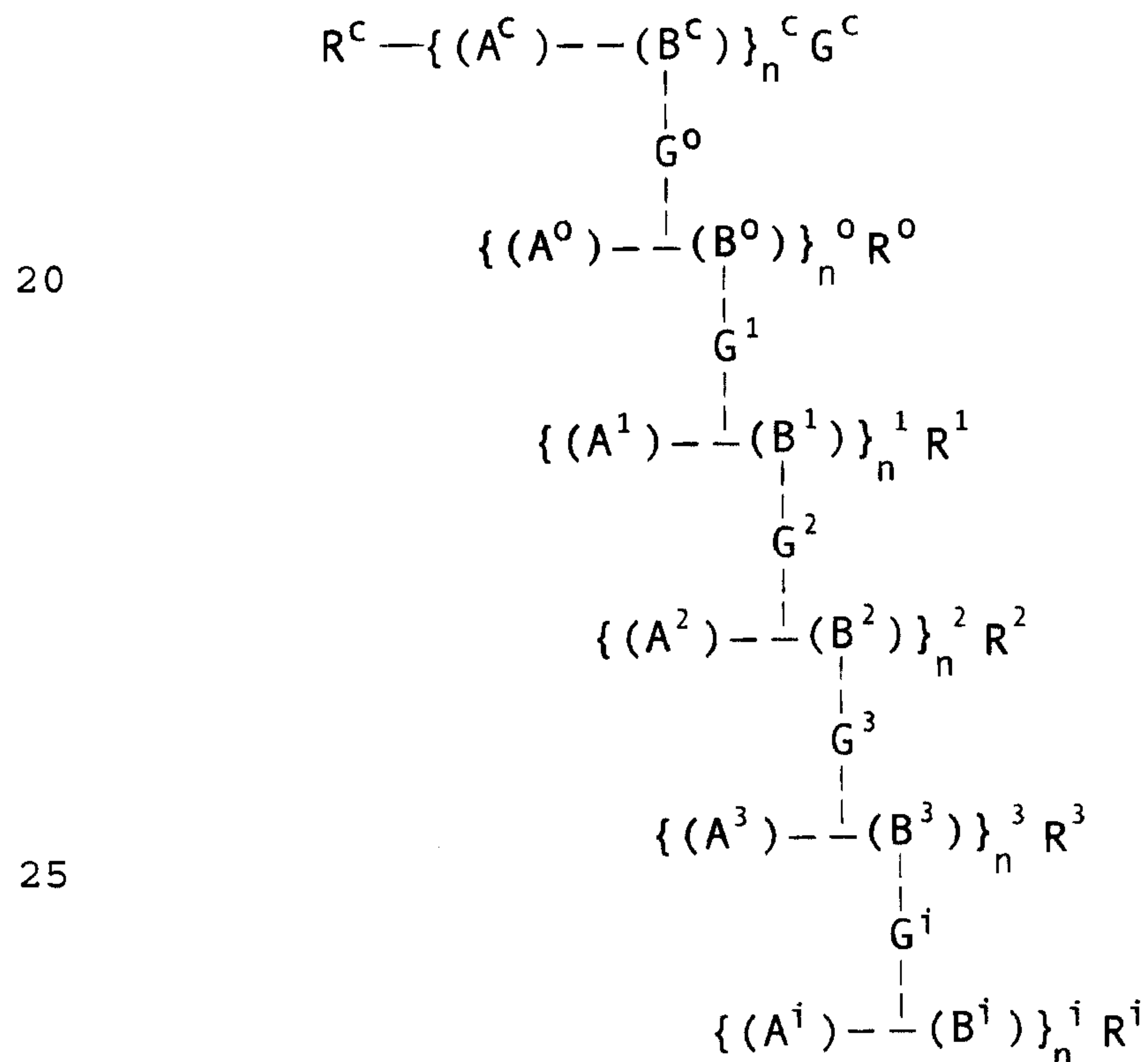
THE INVENTION

Benefits and other perceived advantages are achieved in
accord with the present invention which comprises novel non-
crosslinked, poly-branched polymers, and methods for
manufacturing such polymers. In its broadest scope, this
invention deals with poly-branched polymers having at least
one branch referred to herein as a "core branch" emanating
from a core molecule, said branch being essentially linear,
and having at least one end chemically coupled to the core
molecule, with the other end of the branch terminating in a
group from a molecule used to initiate the reaction by which
the branch was prepared, and at least one second branch which
is branched from the core branch, said second branch, or
branches, being essentially linear, and having at least one
end chemically coupled to the core branch, with the other end

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of the branch terminating in a group selected from a molecule used to prepare the second branch polymer, which when subjected to iterative polymer grafting steps (i.e. generations, which will be delineated further herein), form
 5 three-dimensional organizations of ordered organic molecules. These polymers are hereinafter referred to as "comb-burst" structures in that they are prepared from comb-like core molecules, but after subsequent grafting of additional branches pursuant to the processes of this
 10 invention, tend to have the appearance in two dimensions of a woven wire fence, which when viewed in three dimensions gives a topology having a starburst-like appearance. Hence, "comb-burst".

According to one aspect of the present invention,
 15 there is provided a composition of matter comprising non-crosslinked poly-branched polymers having the general formula

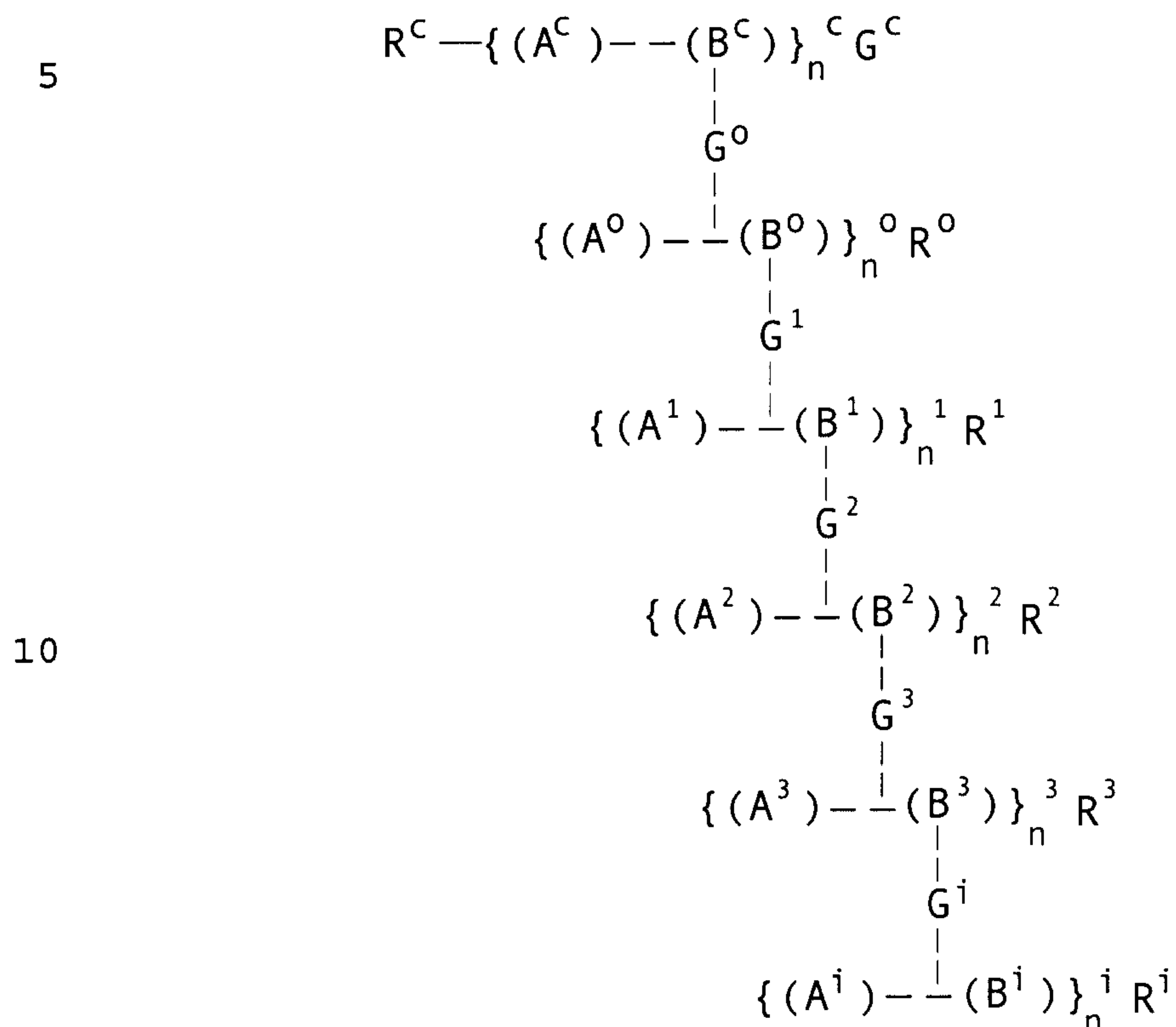


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wherein R^c is a non-reactive end group and each R^0 , R^1 , R^2 , R^3 , and R^i is a residual moiety derived from initiators selected from a group consisting of free radical initiators, cationic initiators, anionic initiators, and group transfer initiators; i represents repetitive linear polymers having the unit formula $\{(A^i) \text{--} (B^i)\}$; A^c , A^0 , A^1 , A^2 , A^3 , and A^i are non-reactive comonomers or, oligomers or polymers formed from a polymerizable monomer, said oligomers or polymers being capable of withstanding the conditions required for preparation of a graft polymer; B^c , B^0 , B^1 , B^2 , B^3 , and B^i are protected or unprotected reactive nucleophilic or electrophilic monomers, or oligomers or polymers formed from a polymerizable monomer, said oligomers or polymers being capable of withstanding the conditions required for preparation of a graft polymer; G^0 , G^1 , G^2 , G^3 and G^i are grafting components which represent bonding between adjacent units of the repetitive linear polymers, said bonding being to either an A segment or a B segment; G is a terminating group; n^c is the degree of polymerization of a core initiator; n^0 is the degree of polymerization of a first comb branch; n^1 is the degree of polymerization of a first generation comb-burst branch; n^2 is the degree of polymerization of a second generation comb-burst branch; n^3 is the degree of polymerization of a third generation comb-burst branch; n^i is the degree of polymerization of the i^{th} generation comb-burst polymer having at least one branch point; wherein $n^i \geq 2$ for the case where $i = c, 0, \text{ and } 1$, and $n^i \geq 2$ if n^{i-1} is $>$ zero, the largest i for which n^i does not equal zero is the total number of generational levels of the polymer wherein the superscripts $c, 0, 1, 2, 3$ and i designate comb-burst generation level; the unit ratio of A segments to B segments in any $\{(A) \text{--} (B)\}$ segment of the polymer is 0 to 1:100 to 1.

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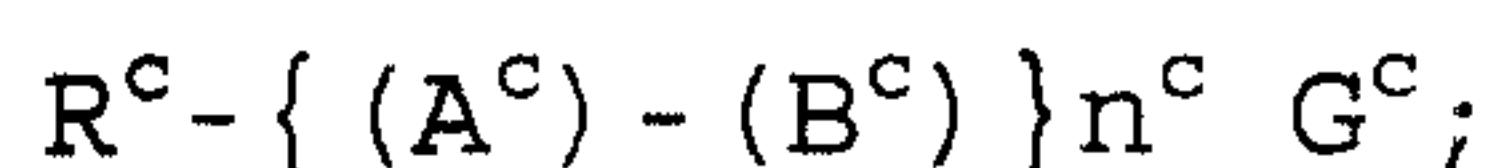
According to another aspect of the present invention, there is provided a process for preparing non-crosslinked poly-branched polymers having the general formula



wherein R^c is a non-reactive end group and each R^0 , R^1 , R^2 , R^3 , and R^i is a residual moiety derived from initiators selected from a group consisting of free radical initiators, cationic initiators, anionic initiators, and group transfer initiators; i represents repetitive linear polymers having the unit formula $\{ (A^i) - (B^i) \}$; A^c , A^0 , A^1 , A^2 , A^3 , and A^i are non-reactive comonomers or, oligomers or polymers formed from a polymerizable monomer, said oligomers or polymers being capable of withstanding the conditions required for preparation of a graft polymer; B^c , B^0 , B^1 , B^2 , B^3 , and B^i are protected or unprotected reactive nucleophilic or electrophilic monomers, or oligomers or polymers formed from a polymerizable monomer, said oligomers or polymers being capable of withstanding the conditions required for

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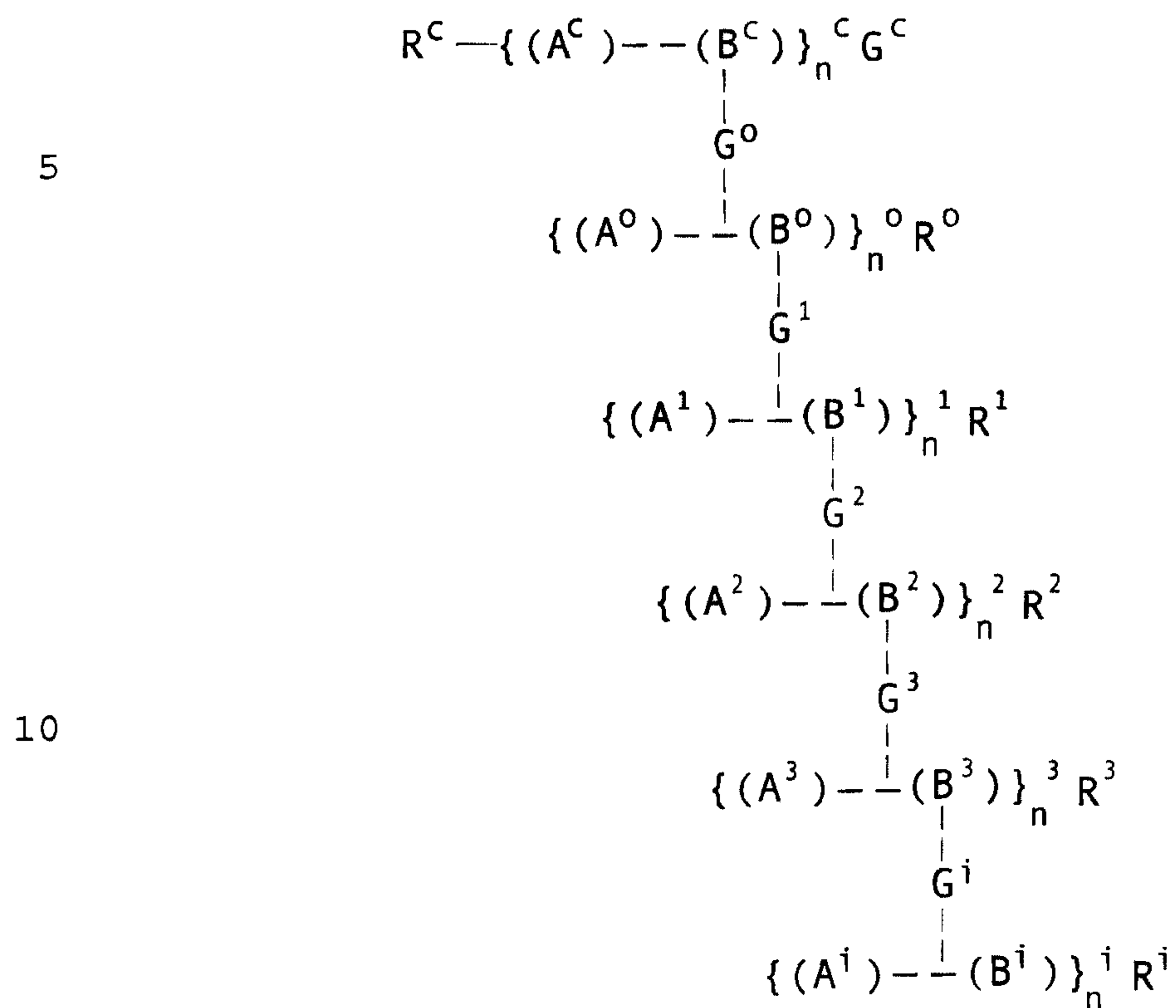
preparation of a graft polymer; G^0 , G^1 , G^2 , G^3 and G^i are grafting components which represent bonding between adjacent units of the repetitive linear polymers, said bonding being to either an A segment or a B segment; G^c is a terminating group; n^c is the degree of polymerization of a core initiator; n^0 is the degree of polymerization of a first comb branch; n^1 is the degree of polymerization of a first generation comb-burst branch; n^2 is the degree of polymerization of a second generation comb-burst branch; n^3 is the degree of polymerization of a third generation comb-burst branch; n^i is the degree of polymerization of the i^{th} generation comb-burst polymer having at least one branch point; wherein $n^i \geq 2$ for the case where $i = c, 0, \text{ and } 1$, and $n^i \geq 2$ if n^{i-1} is $>$ zero, the largest i for which n^i does not equal zero is the total number of generational levels of the polymer wherein the superscripts $c, 0, 1, 2, 3, \text{ and } i$ designate comb-burst generation level; the unit ratio of A segments to B segments in any $\{(A) - (B)\}$ segment of the polymer is 0 to 1:100 to 1, the process comprising (I) forming a linear initiator core having at least one reactive site and having the general formula



(II) reacting essentially all of the sites (B^c) of (I) with a reactive polymer having the unit formula $G^0\{(A^0) - (B^0)\}n^0R^0$ to form multiple branches that contain at least one multiple reactive site on each branch using protection-deprotection reactions to ensure that the unit formula $G^0\{(A^0) - (B^0)\}n^0R^0$ reacts with all (B^c) sites of (I) but that no reactions occur at the reactive sites B^0 ; (III) repeat (II) sequentially to form successive generations of reactive branches to give the desired non-crosslinked poly-branched polymers.

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This invention therefore comprises a composition of matter comprising non-crosslinked poly-branched polymers having the general formula



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wherein R^c is a non-reactive end group and each R^0 , R^1 , R^2 , R^3 , and R^i is selected from initiators selected from a group consisting of free radical initiators, cationic initiators, anionic initiators, and group transfer initiators;

5 i represents repetitive linear polymers having the unit formula $\{(A^1)-(B^1)\}$; A^c , A^0 , A^1 , A^2 , A^3 , and A^i are non-reactive comonomers or, oligomers or polymers formed from a polymerizable monomer, said oligomers or polymers being capable of withstanding the conditions required for

10 preparation of a graft polymer; B^c , B^0 , B^1 , B^2 , B^3 , and B^i are protected or unprotected reactive nucleophilic or electrophilic monomers or, oligomers or polymers formed from a polymerizable monomer, said oligomers or polymers being capable of withstanding the conditions required for

15 preparation of a graft polymer; G is a terminating group or a grafting component; n^c is the degree of polymerization of a core initiator; n^0 is the degree of polymerization of a first comb branch; n^1 is the degree of polymerization of a first generation comb-burst branch; n^2 is the degree of

20 polymerization of a second generation comb-burst branch; n^3 is the degree of polymerization of a third generation comb-burst branch, n^i is the degree of polymerization of the i^{th} generation comb-burst polymer having at least one branch point; wherein $n^i \geq 2$ for the case where $i = c, 0, \text{ and } 1$, and

25 $n^i \geq 2$ if n^{i-1} is $>$ zero, the largest i for which n^i does not equal zero is the total generation level of the polymer

wherein the superscripts c, ⁰, 1, 2, 3, and i designate comb-
burst generation level; the unit ratio of A units to B units
in any {(A)--(B)} segment of the polymer is 0 to 1:100 to 1.

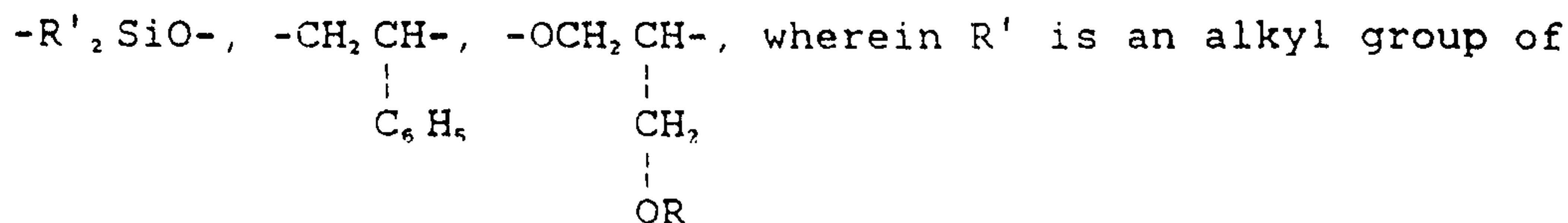
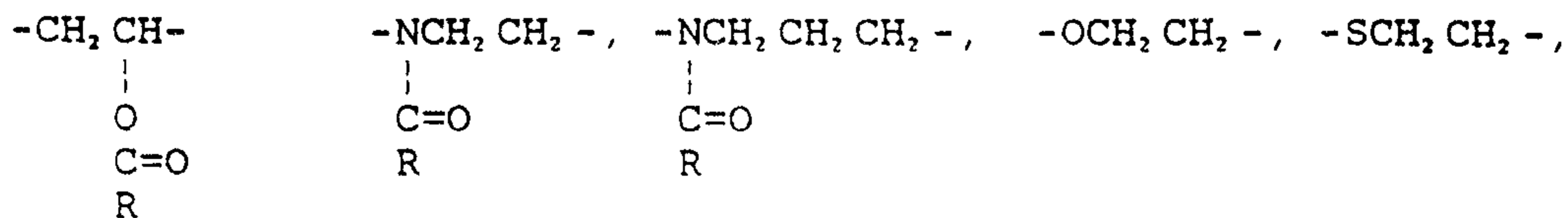
As indicated above, each of R⁰, R¹, R², R³, and Rⁱ in
these inventive polymers is selected as a moiety from a
radical initiator, a moiety from a cationic initiator, a
moiety from an anionic initiator, or a group transfer
initiator. R⁰- Rⁱ can be for example hydrogen, an alkyl
group, Lewis acids, or the like.

The Gⁱ group is the grafting component formed by the
reaction of the living end, or a derivative of the living
end, of the ith generation oligomer with the reactive groups
of the (i-1) generation material. Thus, an anionic oligomer
may be reacted directly with an electrophilic precursor
generation, or it may be terminated by, for example, a
halogen such as chlorine, bromine, or iodine, to create an
electrophilic end group for grafting to a nucleophilic
precursor. Similarly, a cationic oligomer may be reacted
directly with a nucleophilic precursor generation, or
terminated with, for example, water, hydrogen sulfide, or an
amine to give a nucleophilic end group for reaction with an
electrophilic precursor. In the case of G^c, the "graft" is
to a monofunctional molecule, which may be as simple as
quenching the active end with a proton or hydroxide, as would
be the case with normal termination of ionic oligomers with
water, or trapping with a specific molecule in order to

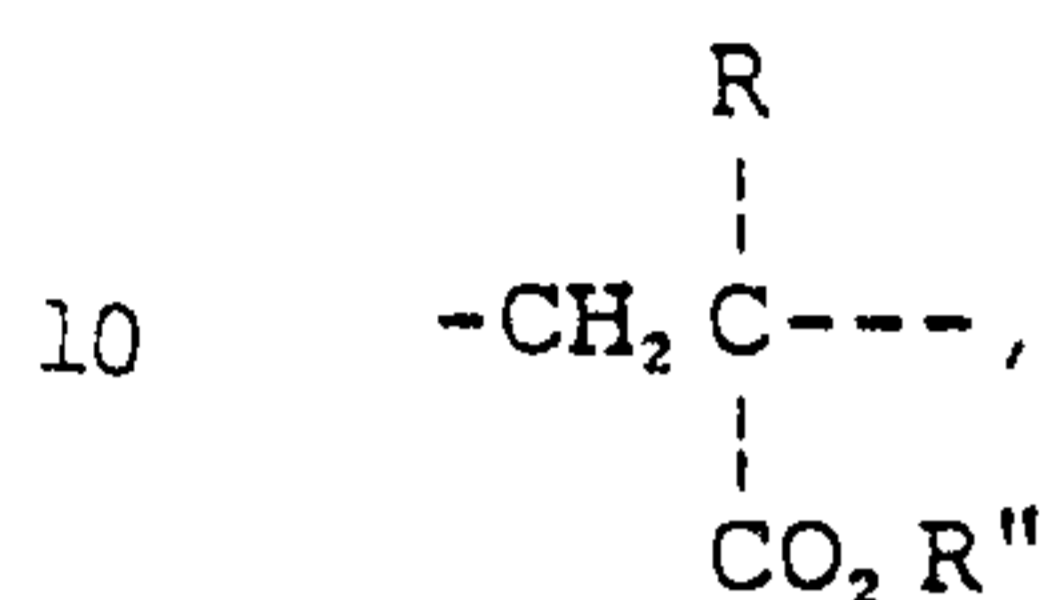
introduce a single desired functional group to the molecule. Other telechelic groups suitable for grafting purposes may be found in Goethals, "Telechelic Polymers"; Syn. Appln., CRC Press (1989).

The oligomeric and polymeric segments of these materials can be homopolymers or copolymers, it being understood that the formulae herein represent bonding of the grafting G groups to either segment A, if it is present, or to segment B, and it being further understood that the grafting to any A segment is at the terminal end of the molecule, any other segment A grafting would result in the potential for crosslinking the polymers, which is not part of the invention herein. Also, for purposes of this invention, each A segment can be monomeric or, oligomers or polymers formed from polymerizable monomers, the only condition being that the said monomers, oligomers and polymers must be capable of withstanding the conditions required for preparation of subsequent graft junctures. As illustrated in the formulae, the bond from G to the next generation is indicated by a vertical line about halfway between the A segments and the B segments to illustrate that G can be bonded to either A, if it is present, or to B, which is always present in the molecule.

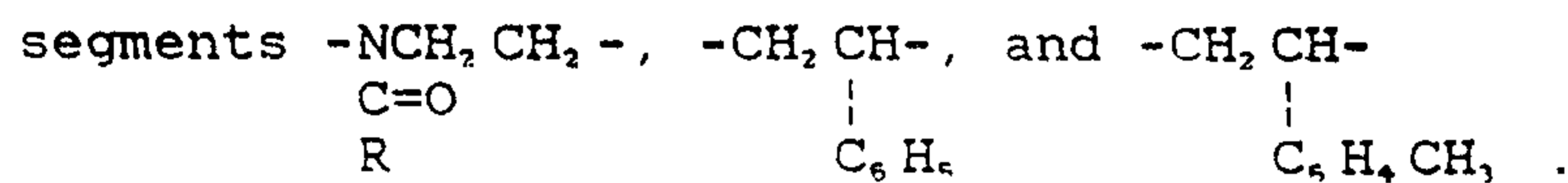
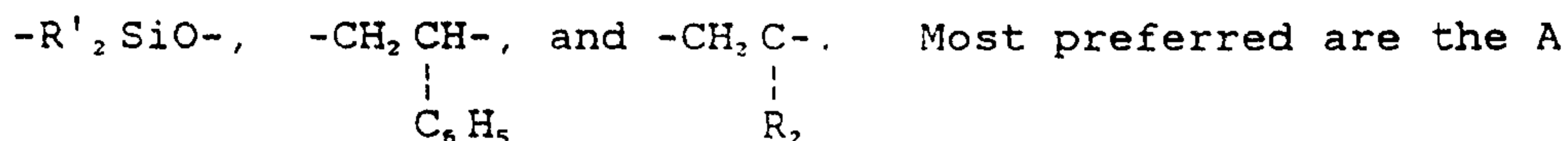
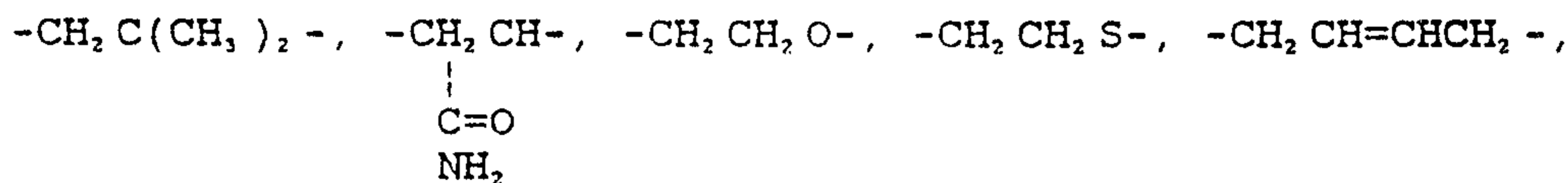
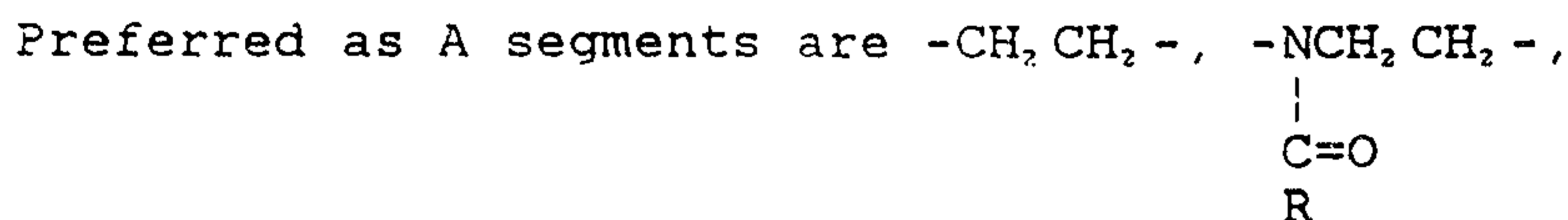
Segments of A include for example, $-\text{CH}_2\text{CH}_2-$,
 $-\text{CH}_2\text{CH}=\text{CHCH}_2-$, $-\text{CH}_2\text{C}(\text{CH}_3)_2-$, $-\text{CH}_2\text{CH}(\text{CN})-$, $-\text{CH}_2\text{CH}-$, $-\text{CH}_2\text{CH}-$,
 $\begin{array}{c} | \\ \text{C}=\text{O} \\ \text{NH}_2 \end{array}$ $\begin{array}{c} | \\ \text{O} \\ \text{R} \end{array}$



1 to 4 carbon atoms, aryls, arylalkyl, hydrogen, or carboalkoxy and R is an alkyl group of 1 to 4 carbon atoms, aryls, or hydrogen;



wherein R has the same meaning as set forth above, and wherein R'' can be an alkyl group of 1 to 4 carbon atoms.



25 Each B segment can be monomeric, or oligomers or polymers formed from polymerizable monomers, wherein said monomers, oligomers and polymers must be capable of

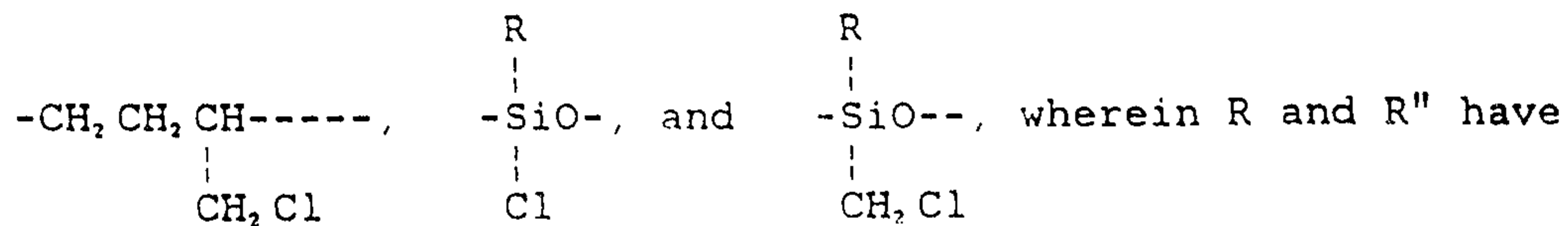
withstanding the conditions required for preparation of a graft polymer and further, the B segments must contain at least one unit which is nucleophilic or electrophilic in character.

The groups B contain the reactive sites to which the oligomers may be grafted. In many cases, these groups may need to be present in latent or masked form if they would otherwise be incompatible with the oligomerization process. For example, polymerization of ethyleneimine leads to highly branched polyethyleneimine oligomers which are not useful for this invention because the secondary amines formed are also reactive under the polymerization conditions. Oxazoline polymerization leads to linear polyethyleneimine in a protected form, and the secondary amines can be unmasked for grafting by hydrolysis. For alkylene oxide oligomerizations, hydroxyl groups intended for use as future graft sites would need to be masked as, for example, an ether to preclude the possibility of forming highly cross-linked gel systems. An example of a latent reactive site would be an alcohol group of a polyol which would require activation by conversion to a halide or sulfonate to allow reaction with anionic oligomer.

Thus, B as a nucleophile can be selected from such groups as $\begin{array}{c} -\text{NCH}_2\text{CH}_2 \\ | \\ \text{H} \end{array}$, $\begin{array}{c} -\text{CH}_2\text{CH}- \\ | \\ \text{NHR} \end{array}$, $-\text{CH}_2\text{CH}(\text{OH})-$, $-\text{CH}_2\text{CH}(\text{SH})-$,

$-\text{OCH}_2\text{CH}(\text{CH}_2\text{OH})-$, and $\begin{array}{c} -\text{NCH}_2\text{CH}_2\text{CH}_2- \\ | \\ \text{H} \end{array}$, while B as an

electrophile can be selected from such groups as



5

the meanings set forth above.

It should be understood that homopolymers consist of only the B segment, while copolymers can be had by combining the B segments with the A segments. Copolymers can also be prepared by using different monomers for the B segment of different generations, for example B¹ being different from B².

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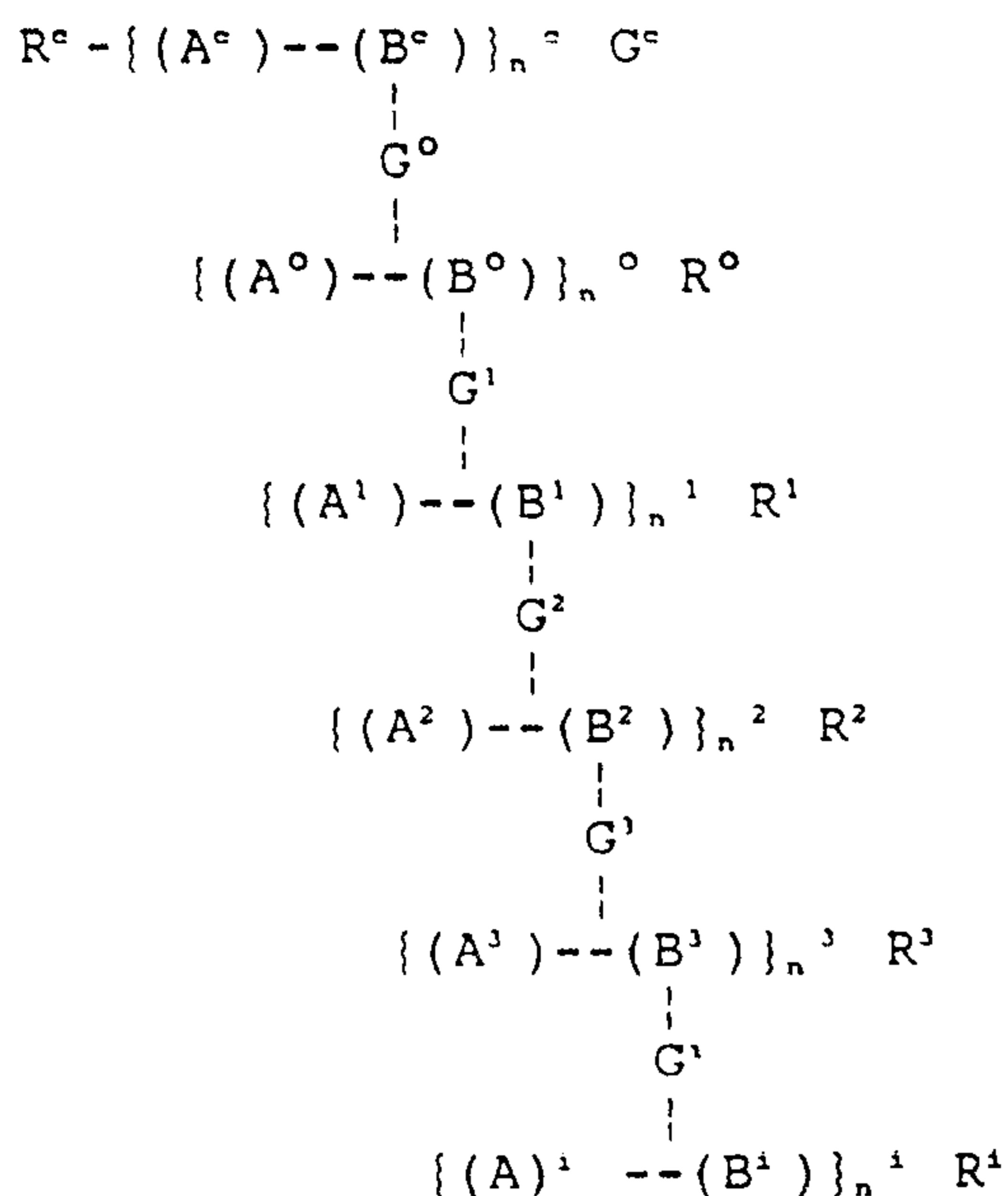
The inventors herein contemplate that for purposes of this invention, there must be at least one B segment and therefore the ratio of A segments to B segments ranges from 0 to 1 to 100 to 1.

15

This invention also comprises a process for preparing non-crosslinked poly-branched polymers having the general formula

20

25



wherein R^c is a non-reactive end group and wherein each R^0 ,
 R^1 , R^2 , R^3 , and R^4 is selected from initiator types selected
 from a group consisting of free radical initiators, cationic
 initiators, anionic initiators, and group transfer
 initiators; (i) represents repetitive linear polymers having
 the unit formula $\{(A^i) - (B^i)\}$; A^c , A^0 , A^1 , A^2 , A^3 , and A^4 are
 non-reactive comonomers or, oligomers or polymers formed from
 a polymerizable monomer, said oligomers or polymers being
 capable of withstanding the conditions required for
 preparation of a graft polymer; B^c , B^0 , B^1 , B^2 , B^3 , and B^4
 are protected or unprotected reactive nucleophilic or
 electrophilic monomers or, oligomers or polymers formed from
 a polymerizable monomer, said oligomers or polymers being
 capable of withstanding the conditions required for
 preparation of a graft polymer; G is a terminating group or a

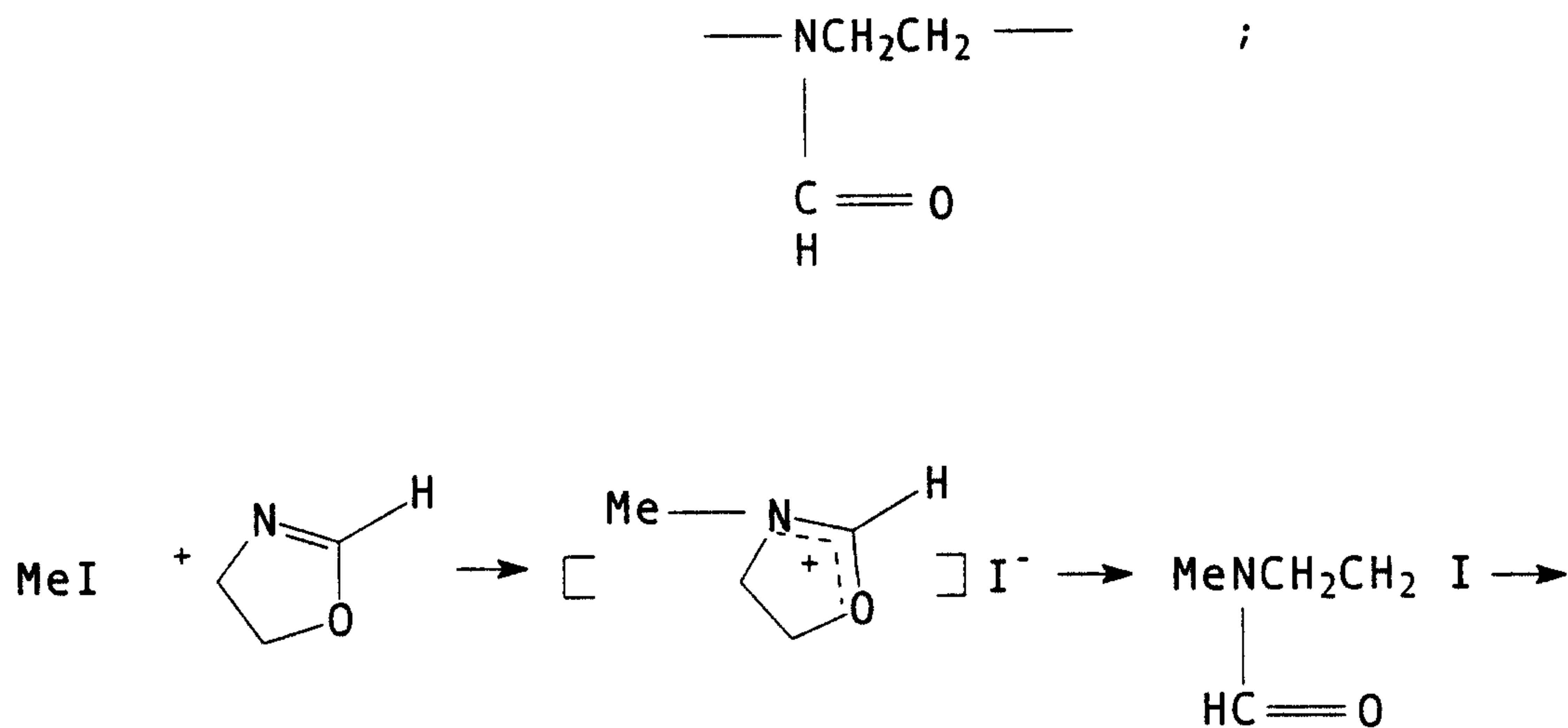
grafting component; n^c is the degree of polymerization of a core initiator; n^0 is the degree of polymerization of a first comb branch; n^1 is the degree of polymerization of a first generation comb-burst branch; n^2 is the degree of polymerization of a second generation comb-burst branch; n^3 is the degree of polymerization of a third generation comb-burst branch, n^i is the degree of polymerization of the i^{th} generation comb-burst polymer having at least one branch point; wherein $n^i \geq 2$ for the case where $i = c, 0, \text{ and } 1$, and $n^i \geq 2$ if n^{i-1} is $>$ zero, the largest i for which n^i does not equal zero is the total generation level of the polymer wherein the superscripts $c, 0, 1, 2, 3$, and i designate comb-burst generation level; the unit ratio of A units to B units in any $\{(A)--(B)\}$ segment of the polymer is 0 to 1:100 to 1, the process comprising (I) forming a linear initiator core having at least one reactive site and having the general formula

$$R^c - \{(A^c) -- (B^c)\} n^c G^c; \text{ (II) reacting all or part of the sites } (B^c) \text{ of (I) with a reactive polymer having the unit formula } G^0 \{(A^0) -- (B^0)\} n^0 R^0 \text{ to form multiple branches that contain at least one reactive site on each branch using protection-deprotection reactions to ensure that the unit formula } G^0 \{(A^0) -- (B^0)\} n^0 R^0 \text{ reacts only with } (B^c) \text{ sites of (I) and that no reactions occur at the reactive sites } B^0; \text{ (III) repeat (II) sequentially to form successive generations of reactive branches to give the desired non-crosslinked poly-branched polymers.}$$

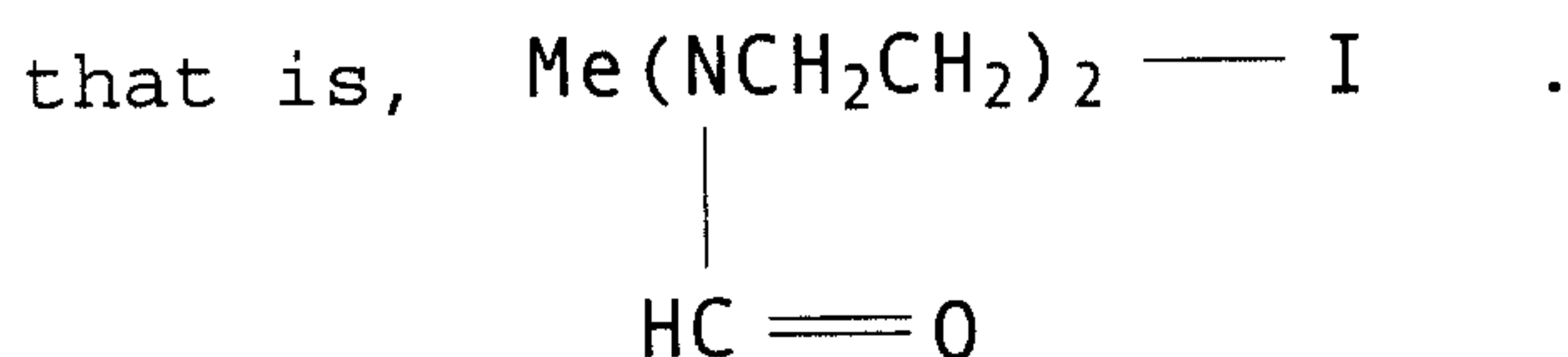
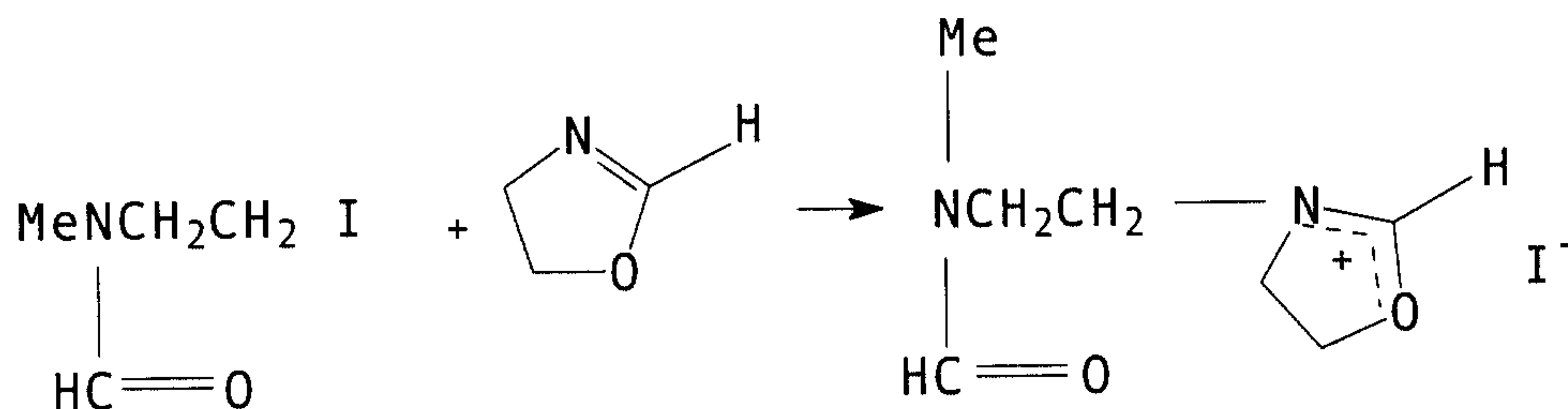
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It should be noted by those skilled in the art that the polymer requires an initiator core (initiator core molecule). This initiator core may or may not be a "living polymer" or "living oligomer", which oligomers and/or polymers are generally known to those skilled in the art. "Living systems" are preferred in order to control polydispersity of the comb-burst dendrimers. Using specific chemistry, the inventors herein can explain this aspect of the invention beginning with reference to "Polymeric Amines And Ammonium Salts", edited by E.J. Goethals, Pergamon Press, (1980), with especial reference to pages 55 et seq. wherein there is taught one method of producing living polymers in a paper entitled "Linear Polyalkylenimines", Saegusa, T. and Kobayashi, S.

Using the example of Saegusa, page 58, one can observe that an initiator such as methyl iodide is first reacted with an oxazoline in the following sequence to give an oligomeric "living oligomer" having, in this case, two protected reactive sites designated as

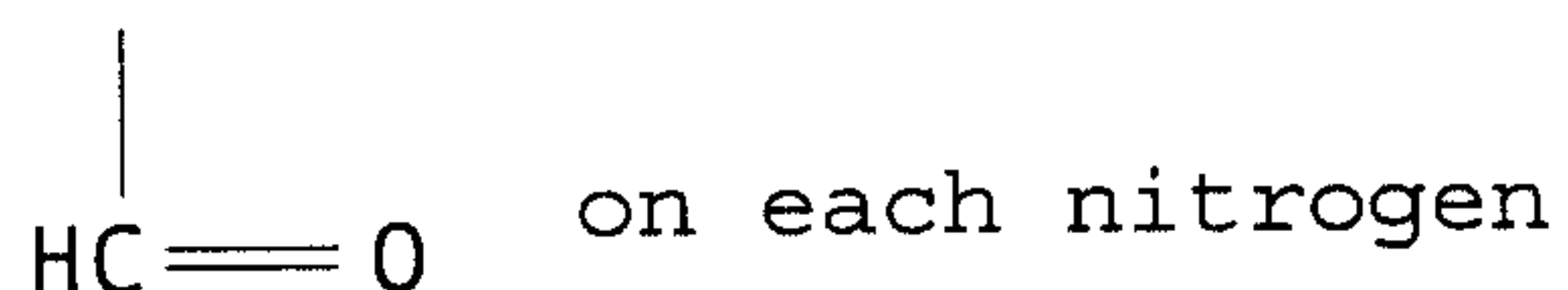


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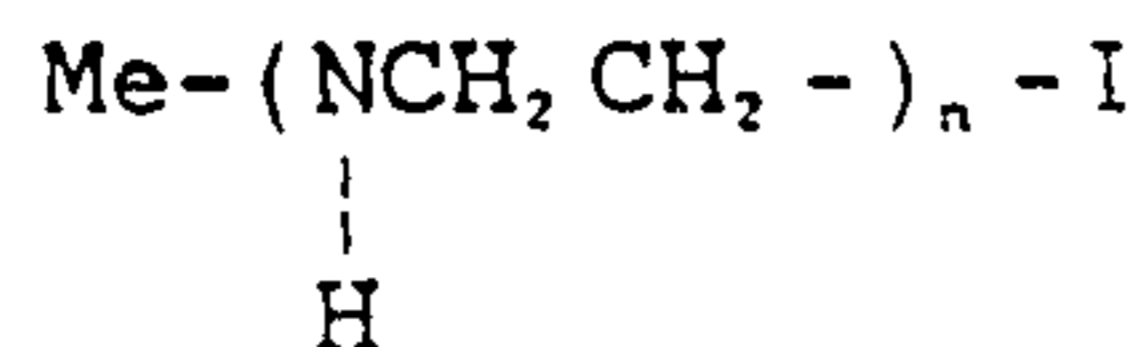


5 With further reference to Fig. 1 of the instant invention, the initiator core in the specific case described just above would be shown in Fig. 1 as $R^c (B^c)_n G^c$; where R^c is methyl and G^c is as described above.

10 Reaction sequences are then chosen to deprotect the nitrogen groups so that each of the two reactive sites adds a reactant possessing its own, new reactive site, or sites, which introduces multiplicity, to obtain a "dendrimer" $\{ (A^o) - (B^o) \}_n - R^o$ of generation 0 (see Fig. 1), wherein "dendrimer" has the same or similar meaning as that
 15 used by Tomalia, et. al. in the article referenced supra. As can be observed from the reaction sequence set forth above, this process requires that protection-deprotection strategies are used to ensure that the reactant reacts with all reactive (B^c) sites, but does not react any (B^o) sites.
 20 Protection-deprotection strategies are generally known to those skilled in the art and great detail does not have to be set forth here. Suffice it to suggest that the living oligomer set forth above has the protective group



of the oligomer whereupon the oligomer is then hydrolyzed with an acid to give polymeric units having reactive amine groups i.e.



5 which are then used as the reactive sites to form the next generation, it being understood that the reactive sites of the polymer being grafted to the amine groups are protected before this reaction takes place, and that they too are hydrolyzed after the grafting reaction to give additional
10 reactive sites for the next generation of branching.

Additional iterative sequences involving addition of new reactants having reactive sites is then undertaken in order to add branches onto branches to form the poly-branched polymer of this invention until the polymers will not form
15 due to steric hinderence referred to as comb-burst dense packing. The article by Tomalia, et al, referenced supra sets forth such technical terms.

One of the inventive processes used to prepare polymers of this invention relies on the polymerization of 2-ethyl-2-oxazoline. Methyl p-toluenesulfonate has been shown to
20 polymerize oxazolines and the polymerization mechanism has been determined to be cationic, producing a "living polymer". This allows the preparation of polymer samples with well defined molecular weight and low polydispersity. The end of
25 the growing polymer chain contains an oxazolinium ion as

disclosed above, that can be trapped by a variety of nucleophiles. To graft the living poly(2-ethyl-2-oxazoline) chains, they are terminated with the secondary amine groups contained on linear poly(ethyleneimine)(LPEI). After grafting onto the linear poly(ethyleneimine) has been accomplished, hydrolysis of the poly(2-ethyl-2-oxazoline) grafts will generate poly(ethyleneimine) branches. This allows further living poly(2-ethyl-2-oxazoline) chains to be grafted onto the poly(ethyleneimine) branches. Repetition of the grafting and hydrolysis forms the inventive polymers with the structures shown herein.

Example 1

A 250 ml one-necked round-bottomed flask equipped with a magnetic stirring bar and a Dean-Stark trap that was surmounted with a reflux condenser was charged with 2.84 gm (15.3 mmole) of methyl tosylate and 125 ml of toluene. The mixture was heated at reflux and solvent was collected until all water had been removed. At this time, 30.0 gm (303 mmoles) of freshly distilled 2-ethyl-2-oxazoline was added all at once and the mixture was refluxed for approximately 4 hours. During this time, in a separate flask, 1.64 gm (38.1 mmole of repeat units) of linear poly(ethyleneimine) was azeotropically dried with toluene. When the poly(ethyleneimine) was dry it was added to the round-bottomed flask containing the oxazoline oligomer and then allowed to reflux

for an additional 3 hours. Any ungrafted living poly(2-ethyl-2-oxazoline) chains were neutralized by the addition of 2.0 ml of water with refluxing for an additional 1 hour. Toluene was removed under reduced pressure to leave a yellowish oily solid that was dissolved in chloroform and precipitated dropwise into diethyl ether. The yellow solid was filtered from solution and dried overnight in a vacuum oven to yield 29.7 gm (94% yield) of grafted poly(2-ethyl-2-oxazoline) as a yellow powder.

Example 2

Into a 500 ml one-necked round-bottomed flask was placed 21.6 gm of the oxazoline from example 1 and 350 ml of water. When the polymer had completely dissolved, 35 ml of concentrated sulfuric acid was added. The flask was equipped with a distillation head and the mixture was heated at reflux and distillate was collected until propionic acid could not be detected. Water was added to the distilling pot when the volume was reduced to less than approximately 75 ml. Upon removal of the propionic acid the distillation head was replaced with a reflux condenser surmounted with a pressure equalized addition funnel charged with 5N NaOH. The base was slowly dripped into the reaction mixture maintained at reflux. When the pH of the reaction mixture was approximately 12, heating was discontinued. At room temperature a solid had formed at the surface of the aqueous mixture. This precipitate was removed and placed in a 250 ml

round-bottomed flask with 175 ml of toluene. The water was removed from the water-toluene azeotrope by distillation. When water removal was complete, the solid became soluble in the refluxing toluene. The hot toluene solution was poured into a 250 ml round-bottomed flask leaving behind insoluble salts. Toluene was removed under reduced pressure to leave a brownish, waxy solid. The sample was dried for approximately 24 hours under vacuum to give 9.14 gm (97% yield) of polymer sample.

Example 3

Using the general method of Example 2, hydrolysis of the graft polymers, was carried out on a separate batch of the graft polymers in the following manner. Five grams (5.0 gm) of the graft copolymer were placed in a 250 ml round-bottomed flask with 100 ml of water and 10 gm of sulfuric acid. The flask was heated with a heating mantle to give a slow distillation of the propionic acid/water azeotrope. The distillation was continued for 2 days, with water being added as necessary to maintain the reaction volume. Approximately 200 ml of distillate was collected over the course of the hydrolysis. The heating was discontinued and 50% NaOH was added slowly to bring the pH to 10. The free polyamine was insoluble in the saturated salt solution, giving a separate phase on top of the aqueous solution. The phases were separated and the polyamine was placed in a 250 ml round-bottomed flask. One hundred fifty ml of toluene was added and

a Dean-Stark trap was attached. After reflux overnight (about 16 hours), no more water was being removed and the polyamine had dissolved in the hot toluene. The hot solution was filtered and the solvent was removed from the filtrate using vacuum and agitation to give branched

5 poly(ethyleneimine) weighing 2.2 gm (100% of theory) as an orange oil. The ^{13}C -NMR spectrum showed a peak for linear poly(ethyleneimine) (49.4 ppm/intensity 8075), residual unhydrolyzed propionamide (9.5 ppm/intensity 156), (26.3 ppm/intensity 180), and primary amine end group (41.7

10 ppm/intensity 61). No peak for a hydroxy terminal group was observed. While the intensities may not be interpreted as a quantitative measure of the groups present, qualitatively, hydrolysis was 80 to 90% complete and grafting was complete within the limits of detection.

15 Example 4

A 2 liter, 3-necked, round-bottomed, glass flask was used with a shaft driven stirrer, instead of magnetic stirring. The initial loading was: water - 250 ml, material prepared essentially by the method of example 3 - 125 gm,

20 sulfuric acid - 150 gm. Additional sulfuric acid, 100 gm was added halfway through the hydrolysis to improve solubility. Internal flask temperature was monitored and a solenoid valve was rigged to add water whenever the temperature rose above 107°C. Thus, constant attention was not necessary and the

25 distillation could be left unattended overnight. The heating

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mantle was also set to shut off at the same temperature so that the flask would not overheat if the water reservoir ran out of water. After 2 days of continuous distillation, 1.6 liters of distillate was collected. The reaction mixture
5 was neutralized and the polymer phase was separated. The crude polymer was purified by dissolving in hot water (1 liter) and precipitated by slow addition to cold water. After two precipitations, the supernatant solution was neutral to Hydrion^R paper. The resulting hydrated polymer
10 was dehydrated via toluene azeotrope as described above to give LPEI (51 gm 94% yield). The ¹³C-NMR spectrum showed LPEI with residual amide carbon intensities 0.5% of the LPEI intensity. Primary amine end group intensity was 0.4% of the LPEI intensity.

15 Example 5

Into a 250 ml round-bottomed glass flask was placed p-toluenesulfonic acid monohydrate (2.0 gm, 11 mmole) and toluene (100 ml). A Dean-Stark trap was attached and the mixture was heated at reflux until water removal was
20 complete. Ethyl oxazoline (10 gm, 100 mmole) was added all at once and the reflux was continued for 2 hours. LPEI (1.0 gm, 23 meq.) was placed in toluene (25 ml) and the mixture was heated to boiling to dissolve the polymer and azeotropically remove trace water in the polymer. The hot
25 LPEI solution was added all at once, to the cloudy oligomer suspension. An orange oil began to precipitate immediately. After 1 hour at reflux, the mixture was cooled and the solvent stripped using vacuum. The residue was dissolved in CH₂Cl₂ (40 ml) and precipitated by a slow addition to ether
30 (500 ml). The solid was collected by filtration and dried in a vacuum oven at 40° to 50°C to give the grafted polymer (12 gm, 92% yield) as a yellow powder. At higher M/I

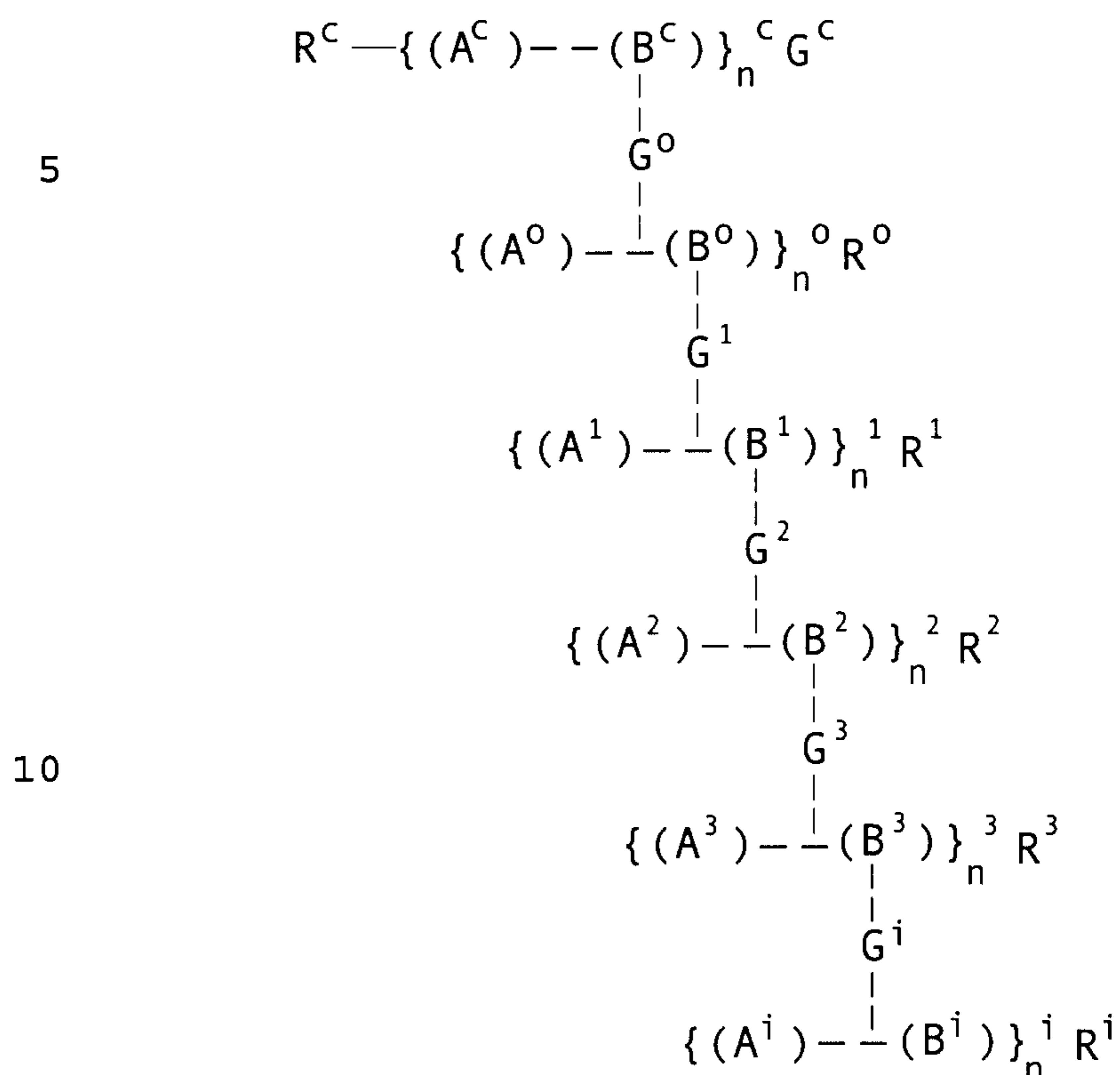
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ratios, the oligomerization time had to be increased to allow complete conversion of the ETOX. For example, intermediate degree of polymerization runs (M/I = 200, olig. time = 3 hours or M/I = 400, olig. time = 6 hours) had low yields due to incomplete conversion. Increasing the reaction time to 12 hours and 24 hours respectively, gave higher conversions and yields. The highest M/I (1000) run, had an oligomerization time of 36 hours, which was not long enough for complete conversion. This gave a material with actual oligomer dp of 700. The ^{13}C -NMR spectrum of the poly-branched polymer derived from this material showed a peak for primary amine end groups which was approaching the limits of detection for the signal/noise ratio. No hydroxyl terminal group was detectable.

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CLAIMS:

1. A composition of matter comprising non-crosslinked poly-branched polymers having the general formula



wherein R^c is a non-reactive end group and each R^0 , R^1 , R^2 , R^3 , and R^i is a residual moiety derived from initiators selected from a group consisting of free radical initiators, cationic initiators, anionic initiators, and group transfer initiators;

i represents repetitive linear polymers having the unit formula $\{ (A^i) - - (B^i) \}$;

A^c , A^0 , A^1 , A^2 , A^3 , and A^i are non-reactive comonomers or, oligomers or polymers formed from a polymerizable monomer, said oligomers or polymers being capable of withstanding the conditions required for preparation of a graft polymer;

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B^c , B^0 , B^1 , B^2 , B^3 , and B^i are protected or unprotected reactive nucleophilic or electrophilic monomers, or oligomers or polymers formed from a polymerizable monomer, said oligomers or polymers being capable of withstanding the conditions required for preparation of a graft polymer;

G^0 , G^1 , G^2 , G^3 and G^i are grafting components which represent bonding between adjacent units of the repetitive linear polymers, said bonding being to either an A segment or a B segment;

G^c is a terminating group;

n^c is the degree of polymerization of a core initiator;

n^0 is the degree of polymerization of a first comb branch;

n^1 is the degree of polymerization of a first generation comb-burst branch;

n^2 is the degree of polymerization of a second generation comb-burst branch;

n^3 is the degree of polymerization of a third generation comb-burst branch,

n^i is the degree of polymerization of the i^{th} generation comb-burst polymer having at least one branch point;

wherein $n^i \geq 2$ for the case where $i = c, 0$, and 1 , and $n^i \geq 2$ if n^{i-1} is $>$ zero, the largest i for which n^i does not equal zero is the total number of generational levels of

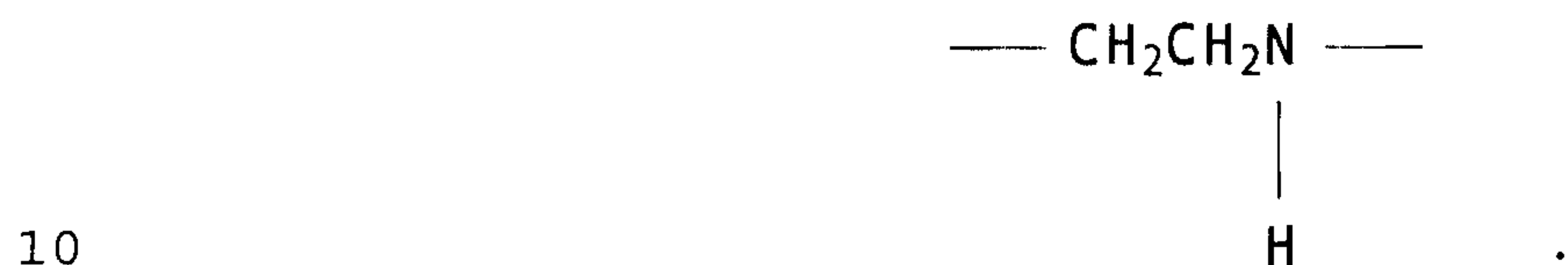
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the polymer wherein the superscripts c, °, 1, 2, 3 and i designate comb-burst generation level;

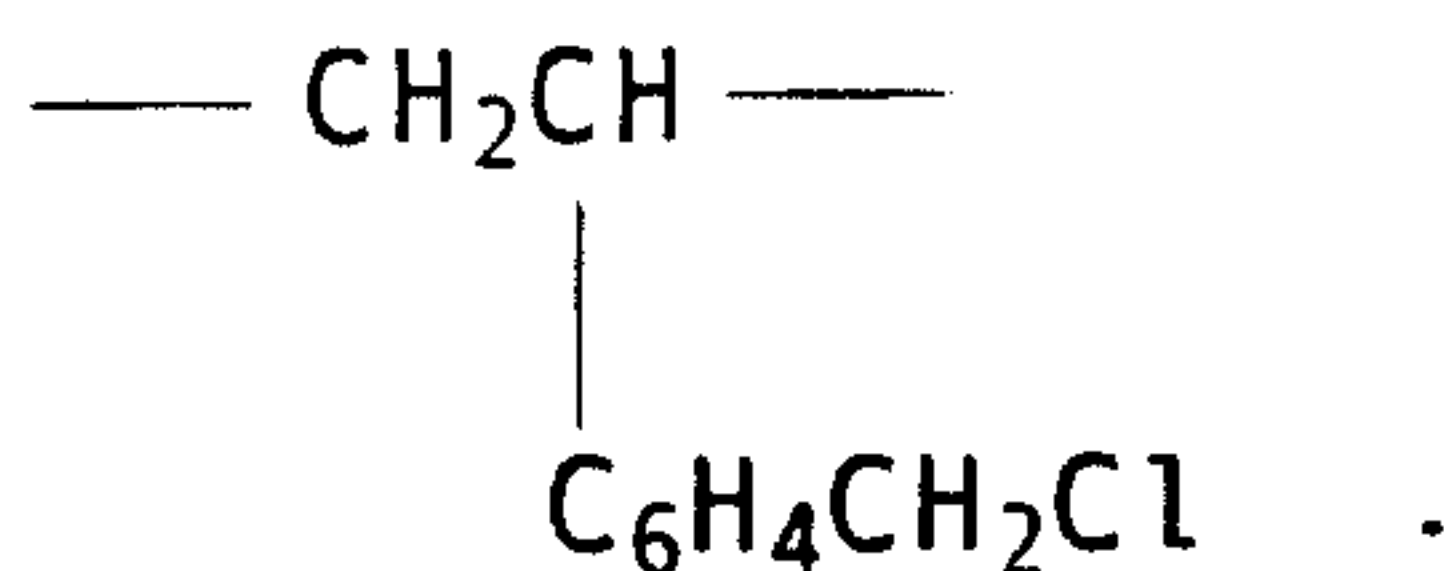
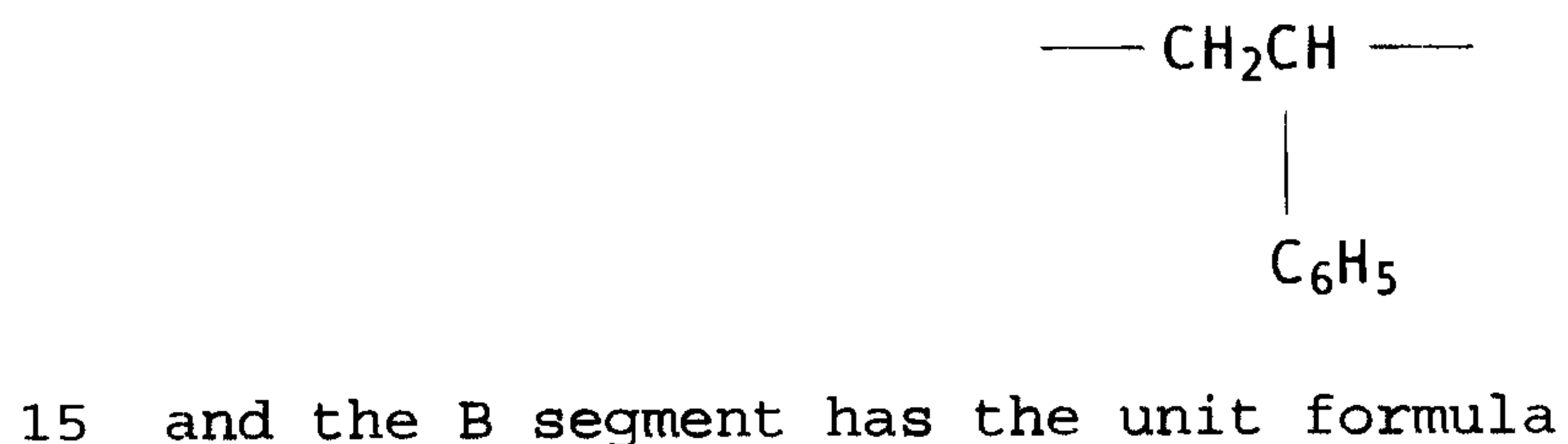
the unit ratio of A segments to B segments in any { (A) -- (B) } segment of the polymer is 0 to 1:100 to 1.

5 2. A composition of matter as claimed in claim 1 which is a hydrolysis product.

3. A composition of matter as claimed in claim 1 wherein the B segment has the unit formula

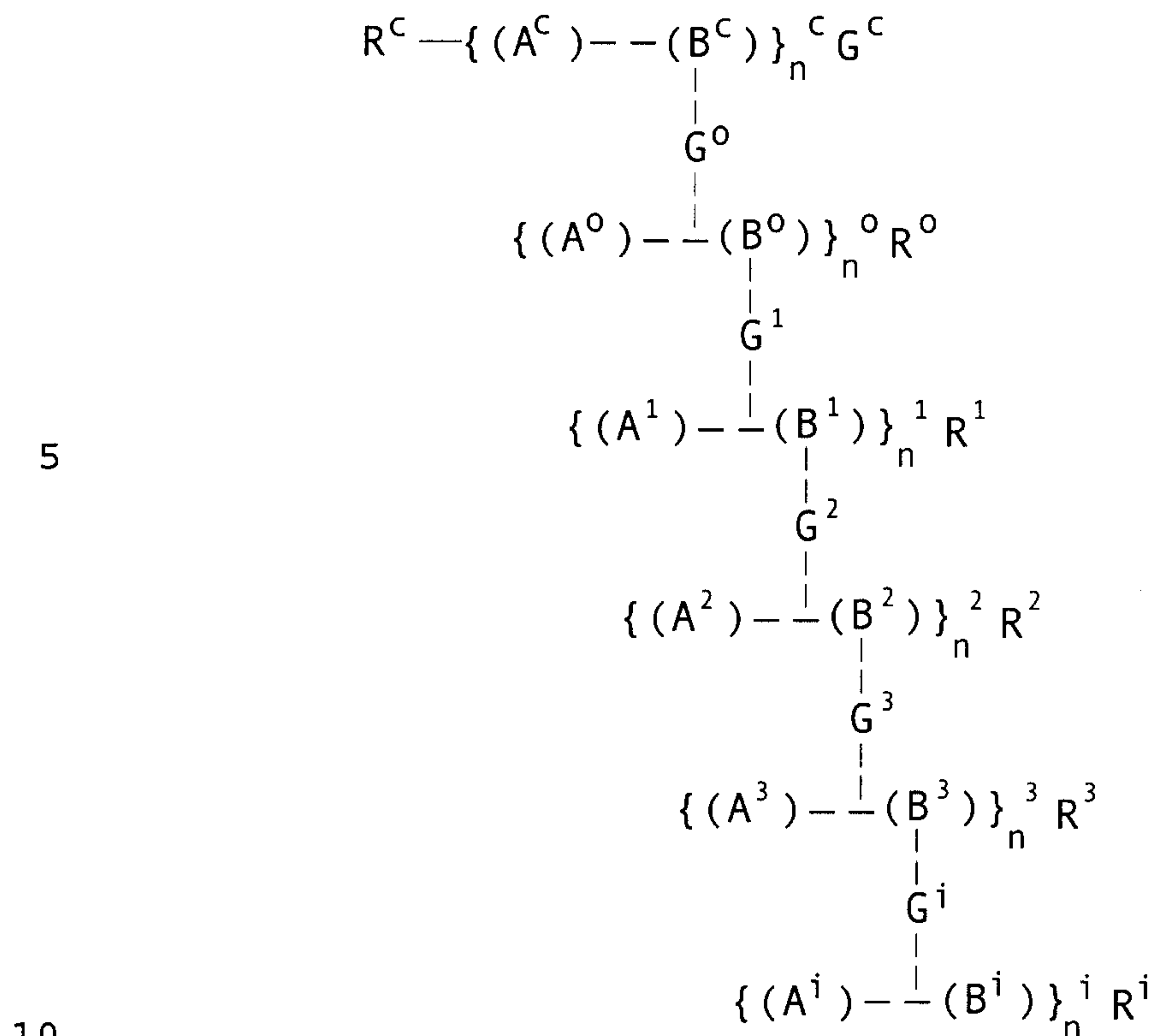


4. A composition of matter as claimed in claim 1 wherein the A segment has the unit formula



5. A process for preparing non-crosslinked poly-branched polymers having the general formula

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wherein R^c is a non-reactive end group and each R^0 , R^1 , R^2 , R^3 , and R^i is a residual moiety derived from initiators selected from a group consisting of free radical initiators, cationic initiators, anionic initiators, and group transfer
15 initiators;

i represents repetitive linear polymers having the unit formula $\{ (A^i) - (B^i) \}$;

A^c , A^0 , A^1 , A^2 , A^3 , and A^i are non-reactive comonomers or, oligomers or polymers formed from a
20 polymerizable monomer, said oligomers or polymers being capable of withstanding the conditions required for preparation of a graft polymer;

B^c , B^0 , B^1 , B^2 , B^3 , and B^i are protected or unprotected reactive nucleophilic or electrophilic monomers,
25 or oligomers or polymers formed from a polymerizable

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monomer, said oligomers or polymers being capable of withstanding the conditions required for preparation of a graft polymer;

G^0 , G^1 , G^2 , G^3 and G^i are grafting components which represent bonding between adjacent units of the repetitive linear polymers, said bonding being to either an A segment or a B segment;

G^c is a terminating group;

n^c is the degree of polymerization of a core initiator;

n^0 is the degree of polymerization of a first comb branch;

n^1 is the degree of polymerization of a first generation comb-burst branch;

n^2 is the degree of polymerization of a second generation comb-burst branch;

n^3 is the degree of polymerization of a third generation comb-burst branch,

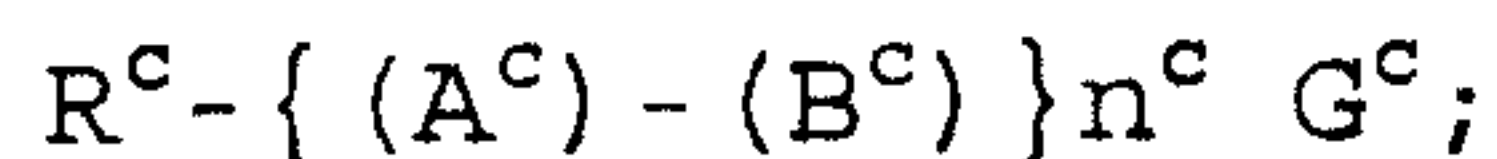
n^i is the degree of polymerization of the i^{th} generation comb-burst polymer having at least one branch point;

wherein $n^i \geq 2$ for the case where $i = c, 0$, and 1 , and $n^i \geq 2$ if n^{i-1} is $>$ zero, the largest i for which n^i does not equal zero is the total number of generational levels of the polymer wherein the superscripts $c, 0, 1, 2, 3$, and i designate comb-burst generation level;

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the unit ratio of A segments to B segments in any { (A) -- (B) } segment of the polymer is 0 to 1:100 to 1, the process comprising

(I) forming a linear initiator core having at least one reactive site and having the general formula



(II) reacting essentially all of the sites (B^c) of (I) with a reactive polymer having the unit formula G^o{ (A^o) - (B^o) }_nR^o to form multiple branches that contain at least one multiple reactive site on each branch using protection-deprotection reactions to ensure that the unit formula G^o{ (A^o) - (B^o) }_nR^o reacts with all (B^c) sites of (I) but that no reactions occur at the reactive sites B^o;

(III) repeat (II) sequentially to form successive generations of reactive branches to give the desired non-crosslinked poly-branched polymers.

6. A process as claimed in claim 5 wherein linear polyethyleneimine is reacted with oxazoline oligomers and is grafted thereby.

7. A process as claimed in claim 6 wherein the oxazoline oligomer is poly-2-alkyl substituted oxazoline.

8. A process as claimed in claim 6 wherein the oxazoline oligomer is poly-2-aryl substituted oxazoline.

9. A process as claimed in claim 6 wherein the grafted polymer is hydrolyzed after grafting.

10. A process as claimed in claim 7, wherein the

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grafted polymer is hydrolyzed after grafting.

11. A process as claimed in claim 8, wherein the grafted polymer is hydrolyzed after grafting.

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PATENT AGENTS

FIG. 1

