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(54) Title: CATALYTIC POLYMERIZATION PROCESS

(57) Abstract

This invention relates to a process for controlling the architecture of copolymers of at least two unsaturated monomers, made by free-radical polymerization in the presence of a cobalt-containing chain transfer agent, including the control of molecular weight, degree of branching and vinyl end group termination, by varying at least one of the variables of molar ratio of monomers, their relative chain transfer constants, polymerization temperature and degree of conversion and amount of cobalt chain transfer agent; and polymers made thereby.
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Catalytic chain transfer is an effective way to control the molecular weight of polymers of methacrylates and styrenes. It is known that chain transfer catalysis (CTC) products contain a terminal vinylidene bond. This feature makes these products attractive as macromonomers for a variety of applications. However, CTC has not been known to be applicable for reduction of molecular weight in the polymerizations of other vinylic monomers such as acrylates.

Copolymerizations of methacrylate monomers with monosubstituted monomers in the presence of cobalt have been described in the art. However, the monosubstituted monomer is almost always present as a minor component. U.S. 4,680,354 describes molecular weight reduction using various Co(II) complexes in MMA-BA, MMA-EA and MMA-BA-St copolymerizations, wherein the abbreviations represent:

MMA=methyl methacrylate
BA=butyl acrylate
EA=ethyl acrylate
St=styrene.

U.S. 5,324,879 describes molecular weight reduction with Co(III) complexes in EA, St, and vinyl acetate (VAc) polymerizations, and MMA-EA copolymerization.

U.S. 4,680,352 describes molecular weight reduction and macromonomer (polymers or copolymers with unsaturated end-groups) synthesis in copolymerizations with acrylates and styrene with various Co(II) complexes. Various terpolymerizations are cited therein; however, no evidence of the nature or existence of terminal double bonds is given.

Gruel et al., Polymer Preprints, 1991, 32, p. 545, reports the use of Co(II) cobaloximes in low conversion St-MMA copolymerizations at low temperatures with end group analysis.

The references cited above cover the copolymerization of acrylates and styrene with methacrylate monomers, but do not disclose synthetic conditions for production of high purity macromonomers based on acrylates and styrene, nor branching of the resulting products. The conditions disclosed are unlikely to yield high purity macromonomers for systems composed predominantly of monosubstituted monomers. Disclosed temperatures of less than 80°C are likely to
provide substantial amounts of undesired graft copolymer at high conversion rates.

**SUMMARY OF THE INVENTION**

This invention concerns an improvement in a process for the free-radical polymerization of at least two unsaturated monomers to form a polymer whose molecular architecture comprises properties of molecular weight, branching, and vinyl-terminated end groups, the monomers having the formula

$$\text{CH}_2-\text{CXY}$$

wherein

X is selected from the group consisting of H, CH$_3$, and CH$_2$OH;

Y is selected from the group consisting of OR, O$_2$CR, halogen, CO$_2$H, COR, CO$_2$R, CN, CONH$_2$, CONHR, CONR$_2$ and R';

R is selected from the group consisting of substituted and

unsubstituted alkyl, substituted and unsubstituted aryl, substituted and

unsubstituted heteroaryl, substituted and unsubstituted aralkyl, substituted and

unsubstituted alkaryl, and substituted and unsubstituted organosilyl, the

substituents being the same or different and selected from the group consisting of

carboxylic acid, carboxylic ester, epoxy, hydroxyl, alkoxy, primary amino,

secondary amino, tertiary amino, isocyanato, sulfonic acid and halogen; and the

number of carbons in said alkyl groups is from 1 to 12; and

R' is selected from the aromatic group consisting of substituted and

unsubstituted aryl, substituted and unsubstituted heteroaryl, the substituents being

the same or different and selected from the group consisting of carboxylic acid,

carboxylic ester, epoxy, hydroxyl, alkoxy, primary amino, secondary amino,

tertiary amino, isocyanato, sulfonic acid, substituted and unsubstituted alkyl,

substituted and unsubstituted aryl, substituted and unsubstituted olefin and

halogen;

by contacting said monomers with a cobalt-containing chain transfer

agent and a free radical initiator at a temperature from about 80° to 170°C;

the improvement which comprises controlling polymer architecture

by introducing into the presence of the chain transfer agent at least one each of

monomers A and B in the molar ratio of A:B, said molar ratio lying in the range of

about 1,000:1 to 2:1, wherein for monomer A X is H and for monomer B X is

methyl or hydroxymethyl; by one or more of the following steps:

I decreasing the ratio of A:B from about 1,000:1 toward 2:1;

II increasing the temperature from above 80°C toward 170 °C;
III  increasing the conversion of monomer to polymer toward 100%
   from less than about 50%;
IV  decreasing the ratio of the chain transfer constant of A:B to below
   1; and
V  increasing the concentration of cobalt chain transfer agent;

whereby:
   to effect lower molecular weight, employ at least one of steps I, II, IV and
   V;
10   to effect a higher degree of vinyl-terminated end groups, employ at least
   one of steps I, II, IV, and V; and
   to effect increased branching, employ at least one of steps I, II, IV, and V
   with step III.

The nature of the derived products changes as a function of time. In the
15   initial stages, linear macromonomers with one monomer-A in the terminal
   position can be obtained as essentially the only product. If the cobalt CTC
   catalyst levels are relatively low then CTC does not occur after every B-monomer
   insertion and the product mixture can include monomer-B units in the polymer
   chain as well as in the terminal position.

Cobalt chain transfer agent is employed in the form of cobalt complexes.
20   Their concentrations are provided in the Examples in terms of ppm by weight of
   total reaction mass. Concentration will vary from 10 ppm to 1,500 ppm,
   preferably 10 to 1,000 ppm.

Later in the course of the reaction, when the concentration of the two
25   above products is increased, then they can be reincorporated into a growing
   polymer chain. Thus, mono-branched product is obtained in the later stages of the
   reaction, usually around 90% conversion. At conversions above 95%, branches
   begin to appear on the branches, and the polymer becomes hyperbranched as
   conversions approach 100%.

Preferred monomers A are selected from the group consisting of
30   acrylates, acrylonitrile and acrylamides;

and preferred monomers B are selected from the group:
   a) substituted or unsubstituted α-methylstyrenes;
35   b) substituted or unsubstituted alkyl methacrylates, where alkyl is
   $C_1$-$C_{12}$;
   c) methacrylonitrile;
   d) substituted or unsubstituted methacrylamide;
e) 2-chloropropene,
f) 2-fluoropropene,
g) 2-bromopropene,
h) methacrylic acid,
i) itaconic acid,
j) itaconic anhydride, and
k) substituted or unsubstituted styrenics.

If branched polymers are the desired product, it is possible to initiate the
described process in the presence of preformed macromonomers. They can be of
the type described in this patent. They can also be macromonomers based entirely
upon methacrylates or the related species described previously in U.S. 4,680,354.
Such a process would lead to products fitting the description above, but would
allow for greater control over the polymer end-groups.

The branched polymers made by said process are polymers of this
invention having the formula:

\[
\begin{align*}
\text{Y} & = \text{as earlier defined;} \\
n & = 1-20, \ m = 1-5, \ p = 1-20, \text{ and } n + m + p \geq 3, \text{ and} \\
Z & \text{ is selected from the group CH}_2\text{CHYCH}_3, \text{ CH}_2\text{CMeYCH}_3, \text{ and, optionally,} \\
\text{Y} & = \text{as earlier defined;} \\
m' & = 0-5, \ p' = 0-20; \ n + m' + p' \geq 2; \\
\text{and if } m \text{ or } m' > 1, \text{ the } m \text{ or } m' \text{ insertions respectively are not consecutive.}
\end{align*}
\]

This invention also concerns a process comprising selecting A and B
so the ratio of their chain transfer constants is less than 1, whereby functionality
derived from Monomer B will be located on the vinyl-terminated end of the
polymer.

This invention also concerns an improved process for the free-radical
polymerization of at least two unsaturated monomers having the formula

\[
\text{CH}_2\equiv\text{CXY}
\]
wherein

\[ \text{X is selected from the group consisting of H, CH}_3\text{, and CH}_2\text{OH;} \]
\[ \text{Y is selected from the group consisting of OR, O}_2\text{CR, halogen, CO}_2\text{H,} \]
\[ \text{CO}_2\text{R, CN, CONH}_2, \text{CONHR, CONR}_2, \text{COR and R'}; \]
\[ \text{R is selected from the group consisting of substituted and} \]
\[ \text{unsubstituted alkyl, substituted and unsubstituted aryl, substituted and} \]
\[ \text{unsubstituted heteroaryl, substituted and unsubstituted aralkyl, substituted and} \]
\[ \text{unsubstituted alkaryl, and substituted and unsubstituted organosilyl, the} \]
\[ \text{substituents being the same or different and selected from the group consisting of} \]
\[ \text{carboxylic acid, carboxylic ester, epoxy, hydroxyl, alkoxy, primary amino,} \]
\[ \text{secondary amino, tertiary amino, isocyanato, sulfonic acid and halogen, and the} \]
\[ \text{number of carbons in said alkyl groups is from 1 to 12; and} \]
\[ \text{R' is selected from the aromatic group consisting of substituted and} \]
\[ \text{unsubstituted aryl, substituted and unsubstituted heteroaryl, the substituents being} \]
\[ \text{the same or different and selected from the group consisting of carboxylic acid,} \]
\[ \text{carboxylic ester, epoxy, hydroxyl, alkoxy, primary amino, secondary amino,} \]
\[ \text{tertiary amino, substituted and unsubstituted alkyl, substituted and unsubstituted} \]
\[ \text{aryl, substituted and unsubstituted olefin and halogen;} \]
\[ \text{by contacting said monomers with a cobalt-containing chain transfer} \]
\[ \text{agent and a free radical initiator at a temperature from about 80}^\circ\text{C to}170^\circ\text{C;}} \]
\[ \text{the improvement which comprises controlling molecular weight of the} \]
\[ \text{polymer architecture by introducing into the presence of the chain transfer agent at} \]
\[ \text{least one each of monomers C and D in the molar ratio of C:D in the range of} \]
\[ \text{about 1,000:1 to}2:1, \text{in which for monomer C, X is H and Y} \neq \text{R'} \text{and for} \]
\[ \text{monomer D, X is H and Y} = \text{R'} \text{by:} \]
\[ \text{decreasing the ratio of C:D from about 1,000:1 toward 2:1; or} \]
\[ \text{increasing the temperature from above}80^\circ\text{C toward}170^\circ\text{ C.} \]
\[ \text{Preferred monomers A are selected from the group consisting of} \]
\[ \text{acrylates, acrylonitrile and acrylamides;} \]
\[ \text{and preferred monomers B are substituted and unsubstituted styrenics.} \]
\[ \text{The polymers made by said process improvement are polymers of this} \]
\[ \text{invention having the formula:} \]
\[ \text{where} Y \neq \text{R'} \text{and} n \geq 1. \]
This invention also concerns a process improvement for polymerizing monomer(s) in the presence of an excess of a nonpolymerizable olefin, \( Y^{1}Y^{2}C=CY^{3}Y^{4} \). The product in the initial stages of the polymerization will be composed primarily of

\[
\begin{align*}
\text{H} & \quad \text{C} \quad \text{H} \\
\text{Y}^{2} & \quad \text{Y}^{4} \quad \text{Y} & \quad \text{C} \quad \text{H}_{2} \quad \text{C} \quad \text{H}_{2} \quad \text{C} \quad \text{CH}_{2}
\end{align*}
\]

wherein:

\( Y^{1} \) and \( Y^{3} \), and optionally \( Y^{2} \) and \( Y^{4} \), are each independently selected from the group consisting of -CH(O), -CN, -C(O)OR, -C(O)NR, alkyl, aryl, substituted alkyl, substituted aryl; or

where \( Y^{1} \) and \( Y^{3} \) or \( Y^{2} \) and \( Y^{4} \) are combined in a cyclic structure which includes any of the above functionalities, or can be -C(O)-(CH_{2})_{x}-, -C(O)-O-(CH_{2})_{x}-, -C(OO)-C(O)-, -C(O)(CH_{2})_{x}-, -C(O)NR-CH_{2}X-, wherein \( x=1-12 \), \( R^{1}, R^{2}, R^{3}, R^{4} \), or \( R^{5} \) are hydrogen, alkyl, aryl, substituted alkyl, or substituted aryl; and where at least one of \( Y^{1} \) and \( Y^{3} \) is selected from the group consisting of -CH(O), -CN, -C(O)OR, -C(O)NR, aryl, substituted aryl; and the remaining of \( Y^{2} \) and \( Y^{4} \) are -H.

The polymers made by said process improvement are polymers of this invention produced at later stages of the polymerization process having the formula:

\[
\begin{align*}
\text{H} & \quad \text{C} \quad \text{H} \\
\text{Y}^{2} & \quad \text{Y}^{4} \quad \text{H} & \quad \text{C} \quad \text{H} \quad \text{C} \quad \text{H} \quad \text{C} \quad \text{CH}_{2}
\end{align*}
\]

where \( Z = H, CH_{3}, CH_{2}CHYCH_{3}, CH_{2}CMYCH_{3} \), or

\[
\begin{align*}
\text{H} & \quad \text{C} \quad \text{H} \\
\text{Y}^{2} & \quad \text{Y}^{4} \quad \text{H} & \quad \text{C} \quad \text{H} \quad \text{C} \quad \text{H} \quad \text{C} \quad \text{CH}_{2}
\end{align*}
\]

k = 0 or 1, n = 0-20, m = 0-5, p = 0-20; and \( k + n + m + p \geq 2 \); if \( m > 1 \), then it is not intended to imply that the m insertions are consecutive;

\( Y \) is selected from the group consisting of OR, O_{2}CR, halogen, CO_{2}H, COR, CO_{2}R, CN, CONH_{2}, CONHR, CONR_{2} and \( R' \); and

\( Y^{1} \) to \( Y^{4} \) and \( R \) and \( R' \) are as defined above.
DETAILS OF THE INVENTION

We have discovered that, with addition of small amounts of an \( \alpha \)-methylvinyl monomer and appropriate choice of reaction conditions, polymerization of monosubstituted monomers in the presence of a metal complex can provide high yield of macromonomers. These macromonomers can subsequently be used for the synthesis of a wide range of block and graft copolymers.

This invention concerns a method for the synthesis of \( \omega \)-unsaturated macromonomers composed predominantly of monosubstituted monomers. The macromonomers are prepared by polymerizing a monosubstituted monomer as the major component (for example styrene) in the presence of a disubstituted \( \alpha \)-methylvinyl monomer (for example, \( \alpha \)-methylstyrene, herein also referred to as "AMS") and a catalytic amount of a cobalt complex [for example, Co(II)(DMG-BF2)2] called CoII in Scheme 1. Reaction Scheme 1 illustrates the process where monomer A = styrene and monomer B = \( \alpha \)-methylstyrene. The process is applicable to a wide range of monosubstituted monomers (for example acrylate esters, vinyl acetate (VAc)) and other non-\( \alpha \)-methylvinyl monomers.

Scheme 1:

In Scheme 1, "Ph" represents a phenyl group, and "m" designates the number of monomer units in the polymer, and is \( \geq 1 \).

The key features of the invention are the addition of small amounts of \( \alpha \)-methylvinyl monomers and the use of high reaction temperatures in the presence of chain transfer catalysts.

The incorporation of \( \alpha \)-methylvinyl monomers into the recipe allows formation of the desired macromonomer end group. In the absence of the \( \alpha \)-methylvinyl monomer, polymerization of monosubstituted monomers give polymers with internal double bonds (styrenic monomer) or a stable alkyl-cobalt species (acrylate monomers) as chain ends.
The use of high reaction temperatures (>100 °C) favors the formation of pure linear macromonomers from monosubstituted monomers (for example acrylates, vinyl esters, and styrene). At lower temperatures we have shown that the formed macromonomers can react further by copolymerization to give branched polymers. Even though the macromonomers can undergo further reaction, at reaction temperatures >100 °C, the radicals so formed do not propagate to give branched polymers. Rather, they fragment to give back a macromonomer. It is possible that this chemistry will also reduce the polydispersity of the final product.

The invention also provides a route to block or graft copolymers as illustrated in Scheme 2. The product derived by copolymerization of the macromonomer in the presence of monomers can be determined by appropriate choice of the monomer and the reaction conditions.

Scheme 2:

In Scheme 2, "Ph" represents a phenyl group; "m", "n" and "o" designate the number of monomer units in the polymer; and X and Y are as defined above.

We have demonstrated that styrene macromonomers prepared by the above mentioned copolymerization route give chain transfer (by an addition fragmentation mechanism) and have acceptable chain transfer constants at
temperatures >100 °C. They should therefore be useful in the preparation of block
copolymers.

One further aspect of the invention is that by appropriate choice of the
α-methylvinyl monomer the method is also a route to end-functional polymers.

For example, use of a hydroxyethyl- or glycidyl-functional monomer would yield
polymers with ω-hydroxy or ω-epoxy groups, respectively.

This method enables the versatility and robustness of the cobalt
technology to be utilized to form macromonomers that are comprised
predominantly of monosubstituted monomers. Additionally, it provides the key
step in a new and less expensive route to end-functional and block or graft
copolymers based on monosubstituted monomers. Copolymerizations of
monosubstituted monomers with other α-methylvinyl monomers (for example α-
methylstyrene) in the presence of cobalt are contemplated.

The choice of the α-methylvinyl comonomer is important in
macromonomer synthesis. It must be chosen so that the reactivity towards cobalt
("catalytic chain transfer constant") of the derived propagating species is
substantially greater than that of the propagating species derived from the
monosubstituted monomer.

Two factors influence this reactivity.

a) The rate of the chain transfer reaction between the propagating
   species and the cobalt complex;

b) The relative concentrations of the propagating species. This is
determined not only by the monomer concentration but also by
   the propagation rate constants and reactivity ratios.

While methacrylate esters can be used as α-methylvinyl comonomers
(see examples), in copolymerization with styrene, the values of the reactivity
ratios and propagation rate constants will favor the formation of styryl chain ends.
The product then has an internal rather than the desired terminal double bond.

Methacrylate esters are acceptable comonomers in, for example, acrylate
polymerizations.

Thus, the use of α-methylvinyl comomers (for example, α-methylstyrene, methacrylonitrile) which have low propagation rate constants
and high chain transfer rate constants are preferred.

There are substantial cost improvements over alternative technologies
which involve the use of stoichiometric amounts of an organic transfer agent. The
ability to use acrylate/styrenic rich macromonomers, in contexts similar to those
developed for methacrylate monomers products by cobalt mediated processes. for
example, in graft, star, block and branched copolymer syntheses, further extends the value of the process.

The nature of the derived products changes as a function of time. In the initial stages, the product

\[
\begin{align*}
\text{H} & \quad \text{(H)} \\
\text{C} & \quad \text{(C)} \\
\text{H}_2 & \quad \text{(Y)} \\
\text{C} & \quad \text{(C)} \\
\text{H}_2 & \quad \text{(Y)} \\
\text{CH}_2 & \\
\end{align*}
\]

n

\[
\begin{align*}
\text{H} & \quad \text{(C)} \\
\text{C} & \quad \text{(C)} \\
\text{H}_2 & \quad \text{(Y)} \\
\text{CH}_2 & \\
\end{align*}
\]

m

\[
\begin{align*}
\text{H} & \quad \text{(H)} \\
\text{C} & \quad \text{(C)} \\
\text{H}_2 & \quad \text{(Y)} \\
\text{C} & \quad \text{(C)} \\
\text{H}_2 & \quad \text{(Y)} \\
\text{CH}_2 & \\
\end{align*}
\]

p

\[
\begin{align*}
\text{H} & \quad \text{(C)} \\
\text{C} & \quad \text{(C)} \\
\text{H}_2 & \quad \text{(Y)} \\
\text{CH}_2 & \\
\end{align*}
\]

Later in the course of the reaction, when the concentration of the two above products is increased, they can be reincorporated into a growing polymer chain. Thus, the product

\[
\begin{align*}
\text{H} & \quad \text{(CH}_2\text{C)} \\
\text{Y} & \quad \text{(Y)} \\
\text{(CH}_2\text{C)} & \quad \text{(CH}_2\text{C)} \\
\text{Y} & \quad \text{(Y)} \\
\text{(CH}_2\text{C)} & \quad \text{(CH}_2\text{C)} \\
\text{Y} & \quad \text{(Y)} \\
\text{CH}_2 & \quad \text{CCH}_2 \\
\end{align*}
\]

where Z can include -H, -CH\textsubscript{3}, CH\textsubscript{2}CHYCH\textsubscript{3}, CH\textsubscript{2}CM\textsubscript{e}YCH\textsubscript{3}, or

\[
\begin{align*}
\text{H} & \quad \text{(C)} \\
\text{H}_2 & \quad \text{(Y)} \\
\text{(C)} & \quad \text{(C)} \\
\text{H}_2 & \quad \text{(Y)} \\
\text{(C)} & \quad \text{(C)} \\
\text{H}_2 & \quad \text{(Y)} \\
\text{(C)} & \quad \text{(C)} \\
\text{H}_2 & \quad \text{(Y)} \\
\end{align*}
\]

n

\[
\begin{align*}
\text{H} & \quad \text{(C)} \\
\text{H}_2 & \quad \text{(Y)} \\
\text{(C)} & \quad \text{(C)} \\
\text{H}_2 & \quad \text{(Y)} \\
\text{(C)} & \quad \text{(C)} \\
\text{H}_2 & \quad \text{(Y)} \\
\end{align*}
\]

m

\[
\begin{align*}
\text{H} & \quad \text{(C)} \\
\text{H}_2 & \quad \text{(Y)} \\
\text{(C)} & \quad \text{(C)} \\
\text{H}_2 & \quad \text{(Y)} \\
\end{align*}
\]

p
is obtained. In the early stages of the reaction, Z is most often H, but as the reaction proceeds toward 90% conversion, Z begins to include more of the higher molecular weight species as branches. At conversions above 95%, branches begin to appear on the branches, and the polymer becomes hyperbranched as conversions approach 100%.

Metal complexes are those that give catalytic chain transfer with α-methylvinyl monomers. Examples include, but are not limited to, cobalt(II) and cobalt(III) chelates:

\[
\text{Co(II)(DPG-BF}_2\text{)}_2 \quad J=K=\text{Ph}, \ L=\text{ligand}
\]
\[
\text{Co(II)(DMG-BF}_2\text{)}_2 \quad J=K=\text{Me}, \ L=\text{ligand}
\]
\[
\text{Co(II)(EMG-BF}_2\text{)}_2 \quad J=\text{Me}, \ K=\text{Et}, \ L=\text{ligand}
\]
\[
\text{Co(II)(DEG-BF}_2\text{)}_2 \quad J=K=\text{Et}, \ L=\text{ligand}
\]
\[
\text{Co(II)(CHG-BF}_2\text{)}_2 \quad J=K=-(\text{CH}_2\text{)}_4\text{Me}, \ L=\text{ligand}
\]

\[
\text{QCo(III)(DPG-BF}_2\text{)}_2 \quad J=K=\text{Ph}, \ R=\text{alkyl}, \ L=\text{ligand}
\]
\[
\text{QCo(III)(DMG-BF}_2\text{)}_2 \quad J=K=\text{Me}, \ R=\text{alkyl}, \ L=\text{ligand}
\]
\[
\text{QCo(III)(EMG-BF}_2\text{)}_2 \quad J=\text{Me}, \ K=\text{Et}, \ R=\text{alkyl}, \ L=\text{ligand}
\]
\[
\text{QCo(III)(DEG-BF}_2\text{)}_2 \quad J=K=\text{Et}, \ R=\text{alkyl}, \ L=\text{ligand}
\]
\[
\text{QCo(III)(CHG-BF}_2\text{)}_2 \quad J=K=-(\text{CH}_2\text{)}_4\text{Me}, \ R=\text{alkyl}, \ L=\text{ligand}
\]
\[
\text{QCo(III)(DMG-BF}_2\text{)}_2 \quad J=K=\text{Me}, \ R=\text{halogen}, \ L=\text{ligand}
\]

L can be a variety of additional neutral ligands commonly known in coordination chemistry. Examples include water, amines, ammonia, phosphines, The catalysts can also include cobalt complexes of a variety of porphyrin
molecules such as tetrphenylporphyrin, tetraanisylporphyrin, tetramesitylporphyrin and other substituted species.

\[ \alpha\text{-Methylvinyl monomers (B monomers) have the general structure} \]

\[
Y \quad \text{CH}_3 \quad \text{CH}_2\text{OH} \quad Y
\]

where \( Y \) is as described above in the "Summary". \( R \) is an optionally substituted alkyl (such as fluoroalkyl, hydroxyalkyl, or epoxyalkyl), organosilyl, or aryl group. Preferred examples of \( \alpha \)-methylvinyl monomers (B monomers) include methacrylate esters, \( \alpha \)-methylstyrene and methacyronitrile.

“\( A \)” monomers have the general structure:

\[
Y
\]

where \( Y \) is as described above in the "Summary".

The enhanced utility of the polymerization method discussed in this invention is that it extends each of these general CTC methodologies:

i) molecular weight control is extended from methacrylates and styrenes to include acrylates, vinyl esters, and other higher activity monomer species;

ii) macromonomer synthesis is extended to the monomers in (i) while retaining the desirable vinyl termination of the resulting species;

iii) end-functional polymer synthesis is also extended to the monomers in (i);

iv) the use of macromonomers as chain transfer agents is extended to include monomer classes heretofore unavailable through CTC technology; and

v) not only are a wider range of block and graft copolymers available through the use of CTC technology, but now it is possible to prepare branched and even hyperbranched species through single-pot reactions.

It is preferred to employ free-radical initiators and solvents in the process of this invention. The process can be run in batch, semi-batch, continuous, bulk, emulsion or suspension mode.

Most preferred \( A \)-monomers are:
methyl acrylate, ethyl acrylate, propyl acrylate (all isomers), butyl acrylate (all isomers), 2-ethylhexyl acrylate, isobornyl acrylate, acrylic acid, benzyl acrylate, phenyl acrylate, acrylonitrile, glycidyl acrylate, 2-hydroxyethyl acrylate, hydroxypropyl acrylate (all isomers), hydroxybutyl acrylate (all isomers), diethylaminoethyl acrylate, triethylene glycol acrylate, N-tert-butyl acrylamide, N-n-butyl acrylamide, N-methyl-ol acrylamide, N-ethyl-ol acrylamide, trimethoxysilylpropyl acrylate, triethoxysilylpropyl acrylate, tributoxysilylpropyl acrylate, dimethoxymethylsilylpropyl acrylate, diethoxymethylsilylpropyl acrylate, dibutoxymethylsilylpropyl acrylate, diisopropoxymethylsilylpropyl acrylate, dimethoxysilylpropyl acrylate, diethoxysilylpropyl acrylate, dibutoxysilylpropyl acrylate, diisopropoxysilylpropyl acrylate, vinyl acetate, styrene, diethylamino styrene, P—methy1styrene, vinyl benzoic acid, vinylbenzinsulfonic acid, vinyl propionate, vinyl butyrate, vinyl benzoate, vinyl chloride, vinyl fluoride, vinyl bromide.

Most preferred B-monomers are:
methyl methacrylate, ethyl methacrylate, propyl methacrylate (all isomers), butyl methacrylate (all isomers), 2-ethylhexyl methacrylate, isobornyl methacrylate, methacrylic acid, benzyl methacrylate, phenyl methacrylate, methacrylonitrile, alpha methyl styrene, trimethoxysilylpropyl methacrylate, triethoxysilylpropyl methacrylate, tributoxysilylpropyl methacrylate, dimethoxymethylsilylpropyl methacrylate, diethoxymethylsilylpropylmethacrylate, dibutoxysilylpropyl methacrylate, diisopropoxymethylsilylpropyl methacrylate, dimethoxysilylpropyl methacrylate, diethoxysilylpropyl methacrylate, dibutoxysilylpropyl methacrylate, diisopropoxysilylpropyl methacrylate, isopropenyl butyrate, isopropenyl acetate, isopropenyl benzoate, isopropenyl chloride, isopropenyl fluoride, isopropenyl bromideitaconic aciditaconic anhydridedimethyl itaconate. methyl itaconateN-tert-butyl methacrylamide, N-n-butyl methacrylamide, N-methyl-ol methacrylamide, N-ethyl-ol methacrylamide, isopropenylbenzoic acid (all isomers), diethy lamino alphamethyl styrene (all isomers), para-methyl-alpha-methy1styrene (all isomers), diisopropenylbenzene (all isomers), isopropenylbenzene sulfonic acid (all isomers), methyl 2-hydroxymethylacrylate, ethyl 2-hydroxymethylacrylate, propyl 2-hydroxymethylacrylate (all isomers), butyl 2-hydroxymethylacrylate (all isomers), 2-ethylhexyl 2-hydroxymethylacrylate, isobornyl 2-hydroxymethylacrylate, and TM1® dimethyl Meta-Isopropenylbenzyl Isocyanate.

Preferred C monomers are those from the list of A monomers minus the styrenic family.

Preferred D monomers include the following styrenes:
styrene, vinyl benzoic acid (all isomers), diethylamino styrene (all isomers), parameethylstyrene (all isomers), and vinyl benzene sulfonic acid (all isomers).

Typical products of the reaction at lower conversions include the linear products from methyl acrylate and methyl methacrylate:

from butyl acrylate and alpha-methylstyrene:

from hydroxyethyl acrylate and alpha-methylstyrene:

from vinyl benzoate and butyl methacrylate:
Typical products of the reaction at lower conversions include the linear products from butyl acrylate and methyl methacrylate:

\[
\begin{align*}
&\text{H} - \left( \text{CH}_2 - \text{C} - \left( \text{C}_n\text{O}_2\text{Bu} \right) \right) - \text{CH}_2 \\
&\text{H} - \left( \text{CH}_2 - \text{C} - \left( \text{CH}_2 - \text{C} - \left( \text{CH}_2 - \text{C} - \left( \text{C}_n\text{O}_2\text{Me} \right) \right) - \text{CO}_2\text{Me} \right) \right) - \text{CH}_2 \\
\end{align*}
\]

from methyl acrylate and alpha-methylstyrene:

\[
\begin{align*}
&\text{H} - \left( \text{CH}_2 - \text{C} - \left( \text{C}_m\text{O}_2\text{Me} \right) \right) - \text{CH}_2 \\
&\text{H} - \left( \text{CH}_2 - \text{C} - \left( \text{CH}_2 - \text{C} - \left( \text{CH}_2 - \text{C} - \left( \text{C}_m\text{O}_2\text{Me} \right) \right) \right) - \text{CO}_2\text{Me} \right) \right) - \text{CH}_2 \\
&\text{H} - \left( \text{CH}_2 - \text{C} - \left( \text{CH}_2 - \text{C} - \left( \text{CH}_2 - \text{C} - \left( \text{C}_p\text{O}_2\text{Me} \right) \right) \right) \right) - \text{CH}_2 \\
&\text{H} - \left( \text{CH}_2 - \text{C} - \left( \text{CH}_2 - \text{C} - \left( \text{CH}_2 - \text{C} - \left( \text{C}_p\text{O}_2\text{Ph} \right) \right) \right) \right) - \text{CH}_2 \\
&\text{H} - \left( \text{CH}_2 - \text{C} - \left( \text{CH}_2 - \text{C} - \left( \text{CH}_2 - \text{C} - \left( \text{C}_p\text{O}_2\text{Me} \right) \right) \right) \right) - \text{CH}_2 \\
\end{align*}
\]

When the polymerization (for example butyl acrylate as A-monomer and methyl methacrylate as B-monomer) is carried out in the presence of a nonpolymerizable olefin such as 2-pentenenitrile, the product in the initial stages of the polymerization will be:

\[
\begin{align*}
&\text{Bu} - \left( \text{C}_n\text{O}_2\text{Bu} \right) - \text{CO}_2\text{Me} \\
&\text{CN} - \left( \text{H}_2 - \text{C} - \left( \text{H}_2 - \text{C} - \left( \text{H}_2 - \text{C} - \left( \text{C}_n\text{O}_2\text{Bu} \right) \right) \right) \right) - \text{CO}_2\text{Me} \\
\end{align*}
\]

15
and later in the polymerization, the product will be:

\[
\text{Bu} - \text{C} - \left( \text{CH}_2 - \text{C} - \text{CO}_2\text{Bu} \right)_m \text{CN} \\
\text{Bu} - \text{C} - \left( \text{CH}_2 - \text{C} - \text{CO}_2\text{Me} \right)_n \text{CH}_2 - \text{C} - \text{CH}_2
\]

It becomes impractical to draw schematics of any of the higher degrees of branching that are obtained as the conversion of the polymerization approaches 100%.

Oligomers, macromonomers and polymers made by the present process are useful in a wide variety of coating and molding resins. Other potential uses can include cast, blown, spun or sprayed applications in fiber, film, sheet, composite materials, multilayer coatings, photopolymerizable materials, photoresists, surface active agents, dispersants, adhesives, adhesion promoters, coupling agents, compatibilizers and others. End products taking advantage of available characteristics can include, for example, automotive and architectural coatings or finishes, including high solids, aqueous or solvent based finishes.

Polymers, such as those produced in this invention, will find use in, for example, structured polymers for use in pigment dispersants.

K⁺IDS mass spectroscopy is an ionization method that produces pseudomolecular ions in the form of [M]K⁺ with little or no fragmentation. Intact organic molecules are desorbed by rapid heating. In the gas phase, the organic molecules are ionized by potassium attachment. Potassium ions are generated from an aluminosilicate matrix that contains K₂O. All of these experiments were performed on a Finnegan Model 4615 GC/MS quadrupole mass spectrometer (Finnegan MAT (USA), San Jose, CA). An electron impact source configuration operating at 200 °C and a source pressure of <1×10⁻⁶ torr was used. MALDI was also performed on this instrument.

All MW and DP measurements were based on gel permeation chromatography (GPC) using styrene as a standard.
Definitions

The following abbreviations have been used and are defined as:

TAPCo = meso-tetra(4-methoxyphenyl)porphyrin-Co; VAZOR®-88 = 1,1'-azobis(cyclohexane-1-carbonitrile) (DuPont Co., Wilmington, DE); VRO-110 = 2,2'-azobis(2,4,4-trimethylpentane) (Wako Pure Chemical Industries, Ltd., Osaka, Japan);

DP = degree of polymerization. \( M_n \) is number average molecular weight and \( M_w \) is weight average molecular weight. AIBN is azoisobutyronitrile. THF is tetrahydrofuran. MA = methylacrylate.

EXAMPLES

EXAMPLES 1-9

Synthesis of low molecular weight styrene macromonomers

AMS comonomer

Feed polymerization

Examples 1-3 and Control 1 show that molecular weight control is obtained in the absence of added \( \alpha \)-methylstyrene. The products have structure 1 with an internal double bond and do not function as macromonomers.

Solution polymerization of styrene with \( \alpha \)-methylstyrene (10:1) and iPrCo(III)(DMG-BF\(_2\))\(_2\) isopropylecobalt(III)(DMG) (100 ppm) in n-butyl acetate at 125 °C

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-butyl acetate</td>
<td>20.04 g</td>
</tr>
<tr>
<td>styrene (sty)</td>
<td>10.03 g</td>
</tr>
<tr>
<td>( \alpha )-methylstyrene</td>
<td>1.00 g</td>
</tr>
</tbody>
</table>

Shot:

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>iPrCo(III)(DMG-BF(_2))(_2)</td>
<td>1.4 mg</td>
</tr>
<tr>
<td>n-butyl acetate</td>
<td>5.00 g</td>
</tr>
</tbody>
</table>

Feed 1:

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1'-azobis(4-cyclohexanecarbonitrile)</td>
<td>0.093 g</td>
</tr>
<tr>
<td>n-butyl acetate</td>
<td>6.73 g</td>
</tr>
<tr>
<td>iPrCo(III)(DMG-BF(_2))(_2)</td>
<td>4.6 mg</td>
</tr>
</tbody>
</table>

Feed 2:

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>styrene</td>
<td>13.57 g</td>
</tr>
<tr>
<td>( \alpha )-methylstyrene</td>
<td>1.57 g</td>
</tr>
</tbody>
</table>
The butyl acetate was degassed in a 5 neck 250 mL reactor, equipped with condenser, stirred, and N₂ purge. The monomers were added and degassed for a further 10 minutes. The reactor was heated to reflux (ca 125°C) and the shot of iPrCo(III)(DMG-BF₂)₂/solvent added. The monomer and initiator feeds were started immediately. The reactor was sampled at regular intervals to monitor intermediate molecular weights (GPC, THF) and conversions (¹H NMR, CDCl₃). A sample of this low viscosity yellow liquid was precipitated into a twenty fold excess of methanol, and the macromonomer recovered as a fine white powder. \( \tilde{M}_n \) 1270, \( \tilde{M}_w/\tilde{M}_n \) 1.43, 34% conversion. The precipitated samples were examined by ¹H NMR (200 MHz, CDCl₃) to establish the nature of the chain ends.

The unsaturated end groups give rise to signals as follows: styryl end group internal double bond (1): \( \delta_6.1 \cdot \text{-CH(Ph)} = \text{CH-Ph} \); \( \delta_8.3 \cdot \text{-CH(Ph)} = \text{CH=CH-Ph} \). Alpha methyl styrene- (AMS)-derived terminal methylene double bond (2): \( \delta_4.8 \cdot \text{H and } \delta_5.2 \cdot \text{H, } \text{-C(Ph)} = \text{CH}_2 \) (the ratio of the signals at \( \delta_6.1 \) and \( \delta_4.8 \) was found to give the best estimate of terminal double bond content. Although this utilises a signal on the fringe of the broad aromatic resonance \( \delta 7.6-7.2 \), a series of comparisons of the ¹H-NMR molecular weights calculated from the end groups with those obtained by GPC showed that this gave better results than the signal at \( \delta 8.3 \). This may be due to the internal double bond product being a mixture of (1) and (3).

Table 1.1: Polymerization of styrene in presence of AMS and iPrCo(III) (DMG-BF₂)₂ at 125°C

<table>
<thead>
<tr>
<th>Example</th>
<th>Time (min)</th>
<th>[Co(III)] ppm</th>
<th>Sty: AMS</th>
<th>( \tilde{M}_n )</th>
<th>( \tilde{M}_w )</th>
<th>( \tilde{M}_w/\tilde{M}_n )</th>
<th>Conv. %</th>
<th>[2]%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>100</td>
<td>-</td>
<td>1050</td>
<td>2290</td>
<td>2.18</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>100</td>
<td>-</td>
<td>1150</td>
<td>2540</td>
<td>2.21</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>100</td>
<td>-</td>
<td>1100</td>
<td>2590</td>
<td>2.18</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ppt</td>
<td>100</td>
<td>-</td>
<td>1630</td>
<td>1660</td>
<td>1.69</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>50</td>
<td>-</td>
<td>2010</td>
<td>4150</td>
<td>2.06</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>50</td>
<td>-</td>
<td>1720</td>
<td>3980</td>
<td>2.30</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ppt</td>
<td>50</td>
<td>-</td>
<td>1940</td>
<td>1940</td>
<td>2.03</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>25</td>
<td>-</td>
<td>3270</td>
<td>11153</td>
<td>3.41</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>25</td>
<td>-</td>
<td>2710</td>
<td>9540</td>
<td>3.52</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ppt</td>
<td>25</td>
<td>-</td>
<td>2750</td>
<td>2750</td>
<td>3.26</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

¹ Determined by ¹H NMR
² % 2, remainder is 1 and 3 estimated by ¹H NMR
<table>
<thead>
<tr>
<th>Example</th>
<th>Time (min)</th>
<th>[Co(III)] ppm</th>
<th>Sty: AMS</th>
<th>$\tilde{M}_n$</th>
<th>$\tilde{M}_w$</th>
<th>$\tilde{M}_{w/\tilde{M}_n}$</th>
<th>Conv.</th>
<th>[2]%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control 1</td>
<td>60</td>
<td>0</td>
<td>-</td>
<td>32230</td>
<td>54760</td>
<td>1.70</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>0</td>
<td>-</td>
<td>33830</td>
<td>59450</td>
<td>1.76</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>180</td>
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<td>-</td>
<td>38060</td>
<td>63750</td>
<td>1.68</td>
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<td>5</td>
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<td>67150</td>
<td>1.70</td>
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<td>6</td>
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<td>-</td>
<td>37420</td>
<td>67630</td>
<td>1.81</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>360</td>
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<td>-</td>
<td>39420</td>
<td>67070</td>
<td>1.70</td>
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<td>8</td>
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<td>100</td>
<td>10:1</td>
<td>730</td>
<td>1840</td>
<td>2.38</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>60</td>
<td>100</td>
<td>10:1</td>
<td>740</td>
<td>1670</td>
<td>2.25</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>100</td>
<td>10:1</td>
<td>690</td>
<td>1430</td>
<td>2.06</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ppt</td>
<td>100</td>
<td>10:1</td>
<td>1270</td>
<td>1430</td>
<td>1.43</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>60</td>
<td>50</td>
<td>10:1</td>
<td>1170</td>
<td>2540</td>
<td>2.17</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>50</td>
<td>10:1</td>
<td>1040</td>
<td>2300</td>
<td>2.21</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ppt</td>
<td>50</td>
<td>10:1</td>
<td>1470</td>
<td>1470</td>
<td>1.80</td>
<td>56</td>
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</tr>
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<td>6</td>
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<td>1370</td>
<td>2890</td>
<td>2.11</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>25</td>
<td>10:1</td>
<td>1270</td>
<td>2690</td>
<td>2.11</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ppt</td>
<td>25</td>
<td>10:1</td>
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<td>1660</td>
<td>1.89</td>
<td>65</td>
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</tr>
<tr>
<td>Control 2</td>
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<td>10:1</td>
<td>19696</td>
<td>50460</td>
<td>2.56</td>
<td>n.d</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0</td>
<td>10:1</td>
<td>14860</td>
<td>37950</td>
<td>2.55</td>
<td>n.d</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0</td>
<td>10:1</td>
<td>17060</td>
<td>38890</td>
<td>2.28</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>0</td>
<td>10:1</td>
<td>24430</td>
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<td>1.72</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>0</td>
<td>10:1</td>
<td>27440</td>
<td>51420</td>
<td>1.87</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>0</td>
<td>10:1</td>
<td>29400</td>
<td>52930</td>
<td>1.80</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>60</td>
<td>100</td>
<td>5:1</td>
<td>380</td>
<td>930</td>
<td>2.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>100</td>
<td>5:1</td>
<td>140</td>
<td>870</td>
<td>2.10</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>ppt</td>
<td>100</td>
<td>5:1</td>
<td>1310</td>
<td>1310</td>
<td>1.83</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>60</td>
<td>50</td>
<td>5:1</td>
<td>810</td>
<td>1670</td>
<td>2.06</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>50</td>
<td>5:1</td>
<td>780</td>
<td>1530</td>
<td>1.96</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ppt</td>
<td>50</td>
<td>5:1</td>
<td>1180</td>
<td>1180</td>
<td>1.53</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>60</td>
<td>25</td>
<td>5:1</td>
<td>1760</td>
<td>3480</td>
<td>1.98</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>25</td>
<td>5:1</td>
<td>1640</td>
<td>3160</td>
<td>1.93</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ppt</td>
<td>25</td>
<td>5:1</td>
<td>2140</td>
<td>2140</td>
<td>1.60</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Control 3</td>
<td>60</td>
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<td>5:1</td>
<td>16740</td>
<td>32450</td>
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<td></td>
<td>120</td>
<td>0</td>
<td>5:1</td>
<td>19540</td>
<td>35020</td>
<td>1.79</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ppt</td>
<td>0</td>
<td>5:1</td>
<td>19570</td>
<td>19570</td>
<td>1.83</td>
<td></td>
<td>0</td>
</tr>
</tbody>
</table>
EXAMPLES 10-12

Synthesis of high molecular weight styrene macromonomers

AMS comonomer

Feed polymerization

These Examples were run according to the same procedure of Examples 1 through 3.

Table 1.2: Polymerization of styrene in presence of AMS and iPrCo(III)(DMG-BF₃)₂ at 125 °C. Numbers in parenthesis indicate reaction times.

<table>
<thead>
<tr>
<th>Ex.</th>
<th>reaction time (h)</th>
<th>[Co(III)] (ppm)</th>
<th>Sty/AM</th>
<th>S</th>
<th>Mₙ</th>
<th>Mₘ/Mₙ</th>
<th>% conv.</th>
<th>% terminal alkene</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2</td>
<td>8 (0.13/0.37)³</td>
<td>5/1</td>
<td>7455 (120)</td>
<td>2.4</td>
<td>14</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9442 (ppt)</td>
<td>1.95</td>
<td></td>
<td></td>
<td>&gt;70⁵</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>8 (0.13/0.37)³</td>
<td>5/1</td>
<td>4648 (60)</td>
<td>1.81</td>
<td>12</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5160 (ppt)</td>
<td>1.64</td>
<td></td>
<td></td>
<td>&gt;70⁵</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>2</td>
<td>13 (0.25/0.75)³</td>
<td>5/1</td>
<td>2660 (120)</td>
<td>1.87</td>
<td>20</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3300 (ppt)</td>
<td>1.63</td>
<td></td>
<td></td>
<td>&gt;70⁵</td>
<td></td>
</tr>
</tbody>
</table>

EXAMPLES 13-18, Control 4-6

Synthesis of styrene macromonomers

AMS comonomer

Batch polymerizations in sealed tube - Effect of reaction temperature

Batch polymerizations were conducted in sealed tubes to establish the effect of temperature on macromonomer purity (%) 2. Molecular weights and macromonomer purities are similar to those obtained in the feed polymerization experiments (refer Table 1.1).

A mixture of styrene (1.3g, 12.5 mmol), α-methylstyrene (0.15g, 1.27 mmol) (monomer ratio: 10/1), n-butyl acetate (3 g), Vd₄₅-110 (8.9×10⁻⁵ g, 20 ppm) and iPrCo(III)(DMG-BF₃)₂ (for concentrations see Table 1.3) was placed in an ampoule and degassed by 4 freeze-thaw cycles. The ampoule was sealed and the mixture heated at 125 °C for 2 hours. The ampoule was cooled, opened and the reaction mixture reduced in vacuo to a residue which was analysed by ¹H-nmr and GPC.

³ amount, in mg, added in (shot/feed).
⁴ rate of cobalt complex feed twice that for example 10.
⁵ internal methylene was not visible in the ¹H-nmr spectrum.
Table 1.3: Batch polymerization of styrene in presence of AMS and iPrCo(III)(DMG-BF₂)₂ at 125 °C with VR⁻¹¹⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻{-4-7} 13 10/1 50 100 445 1.61 1 - 4 36 14 10/1 50 100 751 1.76 4 - 6 39 15 10/1 25 100 1408 1.79 7 - 9 54

Table 1.4: Batch polymerization of styrene in presence of AMS and iPrCo(III)(DMG-BF₂)₂ at 80 °C with AIBN initiator.

| Example | Sty/AMS ratio | [Co(III)] ppm | M_n | M_w/M_n | % conv | % terminal AMS
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Control 6 10/1</td>
<td>0</td>
<td>32,60</td>
<td>1.97</td>
<td>4</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>16        10/1</td>
<td>100</td>
<td>660</td>
<td>1.30</td>
<td>5</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>17        10/1</td>
<td>50</td>
<td>1090</td>
<td>1.52</td>
<td>7</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>18        10/1</td>
<td>25</td>
<td>1456</td>
<td>1.63</td>
<td>7</td>
<td>45</td>
<td></td>
</tr>
</tbody>
</table>

EXAMPLES 19-22, CONTROL 7-9

Synthesis of styrene macromonomers

AMS comonomer

Batch polymerizations in sealed tube - Effect of cobalt complex

A mixture of styrene (1.0g, 9.6mmol), α-methylstyrene (0.12g, 0.96mmol) (monomer ratio: 10/1), n-butyl acetate (2g), VR⁻¹¹⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻{-4-7} cycles. The ampoule was sealed and the mixture heated at 125 °C for 2 hours. The ampoule was cooled, opened and the reaction mixture reduced in vacuo to a residue which was analysed by ¹H-nmr and GPC.

⁶ Calculated as [terminal AMS units]/[terminal AMS units + terminal Sty units] X 100. From ¹NMR.
Table 1.5: Batch polymerization of styrene in presence of AMS and various cobalt complexes at 125 °C with VR\textsuperscript{8}110 initiator.

<table>
<thead>
<tr>
<th>Example</th>
<th>Co species\textsuperscript{7}</th>
<th>[Co] ppm</th>
<th>Mn</th>
<th>Mw</th>
<th>PD</th>
<th>% conv</th>
<th>% terminal AMS units\textsuperscript{8}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control 7</td>
<td>Co(III)DMG</td>
<td>0</td>
<td>58,288</td>
<td>104,916</td>
<td>1.8</td>
<td>13</td>
<td>0</td>
</tr>
<tr>
<td>19</td>
<td>&quot;</td>
<td>50</td>
<td>1065</td>
<td>1730</td>
<td>1.62</td>
<td>19</td>
<td>71</td>
</tr>
<tr>
<td>Control 8</td>
<td>Co(III)DEG</td>
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<td>72,284</td>
<td>125,129</td>
<td>1.73</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>&quot;</td>
<td>50</td>
<td>1388</td>
<td>2368</td>
<td>1.7</td>
<td>19</td>
<td>85</td>
</tr>
<tr>
<td>Control 9</td>
<td>Co(II) DPG</td>
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<td>122,098</td>
<td>1.7</td>
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<td>0</td>
</tr>
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<td>1454</td>
<td>2532</td>
<td>1.74</td>
<td>23</td>
<td>91</td>
</tr>
<tr>
<td>22</td>
<td>Co(III)DMG</td>
<td>50</td>
<td>1470</td>
<td>-</td>
<td>1.8</td>
<td>39</td>
<td>74</td>
</tr>
</tbody>
</table>

Feed Expt\textsuperscript{9}

EXAMPLES 23-24, CONTROL 10

Synthesis of styrene macromonomers

Methacrylate comonomer

Feed polymerization

The polymerization recipe for examples 23-24 and their control was similar to that given for Examples 1-3 with the modification that BMA was used in place of AMS. Conversions obtained are similar. Good molecular weight control is observed however little specificity for formation of a terminal macromonomer double bond is observed.

\textsuperscript{7} Co(III)DMG = iPrCo(III)(DMG-BF\textsubscript{2})\textsubscript{2}, Co(III)DEG = MeCo(III)(DEG-BF\textsubscript{2})\textsubscript{2}, Co(IIIDPG Co(II)(DPG-BF\textsubscript{2})\textsubscript{2}

\textsuperscript{8} Calculated as [terminal AMS units]/[terminal AMS units + terminal Sty units] X 100 from NMR.

\textsuperscript{9} Data ex Table 1.1
Table 1.7: Polymerization of styrene in presence of BMA and iPrCo(III)(DMG-BF$_2$)$_2$ at 125 °C with 1,1'-azobis(4-cyclohexanecarbonitrile) as initiator

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (min)</th>
<th>[Co(III)] ppm</th>
<th>Sty:BMA$_{10}$</th>
<th>$\bar{M}_n^{11}$</th>
<th>$\bar{M}_w$</th>
<th>$\bar{M}_w$/$\bar{M}_n$</th>
<th>% Conv.$^{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>30</td>
<td>0</td>
<td>10:1</td>
<td>35870</td>
<td>60580</td>
<td>1.69</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0</td>
<td></td>
<td>34970</td>
<td>58090</td>
<td>1.66</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>0</td>
<td></td>
<td>36360</td>
<td>61770</td>
<td>1.70</td>
<td>51</td>
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<td></td>
<td>35750</td>
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<td>1.73</td>
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<td>1.81</td>
<td>2130</td>
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<td>1220</td>
<td>3410</td>
<td>1.82</td>
<td>37</td>
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<td>100</td>
<td>1190</td>
<td>2230</td>
<td>1.88</td>
<td>51</td>
</tr>
<tr>
<td>ppt</td>
<td>100</td>
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<td>1560</td>
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<td>1.69</td>
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</tr>
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<td>60</td>
<td>25</td>
<td>1.97</td>
<td>4800</td>
<td>38</td>
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<tr>
<td></td>
<td></td>
<td>120</td>
<td>25</td>
<td>2.21</td>
<td>3750</td>
<td>53</td>
<td></td>
</tr>
<tr>
<td>ppt</td>
<td>25</td>
<td></td>
<td></td>
<td>4190</td>
<td>8270</td>
<td>1.97</td>
<td></td>
</tr>
</tbody>
</table>

**EXAMPLES 25-30**

5 **Synthesis of styrene macromonomers**

Isopropenyl acetate comonomer

Batch polymerization

Sty/iPA macromonomer formation at 80 °C: A mixture of styrene (1g, 9.6mmol), isopropenyl acetate (0.19g, 1.9mmol) (monomer ratio: 5/1), n-butyl acetate (2g), AIBN (3.19x10$^{-4}$g, 100ppm) and isopropylcobalt(III)DMG (for concentrations see Table 1.8) was placed in an ampoule and degassed by 4 freeze-thaw cycles. The ampoule was sealed and the mixture heated at 80 °C for 2 hours. The ampoule was cooled, opened and the reaction mixture reduced in vacuo to a residue which was analysed by $^1$H-nmr and GPC.

15 $^1$H-nmr (d6-acetone): styryl end group internal double bond (1): $\delta$6.1 -CH(Ph)-CH=CH-Ph; $\delta$3.1 CH(Ph)-CH=CH-Ph.

---

$^{10}$ Molar ratio of comonomers

$^{11}$ Determined by GPC calibrated with narrow polydispersity polystyrene standards.

$^{12}$ Determined by $^1$H NMR
Table 1.8: Sty/iPA macromonomer formation at 80 °C for 2h with AIBN and iPrCo(III)(DMG-BF₂)₂.

<table>
<thead>
<tr>
<th>Example</th>
<th>Sty/iPA ratio</th>
<th>Co(III) ppm</th>
<th>Mn</th>
<th>Mw</th>
<th>PD</th>
<th>% conv</th>
<th>% terminal iPA units¹³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control 11</td>
<td>5/1</td>
<td>0</td>
<td>57,425</td>
<td>91,753</td>
<td>1.6</td>
<td>6.00</td>
<td>0</td>
</tr>
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<td>5/1</td>
<td>400</td>
<td>338</td>
<td>364</td>
<td>1.07</td>
<td>4.00</td>
<td>0</td>
</tr>
<tr>
<td>26</td>
<td>5/1</td>
<td>100</td>
<td>698</td>
<td>1045</td>
<td>1.49</td>
<td>4.00</td>
<td>0</td>
</tr>
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<td>27</td>
<td>5/1</td>
<td>25</td>
<td>5188</td>
<td>11,611</td>
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<tr>
<td>28</td>
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<td>343</td>
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<td>2.00</td>
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</tr>
<tr>
<td>29</td>
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<td>465</td>
<td>586</td>
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<tr>
<td>30</td>
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<td>1560</td>
<td>2825</td>
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<td>3.00</td>
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</tbody>
</table>

EXEMPLARY EXAMPLES 31-45, CONTROLS 13-16

Synthesis of butyl acrylate macromonomers

AMS comonomer at 80 °C

Batch polymerization - Effect of comonomer and complex concentration

A mixture of butyl acrylate (1.3g, 10mmol), a-methylstyrene (50mg, 0.4mmol) (monomer ratio: 25/1), n-butyl acetate (2g), AIBN (3.74x10⁻⁴ g, 100ppm) and isopropylcobalt(III)DMG (for concentration see Table 2.1) was placed in an ampoule and degassed by 4 freeze-thaw cycles. The ampoule was sealed and the mixture heated at 80 °C for 2 hours. The ampoule was cooled, opened and the reaction mixture reduced in vacuo to a residue which was analysed by ¹H-nmr and GPC.

¹H-nmr (d6-acetone): δ 0.9, CH₃; 1.25, CH₂; 1.5, CH₂; 1.95, CH; 2.3, backbone CH₂; 2.55, allyl CH₂; 3.95, OCH₂; 5.0, vinyl H; 5.2, vinyl H; 7.15-7.25, ArH.

¹³ No terminal alkene derived from iPA were detectable by ¹H NMR.
<table>
<thead>
<tr>
<th>Ex.</th>
<th>BA/AM</th>
<th>Co(III) S ratio</th>
<th>BA/AM ppm</th>
<th>$\bar{M}_n^{14}$</th>
<th>PD Conv</th>
<th>% % term. AMS units$^{15}$</th>
<th>% % term. inc.$^{16}$</th>
<th>% % term. alkene$^{17}$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0</td>
<td>23,500</td>
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<td>39</td>
<td>0</td>
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<tr>
<td>31</td>
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<td>475</td>
<td>1.20</td>
<td>3</td>
<td>64</td>
<td>43</td>
<td>100</td>
</tr>
<tr>
<td>32</td>
<td>5/1</td>
<td>50</td>
<td>487</td>
<td>1.20</td>
<td>4</td>
<td>60</td>
<td>38</td>
<td>100</td>
</tr>
<tr>
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<td>5/1</td>
<td>25</td>
<td>495</td>
<td>1.20</td>
<td>4</td>
<td>54</td>
<td>41</td>
<td>100</td>
</tr>
<tr>
<td>Ctrl 14</td>
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<td>0</td>
<td>28,200</td>
<td>1.64</td>
<td>4</td>
<td>0</td>
<td>38</td>
<td>0</td>
</tr>
<tr>
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<td>100</td>
<td>551</td>
<td>1.27</td>
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<td>50</td>
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<td>1.31</td>
<td>5</td>
<td>63</td>
<td>35</td>
<td>100</td>
</tr>
<tr>
<td>36</td>
<td>10/1</td>
<td>25</td>
<td>635</td>
<td>1.33</td>
<td>5</td>
<td>60</td>
<td>36</td>
<td>100</td>
</tr>
<tr>
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<td>0</td>
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<td>37</td>
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<td>92</td>
<td>15</td>
<td>91</td>
</tr>
<tr>
<td>38</td>
<td>25/1</td>
<td>100</td>
<td>961</td>
<td>1.39</td>
<td>5</td>
<td>77</td>
<td>17</td>
<td>96</td>
</tr>
<tr>
<td>39</td>
<td>25/1</td>
<td>50</td>
<td>1062</td>
<td>1.42</td>
<td>6</td>
<td>71</td>
<td>18</td>
<td>100</td>
</tr>
<tr>
<td>40</td>
<td>25/1</td>
<td>25</td>
<td>1152</td>
<td>1.48</td>
<td>7</td>
<td>57</td>
<td>20</td>
<td>100</td>
</tr>
<tr>
<td>Ctrl 16</td>
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<td>56,071</td>
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<td>14</td>
<td>0</td>
<td>12</td>
<td>0</td>
</tr>
<tr>
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<td>400</td>
<td>1168</td>
<td>1.64</td>
<td>10</td>
<td>78</td>
<td>9</td>
<td>80</td>
</tr>
<tr>
<td>42</td>
<td>50/1</td>
<td>200</td>
<td>1207</td>
<td>1.76</td>
<td>10</td>
<td>75</td>
<td>9</td>
<td>85</td>
</tr>
<tr>
<td>43</td>
<td>50/1</td>
<td>100</td>
<td>1481</td>
<td>1.80</td>
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<td>61</td>
<td>9</td>
<td>91</td>
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<td>44</td>
<td>50/1</td>
<td>50</td>
<td>1600</td>
<td>1.82</td>
<td>11</td>
<td>59</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>45</td>
<td>50/1</td>
<td>25</td>
<td>1876</td>
<td>1.96</td>
<td>11</td>
<td>45</td>
<td>10</td>
<td>100</td>
</tr>
</tbody>
</table>

**EXAMPLES 46-54, CONTROLS 17, 18,**

**Synthesis of butyl acrylate macromonomers**

AMS comonomer at 125 °C

Batch polymerization - Effect of reaction temperature

A mixture of butyl acrylate (1.3g, 10mmol), $\alpha$-methylstyrene (50mg, 0.4mmol) (monomer ratio: 25/1), n-butyl acetate (2g), VR$^\text{®}$-110 (3.74x10$^{-4}$ g).

$^{14}$ Polystyrene equivalents.

$^{15}$ Calculated as (terminal AMS units)/(total AMS units) X 100.

$^{16}$ Calculated as (total AMS units)/(total BA units + total AMS) X 100.

$^{17}$ Calculated as (terminal AMS units)/(terminal AMS units + terminal BA units) X 100.

A Value of 100% indicates that terminal BA could not be detected by $^1$H NMR.
100 ppm) and iPrCo(III)(DMG-BF$_2$)$_2$ (for concentration see Table 2.2) was placed in an ampoule and degassed by 4 freeze-thaw cycles. The ampoule was sealed and the mixture heated at 125 °C for 2 hours. The ampoule was cooled, opened and the reaction mixture reduced in vacuo to a residue which was analysed by $^1$H-nmr and GPC.

Table 2.2  Polymerization of butyl acrylate in presence of AMS and iPrCo(III)(DMG-BF$_2$)$_2$ at 125 °C

<table>
<thead>
<tr>
<th>Ex.</th>
<th>BA/AMS ratio</th>
<th>Co(III) ppm</th>
<th>$\bar{M}_n$</th>
<th>PD</th>
<th>% conv</th>
<th>% term. AMS units$^{18}$</th>
<th>% AMS inc.$^{19}$</th>
<th>% terminal alkene$^{20}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control 17 25/1</td>
<td>0</td>
<td>18,069</td>
<td>1.77</td>
<td>36</td>
<td>0</td>
<td>13</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>25/1</td>
<td>200</td>
<td>973</td>
<td>1.58</td>
<td>19</td>
<td>77</td>
<td>12</td>
<td>85</td>
</tr>
<tr>
<td>47</td>
<td>25/1</td>
<td>100</td>
<td>967</td>
<td>1.73</td>
<td>29</td>
<td>68</td>
<td>13</td>
<td>93</td>
</tr>
<tr>
<td>48</td>
<td>25/1</td>
<td>50</td>
<td>1402</td>
<td>1.68</td>
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<td>57</td>
<td>13</td>
<td>100</td>
</tr>
<tr>
<td>49</td>
<td>25/1</td>
<td>25</td>
<td>2230</td>
<td>2.10</td>
<td>3</td>
<td>23</td>
<td>20</td>
<td>100</td>
</tr>
<tr>
<td>Control 18 50/1</td>
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<td>18,891</td>
<td>1.85</td>
<td>6</td>
<td>0</td>
<td>5</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>50/1</td>
<td>400</td>
<td>1069</td>
<td>1.65</td>
<td>21</td>
<td>84</td>
<td>6</td>
<td>not calc.</td>
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<tr>
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<td>200</td>
<td>1200</td>
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<td>21</td>
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<tr>
<td>52</td>
<td>50/1</td>
<td>100</td>
<td>1624</td>
<td>1.81</td>
<td>30</td>
<td>58</td>
<td>6</td>
<td>77</td>
</tr>
<tr>
<td>53</td>
<td>50/1</td>
<td>50</td>
<td>1948</td>
<td>1.92</td>
<td>32</td>
<td>55</td>
<td>6</td>
<td>87</td>
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<tr>
<td>54</td>
<td>50/1</td>
<td>25</td>
<td>3463</td>
<td>2.10</td>
<td>43</td>
<td>32</td>
<td>5</td>
<td>100</td>
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</table>

EXAMPLES 55-58, CONTROL 19

Synthesis of butyl acrylate macromonomers

AMS comonomer at 80°C

Batch polymerization - Effect of cobalt complex

A mixture of butyl acrylate (1.3 g, 10 mmol), a-methylstyrene (24 mg, 0.2 mmol) (monomer ratio: 50/1), n-butyl acetate (2 g), AIBN (3.74 x 10$^{-4}$ g, 100 ppm) and MeCo(III)(DEG-BF$_2$)$_2$ (for concentration see table 2.3) was placed in an ampoule and degassed by 4 freeze-thaw cycles. The ampoule was sealed and the mixture heated at 80°C for 2 hours. The ampoule was cooled, opened and the reaction mixture reduced in vacuo to a residue which was analysed by $^1$H-nmr and GPC.

$^{18}$ Calculated as (terminal AMS units)/(total AMS units) X 100.

$^{19}$ Calculated as (total AMS units)/(total BA units + total AMS) X 100.

$^{20}$ Calculated as (terminal AMS units)/(terminal AMS units + terminal BA units) X 100.
**Table 2.3** Polymerization of butyl acrylate in presence of AMS and \(\text{MeCo(III)}(\text{DEG-BF}_2)_2\) at 80°C

<table>
<thead>
<tr>
<th>Ex.</th>
<th>BA/AMS ratio</th>
<th>Co(III) ppm</th>
<th>(\bar{M}_n)</th>
<th>PD % conv</th>
<th>% term. AMS units(^{21})</th>
<th>% AMS inc.(^{22})</th>
<th>% terminal alkene(^{23})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control 19</td>
<td>50/1</td>
<td>0</td>
<td>49,342</td>
<td>1.74</td>
<td>11</td>
<td>0</td>
<td>25</td>
</tr>
<tr>
<td>55</td>
<td>50/1</td>
<td>200</td>
<td>1128</td>
<td>1.57</td>
<td>4</td>
<td>79</td>
<td>12</td>
</tr>
<tr>
<td>56</td>
<td>50/1</td>
<td>100</td>
<td>1162</td>
<td>1.66</td>
<td>5</td>
<td>75</td>
<td>12</td>
</tr>
<tr>
<td>57</td>
<td>50/1</td>
<td>50</td>
<td>1647</td>
<td>1.70</td>
<td>10</td>
<td>57</td>
<td>12</td>
</tr>
<tr>
<td>58</td>
<td>50/1</td>
<td>25</td>
<td>2369</td>
<td>1.85</td>
<td>11</td>
<td>31</td>
<td>13</td>
</tr>
</tbody>
</table>

**EXAMPLES 59-63, CONTROL 20**

BA/AMS macromonomer formation at 80°C with \(\text{Co(II)}(\text{DPG-BF}_2)_2\).

A mixture of butyl acrylate (1.3g, 10mmol), \(\alpha\)-methylstyrene (24mg, 0.2mmol) (monomer ratio: 50/1), n-butyl acetate (2g), AIBN (3.74x10\(^{-4}\)g, 100ppm) and \(\text{Co(II)}(\text{DPG-BF}_2)_2\) (for concentrations see Table 2.4) was placed in an ampoule and degassed by 4 freeze-thaw cycles. The ampoule was sealed and the mixture heated at 80°C for 2 hours. The ampoule was cooled, opened and the reaction mixture reduced under vacuum to a residue which was analysed by \(^1\)H-nmr and GPC.

**Table 2.4** Polymerization of butyl acrylate in presence of AMS (50/1) and \(\text{Co(II)}(\text{DPG-BF}_2)_2\) at 80°C

<table>
<thead>
<tr>
<th>Ex.</th>
<th>Co(II) ppm</th>
<th>(\bar{M}_n)</th>
<th>(\bar{M}_w)</th>
<th>PD % conv</th>
<th>% term. AMS units(^{24})</th>
<th>% AMS inc.(^{25})</th>
<th>% terminal alkene(^{26})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control 20</td>
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<td>50,575</td>
<td>104,679</td>
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<td>17</td>
<td>0</td>
<td>9</td>
</tr>
<tr>
<td>59</td>
<td>400</td>
<td>796</td>
<td>1262</td>
<td>1.58</td>
<td>1</td>
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<td>1064</td>
<td>1817</td>
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<td>66</td>
<td>13</td>
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<td>1</td>
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<td>2076</td>
<td>5407</td>
<td>2.10</td>
<td>3</td>
<td>35</td>
<td>13</td>
</tr>
</tbody>
</table>

\(^{21}\) Calculated as (terminal AMS units)/(total AMS units) X 100.

\(^{22}\) Calculated as (total AMS units)/(total BA units + total AMS) X 100.

\(^{23}\) Calculated as (terminal AMS units)/(terminal AMS units + terminal BA units) X 100.

\(^{24}\) Calculated as (terminal AMS units)/(total AMS units) X 100.

\(^{25}\) Calculated as (total AMS units)/(total BA units + total AMS) X 100.

\(^{26}\) Calculated as (terminal AMS units)/(terminal AMS units + terminal BA units) X 100.
EXAMPLES 64-68, CONTROL 21

Synthesis of butyl acrylate macromonomers
MAN comonomer at 80 °C - Batch polymerization

A mixture of butyl acrylate (1g, 7.58mmol), methacrylonitrile (51mg, 0.758mmol), n-butyl acetate (2g), AIBN (3.54x10^{-4} g, 100ppm) and iPrCo(III)(DMG-BF$_2$)$_2$ (for concentration see Table 2.5) was placed in an ampoule and degassed by 4 freeze-thaw cycles. The ampoule was sealed and the mixture heated at 80 °C for 2 hours. The ampoule was cooled, opened and the reaction mixture reduced in vacuo to a residue which was analysed by 1H-nmr and GPC.

$^1$H-nmr (CDCl$_3$): d 0.95, CH$_3$; 1.35, CH$_2$; 1.65, CH$_2$; 1.95, CH; 2.3, backbone CH$_2$; 2.6, allyl CH$_2$; 4.0, OCH$_2$; 5.7, vinyl H; 5.85, vinyl H.

Table 2.5 Polymerization of butyl acrylate in presence of MAN and iPrCo(III)(DMG-BF$_2$)$_2$ at 80 °C

<table>
<thead>
<tr>
<th>Ex.</th>
<th>BA/MAN Ratio</th>
<th>[Co(III)] ppm</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>PD</th>
<th>% conv.</th>
<th>% terminal methylene$^{27}$</th>
</tr>
</thead>
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<td>8</td>
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<tr>
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<td>669</td>
<td>1004</td>
<td>1.50</td>
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<td>86</td>
</tr>
<tr>
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<td>802</td>
<td>1179</td>
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<td>87</td>
</tr>
<tr>
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<td>959</td>
<td>1432</td>
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<td>80</td>
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<td>1036</td>
<td>1676</td>
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<td>76</td>
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<td>25</td>
<td>1301</td>
<td>2008</td>
<td>1.54</td>
<td>8</td>
<td>81</td>
</tr>
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</table>

EXAMPLES 69-83, CONTROLS 22 to 24

Synthesis of butyl acrylate macromonomers
MMA comonomer at 60-125°C - Batch polymerization

BA/MMA macromonomer formation at BA/MMA 10/1.

A mixture of butyl acrylate (1g, 7.58mmol), methyl methacrylate (76mg, 0.758mmol), n-butyl acetate (2g), initiator (see Table 2.6 for initiator type) and isopropylcobalt(III)DMG (for concentration see Table 2.6) was placed in an ampoule and degassed by 4 freeze-thaw cycles. The ampoule was sealed and the mixture heated at the indicated temperature for either 2 or 3 hours. The ampoule was rapidly cooled, opened and the reaction mixture reduced in vacuo to a residue which was analysed by $^1$H-nmr and GPC.

$^{27}$ Calculated as (terminal MAN units)/(terminal MAN units + terminal BA units) X 100.
1H-nmr (CDCl₃): d 0.9, CH₃; 1.35, CH₂; 1.65, CH₂; 1.85, CH; 2.25.
backbone CH₃; 2.55, allyl CH₂; 3.6, OCH₃; 4.0, OCH₂; 5.5, vinyl H; 6.15, vinyl
H.

Table 2.6 Polymerization of butyl acrylate in presence of MMA (10:1) and
iPrCo(III)(DMG-BF₂)₂ at various temperatures

<table>
<thead>
<tr>
<th>Ex. (initiator)</th>
<th>Temp °C</th>
<th>React. Time h</th>
<th>Co(III) ppm</th>
<th>Mₙ</th>
<th>PD % conv</th>
<th>% term. alkene²⁸</th>
<th>% MMA incorp.²⁹</th>
<th>Mₙ cal/mol ob</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ctrl 22 (AIBN)</td>
<td>69</td>
<td>3</td>
<td>400</td>
<td>891</td>
<td>1.55</td>
<td>6</td>
<td>83</td>
<td>18 1.04</td>
</tr>
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<td>70</td>
<td>3</td>
<td>200</td>
<td>1051</td>
<td>1.56</td>
<td>5</td>
<td>87</td>
<td>19 1.05</td>
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<td>71</td>
<td>3</td>
<td>100</td>
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<td>1.70</td>
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<td>91</td>
<td>20 0.83</td>
</tr>
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<td>72</td>
<td>3</td>
<td>50</td>
<td>2610</td>
<td>1.80</td>
<td>7</td>
<td>100</td>
<td>19 0.98</td>
</tr>
<tr>
<td></td>
<td>73</td>
<td>3</td>
<td>25</td>
<td>7702</td>
<td>1.87</td>
<td>16</td>
<td>100</td>
<td>18 1.0</td>
</tr>
<tr>
<td>Ctrl 23 (AIBN)</td>
<td>74</td>
<td>2</td>
<td>0</td>
<td>75,501</td>
<td>2.08</td>
<td>54</td>
<td>0</td>
<td>14 1.0</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>2</td>
<td>400</td>
<td>917</td>
<td>1.31</td>
<td>8</td>
<td>75</td>
<td>17 0.92</td>
</tr>
<tr>
<td></td>
<td>76</td>
<td>2</td>
<td>200</td>
<td>1196</td>
<td>1.43</td>
<td>10</td>
<td>86</td>
<td>17 0.93</td>
</tr>
<tr>
<td></td>
<td>77</td>
<td>2</td>
<td>100</td>
<td>1520</td>
<td>1.50</td>
<td>9</td>
<td>92</td>
<td>18 0.92</td>
</tr>
<tr>
<td></td>
<td>78</td>
<td>2</td>
<td>50</td>
<td>2602</td>
<td>1.66</td>
<td>21</td>
<td>94</td>
<td>17 1.00</td>
</tr>
<tr>
<td>Ctrl 24 (VR⁻¹¹₀)</td>
<td>79</td>
<td>2</td>
<td>25</td>
<td>12,117</td>
<td>1.82</td>
<td>53</td>
<td>100</td>
<td>14 1.09</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>2</td>
<td>400</td>
<td>832</td>
<td>1.51</td>
<td>9</td>
<td>79</td>
<td>16 1.04</td>
</tr>
<tr>
<td></td>
<td>81</td>
<td>2</td>
<td>200</td>
<td>1032</td>
<td>1.73</td>
<td>15</td>
<td>87</td>
<td>17 1.00</td>
</tr>
<tr>
<td></td>
<td>82</td>
<td>2</td>
<td>100</td>
<td>1224</td>
<td>1.60</td>
<td>14</td>
<td>91</td>
<td>17 1.05</td>
</tr>
<tr>
<td></td>
<td>83</td>
<td>2</td>
<td>50</td>
<td>1994</td>
<td>1.70</td>
<td>32</td>
<td>92</td>
<td>15 1.01</td>
</tr>
</tbody>
</table>

EXAMPLES 84-91, CONTROL 25 and 26

Synthesis of functional butyl acrylate macromonomers

HEMA comonomer at 80 °C - Batch polymerization

A mixture of butyl acrylate (1.3g; 10mmol), 2-hydroxyethyl
methacrylate, HEMA (65mg; 0.5mmol) (monomer ratio 20:1), n-butyl acetate
(2g), AIBN (3.74x10⁻⁴g, 100ppm) and isopropylcobalt(III)DMG (for
concentration see Table 2.7) was placed in an ampoule and degassed by 4 freeze-

²⁸ Calculated as (terminal MMA units)/(terminal MMA units + terminal BA units) x 100.
²⁹ Calculated as (total MMA units)/(total MMA units + total BA units) x 100.
thaw cycles. The ampoule was sealed and the mixture heated at 80 °C for 1 or 2 hours. The ampoule was cooled, opened and the reaction mixture reduced in vacuo to a residue which was analysed by $^1$H-nmr and GPC.

$^1$H-nmr (CDCl$_3$): d 0.95, CH$_3$; 1.40, CH$_2$; 1.65, CH$_2$; 1.85, backbone CH; 2.25, backbone CH$_2$; 3.80, CH$_2$; 4.00, CH$_2$; 4.22, CH$_2$; 5.50, external vinyl*; 5.80, 5.90, E&Z internal vinyl*; 6.20, external vinyl*.

(*external vinyl signals due to HEMA derived vinyl end group and internal vinyl signals due to BA derived vinyl group).

Table 2.7 Polymerization of butyl acrylate in presence of HEMA (20:1) and iPrCo(III)(DMG-BF$_2$)$_2$ at 80 °C

<table>
<thead>
<tr>
<th>Example</th>
<th>Reaction Time (hours)</th>
<th>Co(III) ppm</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>PD</th>
<th>% conv</th>
<th>% terminal alkene$^{30}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control 25</td>
<td>1</td>
<td>0</td>
<td>169,846</td>
<td>403,699</td>
<td>2.38</td>
<td>53</td>
<td>0</td>
</tr>
<tr>
<td>84</td>
<td>1</td>
<td>200</td>
<td>1695</td>
<td>3011</td>
<td>1.78</td>
<td>6</td>
<td>80</td>
</tr>
<tr>
<td>85</td>
<td>1</td>
<td>50</td>
<td>12,919</td>
<td>25,390</td>
<td>1.97</td>
<td>23</td>
<td>100</td>
</tr>
<tr>
<td>86</td>
<td>1</td>
<td>25</td>
<td>35,421</td>
<td>68,294</td>
<td>1.93</td>
<td>37</td>
<td>100</td>
</tr>
<tr>
<td>Control 26</td>
<td>2</td>
<td>0</td>
<td>58,522</td>
<td>200,100</td>
<td>3.42</td>
<td>98</td>
<td>0</td>
</tr>
<tr>
<td>87</td>
<td>2</td>
<td>400</td>
<td>1116</td>
<td>2144</td>
<td>1.92</td>
<td>13</td>
<td>71</td>
</tr>
<tr>
<td>88</td>
<td>2</td>
<td>200</td>
<td>1545</td>
<td>3207</td>
<td>2.08</td>
<td>19</td>
<td>73</td>
</tr>
<tr>
<td>89</td>
<td>2</td>
<td>100</td>
<td>2219</td>
<td>5215</td>
<td>2.35</td>
<td>24</td>
<td>78</td>
</tr>
<tr>
<td>90</td>
<td>2</td>
<td>50</td>
<td>21,852</td>
<td>46,133</td>
<td>2.11</td>
<td>79</td>
<td>a</td>
</tr>
<tr>
<td>91</td>
<td>2</td>
<td>25</td>
<td>38,369</td>
<td>95,492</td>
<td>2.49</td>
<td>97</td>
<td>a</td>
</tr>
</tbody>
</table>

$^{a}$ Terminal alkene protons were not visible in $^1$H-nmr spectrum.

EXAMPLES 92-94, CONTROL 27

Synthesis of functional acrylate copolymer macromonomers

AMS comonomer at 80 °C - Batch polymerization

A mixture of butyl acrylate (1.3g; 10mmol), 2-hydroxyethylacrylate, HEA (116mg; 1mmol), α-methylstyrene (26mg; 2.2x10$^{-4}$mol) (monomer ratio 10/1/0.22), n-butyl acetate (2g), AIBN (3.65x10$^{-4}$g, 100ppm) and isopropylcobalt(III)DMG (for concentration see Table 2.8) was placed in an ampoule and degassed by 4 freeze-thaw cycles. The ampoule was sealed and the mixture heated at 80 °C for 2 hours. The ampoule was cooled, opened and the

$^{30}$ Calculated as (terminal HEMA units)/(terminal HEMA units + terminal BA units) X 100.
reaction mixture reduced in vacuo to a residue which was analysed by $^1$H-nmr and GPC.

$^1$H-nmr(CDC$_3$): d 0.90, CH$_3$; 1.30, CH$_2$; 1.50, CH$_3$; 1.80, backbone CH; 2.22, backbone CH$_2$; 3.80, CH$_2$; 3.85, CH$_2$; 4.98, external vinyl*; 5.20.

external vinyl*; 5.80, 5.85, internal vinyl*; 6.60-7.00, internal vinyl*; 7.30, ArH.

("external vinyl signals due to aAMS derived vinyl end group and internal vinyl signals due to BA derived vinyl group)."

Table 2.8 Copolymerization of butyl acrylate and hydroxyethyl acrylate in presence of AMS and iPrCo(III)(DMG-BF$_2$)$_2$ at 80 °C

<table>
<thead>
<tr>
<th>Example</th>
<th>BA/HEA/Co(III) M$_n$ PD (%)</th>
<th>terminal AMS units$^{31}$</th>
<th>terminal AMS inc.$^{32}$</th>
<th>%</th>
<th>%</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AMS ratio ppm Mw/Mn conv</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control 27</td>
<td>10/1/0.22 66,642 1.96</td>
<td>30</td>
<td>0</td>
<td>9</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>92</td>
<td>10/1/0.22 200 1255 1.55</td>
<td>16</td>
<td>72</td>
<td>10</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>93</td>
<td>10/1/0.22 100 1712 1.76</td>
<td>22</td>
<td>19</td>
<td>8</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>94</td>
<td>10/1/0.22 50 1835 1.80</td>
<td>22</td>
<td>49</td>
<td>10</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

EXAMPLES 95-100, CONTROLS 28 and 29

Synthesis of vinyl benzoate macromonomers

BMA comonomer at 80 °C - Batch polymerization

A mixture of vinyl benzoate, VB (1.3g, 8.77mmol), butyl methacrylate (0.125g, 0.877mmol) (monomer ratio: 10/1), n-butyl acetate (3g), AIBN (4.43x10$^{-4}$g, 100ppm) and isopropylcobalt(III)DMG (for concentration see Table 3.1) was placed in an ampoule and degassed by 4 freeze-thaw cycles. The ampoule was sealed and the mixture heated at 80 °C for 2 hours. The ampoule was cooled, opened and the reaction mixture reduced in vacuo to a residue which was analysed by $^1$H-nmr and GPC.

$^1$H-nmr (d6-acetone): δ 0.9, CH$_3$; 1.35, CH$_2$; 1.65, CH$_3$; 1.95, CH; 2.25, backbone CH$_2$; 2.55, allyl CH$_2$; 4.0, OCH$_2$; 5.2, CH; 5.45, vinyl H; 6.15, vinyl H; 6.9-7.7, ArH.

---

$^{31}$ Calculated as (terminal AMS units)/(total AMS units) X 100.

$^{32}$ Calculated as (total AMS units)/(total BA+total HEA units) X 100.

$^{33}$ Calculated as (terminal AMS units)/(terminal AMS units + terminal BA units) X 100.
Table 3.1 Polymerization of vinyl benzoate in presence of BMA and 
iPrCo(III)(DMG-BF₂)₃ at 80°C

<table>
<thead>
<tr>
<th>Example</th>
<th>VB/BMA ratio</th>
<th>[Co(III)] ppm</th>
<th>( \bar{M}_n ) ppm</th>
<th>( \bar{M}_w ) ppm</th>
<th>PD conv.</th>
<th>% terminal methylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control 28</td>
<td>10/1</td>
<td>0</td>
<td>67,070</td>
<td>106,547</td>
<td>1.59</td>
<td>12</td>
</tr>
<tr>
<td>95</td>
<td>10/1</td>
<td>100</td>
<td>3168</td>
<td>4942</td>
<td>1.56</td>
<td>5</td>
</tr>
<tr>
<td>96</td>
<td>10/1</td>
<td>50</td>
<td>6679</td>
<td>12,475</td>
<td>1.87</td>
<td>7</td>
</tr>
<tr>
<td>97</td>
<td>10/1</td>
<td>25</td>
<td>12,344</td>
<td>24,349</td>
<td>1.97</td>
<td>8</td>
</tr>
<tr>
<td>Control 29</td>
<td>5/1</td>
<td>0</td>
<td>86,701</td>
<td>137,600</td>
<td>1.58</td>
<td>19</td>
</tr>
<tr>
<td>98</td>
<td>5/1</td>
<td>100</td>
<td>1720</td>
<td>2526</td>
<td>1.47</td>
<td>8</td>
</tr>
<tr>
<td>99</td>
<td>5/1</td>
<td>50</td>
<td>3464</td>
<td>6151</td>
<td>1.76</td>
<td>7</td>
</tr>
<tr>
<td>100</td>
<td>5/1</td>
<td>25</td>
<td>9094</td>
<td>16,155</td>
<td>1.78</td>
<td>9</td>
</tr>
</tbody>
</table>

- **a** Calculated as (terminal BMA units)/(terminal BMA units+ terminal VB units) X 100.

5

**EXAMPLES 101-108, CONTROLS 30 and 31**

Synthesis of vinyl acetate macromonomers methacrylate comonomers at 80°C -
Butyl methacrylate comonomers at 80°C Batch polymerization
VAc/BMA macromonomer synthesis with monomer ratio of 10/1.

A mixture of vinyl acetate (1g; 11.6mmol), butyl methacrylate
10 (0.165g; 1.16mmol) (monomer ratio: 10/1), n-butyl acetate (2g), AIBN (3.17x10⁻⁴g, 100ppm) and isopropylcobalt(III)DMG (for concentration see Table 3.2) was
placed in an ampoule and degassed by 3 freeze-thaw cycles. The ampoule was
sealed and the mixture heated at 80 °C for 2 hours. The ampoule was cooled,
opened and the reaction mixture reduced in vacuo to a residue which was
15 analysed by \(^1\)H-nmr and GPC.

\(^1\)H-nmr(CDCl₃): d 0.95, CH₃; 1.30, CH₂; 1.60, CH₂; 3.90, CH₂; 5.40,
6.10, external vinyl CH₂*.

(*external vinyl signals due to BMA derived vinyl end group).

34 Calculated as (terminal BMA units)/(terminal BMA units+ terminal VB units) X 100.
**Table 3.2** Polymerization of vinyl benzoate in presence of BMA and iPrCo(III)(DMG-BF$_2$)$_3$ at 80°C (VAc:BMA = 10:1)

<table>
<thead>
<tr>
<th>Example</th>
<th>Co(III) ppm</th>
<th>$M_n$</th>
<th>PD</th>
<th>% conv</th>
<th>%BMA terminal$^{35}$</th>
<th>BMA$^{36}$ (%)</th>
<th>% term. alkene$^{37}$</th>
<th>$\bar{M}_n$ calc/obs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>30</td>
<td>62,363</td>
<td>1.78</td>
<td>10</td>
<td>0</td>
<td>67</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>101</td>
<td>400</td>
<td>499</td>
<td>1.40</td>
<td>5</td>
<td>33</td>
<td>80</td>
<td>100</td>
<td>0.9</td>
</tr>
<tr>
<td>102</td>
<td>200</td>
<td>1917</td>
<td>1.37</td>
<td>6</td>
<td>16</td>
<td>69</td>
<td>100</td>
<td>0.55</td>
</tr>
<tr>
<td>103</td>
<td>100</td>
<td>2127</td>
<td>2.3</td>
<td>7</td>
<td>7</td>
<td>72</td>
<td>100</td>
<td>1.02</td>
</tr>
<tr>
<td>104</td>
<td>50</td>
<td>4435</td>
<td>3.0</td>
<td>7</td>
<td>4</td>
<td>73</td>
<td>100</td>
<td>1.03</td>
</tr>
<tr>
<td>105</td>
<td>25</td>
<td>10,331</td>
<td>2.88</td>
<td>10</td>
<td>1</td>
<td>71</td>
<td>100</td>
<td>1.3</td>
</tr>
</tbody>
</table>

*VAc/MMA macromonomer synthesis with monomer ratio of 5/1.*

A mixture of vinyl acetate (0.75g; 8.77mol), methyl methacrylate (0.175g; 1.75mmol) (monomer ratio: 5/1), n-butyl acetate (2g), AIBN (2.93x10$^{-4}$g, 100ppm) and isopropylcobalt(III)DMG (for concentration see Table 3.3) was placed in an ampoule and degassed by 3 freeze-thaw cycles. The ampoule was sealed and the mixture heated at 80°C for 2 hours. The ampoule was cooled, opened and the reaction mixture reduced *in vacuo* to a residue which was analysed by $^1$H-nmr and GPC.

$^1$H-nmr (d$_4$-acetone): δ 0.6-2.1, CH$_3$CO$_2$ and backbone CH$_2$; 3.60, COOCH$_3$; 4.80-5.30, multiplet, various methine signals; 5.42, 6.10 external vinyl CH$_2$*. (*external vinyl signal due to MMA derived vinyl end group).

---

$^{35}$ Calculated as [terminal BMA units]/[total BMA units incorporated] X 100.

$^{36}$ Calculated as (total BMA units)/(total VAc units + total BMA units) X 100.

$^{37}$ VAc derived internal alkene not detectable by $^1$H-nmr.
Table 3.3 Polymerization of vinyl acetate in presence of MMA and iPrCo(III)(DMG-BF₂)₂ at 80°C (VAc:MMA = 5:1)

<table>
<thead>
<tr>
<th>Example</th>
<th>Co(III) ppm</th>
<th>Mₙ</th>
<th>PD</th>
<th>% conv</th>
<th>% MMA terminal inc.³⁹</th>
<th>% MMA alkene⁴⁰</th>
<th>Mₙ calc obs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control 31</td>
<td>0</td>
<td>40,448</td>
<td>1.87</td>
<td>8</td>
<td>0</td>
<td>87</td>
<td>0</td>
</tr>
<tr>
<td>106</td>
<td>100</td>
<td>11,806</td>
<td>2.26</td>
<td>5</td>
<td>0.9</td>
<td>87</td>
<td>100</td>
</tr>
<tr>
<td>107</td>
<td>50</td>
<td>12,487</td>
<td>2.38</td>
<td>8</td>
<td>0.8</td>
<td>88</td>
<td>100</td>
</tr>
<tr>
<td>108</td>
<td>25</td>
<td>30,782</td>
<td>1.92</td>
<td>8</td>
<td>0⁴¹</td>
<td>87</td>
<td>0⁴¹</td>
</tr>
</tbody>
</table>

EXAMPLES 109-116, CONTROLS 32 and 33

Synthesis of vinyl acetate macromonomers
isopropenyl acetate, iPA comonomer at 125 °C - Batch polymerization
A mixture of vinyl acetate (1.0g; 11.6mmol), isopropenyl acetate (23mg; 0.232mmol) (monomer ratio: 50/1), n-butyl acetate (2g), VR⁰⁻¹¹₀ (3.4x10⁻⁴g, 100ppm) and isopropylcobalt(III)DMG (for concentration see Table 3.4) was placed in an ampoule and degassed by 3 freeze-thaw cycles. The ampoule was sealed and the mixture heated at 125 °C for 2 hours. The ampoule was cooled, opened and the reaction mixture reduced in vacuo to a residue which was analysed by ¹H-nmr and GPC.
¹H-nmr (CDCl₃): d 1.2-2.1, CH₂ +CH₃CO; 4.7-5.2, multiplet, various backbone methine.

³⁸ Calculated as (terminal MMA units)÷(total MMA units incorporated) X 100.
³⁹ Calculated as (total MMA units)÷(total VAc units + total MMA units) X 100.
⁴⁰ Calculated as (terminal MMA units)÷(terminal VAc units + terminal MMA units) X 100. VAc derived internal alkene not detectable by ¹H-nmr.
⁴¹ Terminal vinyl signals could not be detected by ¹H-nmr.
Table 3.4 Polymerization of vinyl acetate in presence of iPA and iPrCo(III)(DMG-BF₂)₂ at 125°C

<table>
<thead>
<tr>
<th>Example</th>
<th>Vac/iPA ratio</th>
<th>Co(III) ppm</th>
<th>Mₙ</th>
<th>Mₘ</th>
<th>PD conv</th>
<th>% % term. iPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control 32</td>
<td>5/1</td>
<td>0</td>
<td>11,964</td>
<td>21,818</td>
<td>1.82</td>
<td>47</td>
</tr>
<tr>
<td>109</td>
<td>5/1</td>
<td>200</td>
<td>502</td>
<td>983</td>
<td>1.40</td>
<td>2</td>
</tr>
<tr>
<td>110</td>
<td>5/1</td>
<td>100</td>
<td>696</td>
<td>1124</td>
<td>1.61</td>
<td>2</td>
</tr>
<tr>
<td>111</td>
<td>5/1</td>
<td>50</td>
<td>1240</td>
<td>2278</td>
<td>1.84</td>
<td>2</td>
</tr>
<tr>
<td>112</td>
<td>5/1</td>
<td>25</td>
<td>z 4781</td>
<td>11,189</td>
<td>2.34</td>
<td>9</td>
</tr>
<tr>
<td>Control 33</td>
<td>50/1</td>
<td>0</td>
<td>15,271</td>
<td>29,423</td>
<td>1.93</td>
<td>90</td>
</tr>
<tr>
<td>113</td>
<td>50/1</td>
<td>200</td>
<td>772</td>
<td>1329</td>
<td>1.72</td>
<td>2</td>
</tr>
<tr>
<td>114</td>
<td>50/1</td>
<td>100</td>
<td>1295</td>
<td>2517</td>
<td>1.94</td>
<td>3</td>
</tr>
<tr>
<td>115</td>
<td>50/1</td>
<td>50</td>
<td>2353</td>
<td>6484</td>
<td>2.76</td>
<td>5</td>
</tr>
<tr>
<td>116</td>
<td>50/1</td>
<td>25</td>
<td>13,518</td>
<td>23,737</td>
<td>1.76</td>
<td>16</td>
</tr>
</tbody>
</table>

a end group signals observed but reliable quantitation not possible.
b no end group signals detected.

EXAMPLES 117-128, CONTROLS 34 to 36

Synthesis of vinyl acetate macromonomers

isopropenyl chloride comonomer at 125 °C - Batch polymerization

VAc/iPrCl macromonomer formation at 125 °C with VR®-110 and iPrCo(III)(DMG-BF₂)₂

A mixture of vinyl acetate (1g, 11.6mmol), isopropenyl chloride (0.18g, 2.32mmol) (monomer ratio: 5/1), n-butyl acetate (2g), VR®-110 (3.18x10⁻⁴ g, 100ppm) and iPrCo(III)(DMG-BF₂)₂ (for concentration see table 3.5) was placed in an ampoule and degassed by 4 freeze-thaw cycles. The ampoule was sealed and the mixture heated at 125°C for 2 hours. The ampoule was cooled, opened and the reaction mixture reduced in vacuo to a residue which was analysed by ¹H-nmr and GPC.
Table 3.5 Polymerization of vinyl acetate in presence of iPCI and iPrCo(III)(DMG-BF₂)₂ at 125 °C

<table>
<thead>
<tr>
<th>Example</th>
<th>VAc/iPrCl</th>
<th>Co(III) Mₙ</th>
<th>Mₚ</th>
<th>PD</th>
<th>% conv</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ppm</td>
<td>ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control 34</td>
<td>5/1</td>
<td>0</td>
<td>3969</td>
<td>7475</td>
<td>1.88</td>
</tr>
<tr>
<td>117</td>
<td>5/1</td>
<td>200</td>
<td>350</td>
<td>434</td>
<td>1.24</td>
</tr>
<tr>
<td>118</td>
<td>5/1</td>
<td>100</td>
<td>552</td>
<td>1323</td>
<td>2.40</td>
</tr>
<tr>
<td>119</td>
<td>5/1</td>
<td>50</td>
<td>1355</td>
<td>3833</td>
<td>2.82</td>
</tr>
<tr>
<td>120</td>
<td>5/1</td>
<td>25</td>
<td>1791</td>
<td>5143</td>
<td>2.87</td>
</tr>
<tr>
<td>Control 35</td>
<td>50/1</td>
<td>0</td>
<td>15,712</td>
<td>27,346</td>
<td>1.74</td>
</tr>
<tr>
<td>121</td>
<td>50/1</td>
<td>200</td>
<td>717</td>
<td>973</td>
<td>1.35</td>
</tr>
<tr>
<td>122</td>
<td>50/1</td>
<td>100</td>
<td>1230</td>
<td>1843</td>
<td>1.49</td>
</tr>
<tr>
<td>123</td>
<td>50/1</td>
<td>50</td>
<td>2692</td>
<td>4594</td>
<td>1.71</td>
</tr>
<tr>
<td>124</td>
<td>50/1</td>
<td>25</td>
<td>12,243</td>
<td>21,771</td>
<td>1.78</td>
</tr>
</tbody>
</table>

VAc/iPrCl macromonomer formation at 125 °C with VR®-110 and MRCO(III)(DEG-BF₂)₂

A mixture of vinyl acetate (1g, 11.6mmol), isopropenyl chloride (18mg, 0.232mmol) (monomer ratio: 50/1), n-butyl acetate (2g), VR®-110 (3.15x10⁻⁴ g, 100ppm) and MeCo(III)(DEG-BF₂)₂ (for concentration see table 3.6) was placed in an ampoule and degassed by 4 freeze-thaw cycles. The ampoule was sealed and the mixture heated at 125° for 2 hours. The ampoule was opened and the reaction mixture reduced in vacuo to a residue which was analysed by GPC.

Table 3.6 Polymerization of vinyl acetate in presence of iPCI and MeCo(III)(DEG-BF₂)₂ at 125 °C

<table>
<thead>
<tr>
<th>Example</th>
<th>VAc/iPrCl ratio</th>
<th>Co(III) ppm</th>
<th>Mₙ</th>
<th>Mₚ</th>
<th>PD</th>
<th>% conv</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control 36</td>
<td>50/1</td>
<td>0</td>
<td>13,984</td>
<td>24,811</td>
<td>1.77</td>
<td>46</td>
</tr>
<tr>
<td>125</td>
<td>50/1</td>
<td>200</td>
<td>935</td>
<td>1502</td>
<td>1.60</td>
<td>&lt;1</td>
</tr>
<tr>
<td>126</td>
<td>50/1</td>
<td>100</td>
<td>1627</td>
<td>3001</td>
<td>1.84</td>
<td>1</td>
</tr>
<tr>
<td>127</td>
<td>50/1</td>
<td>50</td>
<td>10,605</td>
<td>19,522</td>
<td>1.84</td>
<td>6</td>
</tr>
<tr>
<td>128</td>
<td>50/1</td>
<td>25</td>
<td>12,740</td>
<td>22,831</td>
<td>1.79</td>
<td>10</td>
</tr>
</tbody>
</table>
EXAMPLES 129-132, CONTROL 37
Synthesis of functional styrene macromonomer
TMF®- Cytec Incorporated comonomer
Feed polymerization

A mixture of styrene (1g, 9.6mmol), TMF® (0.2g, 0.96mmol)
(monomer ratio: 10/1), n-butyl acetate (2g), VR®-110 (3.2x10^-4 g, 100ppm) and
isopropylcobalt(III)DMG (at 0, 25, 50, 100 and 200ppm) was placed in an
ampoule and degassed by 4 freeze-thaw cycles. The ampoule was sealed and the
mixture heated at 125 °C for 2 hours. The ampoule was cooled, opened and the
reaction mixture reduced in vacuo to a residue which was analysed by ¹H-nmr and
GPC.

¹H-nmr(d₆-acetone): δ 4.9, external vinyl*; 5.20, external vinyl*; 6.0-
6.2, internal vinyl*; 6.6-7.4, ArH.
(⁎ external vinyl signals due to TMF® derived vinyl end group and internal vinyl
signals due to Sty derived vinyl end group).

Table 4.1: Polymerization of styrene in presence of TMF® and iPrCo(III)(DMG-BF₂)₂ at 125 °C

<table>
<thead>
<tr>
<th>Example</th>
<th>Sty/TMF® ratio</th>
<th>Co(III) ppm</th>
<th>Mn</th>
<th>Mw</th>
<th>PD</th>
<th>% terminal TMI® units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control 37</td>
<td>10/1</td>
<td>0</td>
<td>85,912</td>
<td>133,091</td>
<td>1.67</td>
<td>0</td>
</tr>
<tr>
<td>129</td>
<td>10/1</td>
<td>200</td>
<td>475</td>
<td>602</td>
<td>1.27</td>
<td>47</td>
</tr>
<tr>
<td>130</td>
<td>10/1</td>
<td>100</td>
<td>640</td>
<td>903</td>
<td>1.41</td>
<td>53</td>
</tr>
<tr>
<td>131</td>
<td>10/1</td>
<td>50</td>
<td>887</td>
<td>1373</td>
<td>1.55</td>
<td>60</td>
</tr>
<tr>
<td>132</td>
<td>10/1</td>
<td>25</td>
<td>1274</td>
<td>2155</td>
<td>1.73</td>
<td>75</td>
</tr>
</tbody>
</table>

EXAMPLE 133
A mixture of 2.5 mL MA, 0.5 mL 2-chloro-2-propenol, 14 mg TAPCo, 20 mg
VAZO-88 and 5 mL chloroform was degassed by three freeze-pump-thaw cycles.
The reaction mixture was kept at 90 °C until 10-15% conversion was attained.
GPC analysis showed Mn = 2150, PD = 2.0.

EXAMPLE 134
A mixture of 2.5 mL MA, 0.5 mL ethyl 2-hydroxymethylacrylate, 14 mg TAPCo,
20 mg VAZO-88 and 5 mL chloroform was degassed by three freeze-pump-thaw

42 Calculated as (terminal TMI units)/(terminal TMI units+terminal Sty units).
cycles. The reaction mixture was kept at 90 °C until 10-15% conversion was attained. GPC analysis showed Mn ≈ 1600, PD = 3.2.

EXAMPLE 135

A mixture of 2.5 mL MA, 0.5 mL styrene, 14 mg TAPCo, 20 mg VAZO-88 and 5 mL chloroform was degassed by three freeze-pump-thaw cycles. The reaction mixture was kept at 90 °C until 10-15% conversion was attained. GPC analysis showed Mn ≈ 700, PD = 2.4.

EXAMPLE 136

A mixture of 2.5 mL MA, 0.5 mL 2-hydroxyethyl methacrylate, 14 mg TAPCo, 20 mg VAZO-88 and 5 mL chloroform was degassed by three freeze-pump-thaw cycles. The reaction mixture was kept at 90°C until 10-15% conversion was attained. GPC analysis showed Mn ≈ 2150, PD = 2.0.

CONTROL 38

A mixture of 2.5 mL MA, 14 mg TAPCo, 20 mg VAZO®-88 and 5 mL chloroform was degassed by three freeze-pump-thaw cycles. The reaction mixture was kept at 90°C until 10-15% conversion was attained. GPC analysis showed Mn ≈ 21,700, PD=2.4.

EXAMPLE 137

High Conversion Copolymerization of BA and MMA to Branched and Hyperbranched Polymers

The reincorporation of initially-formed macromonomers back into the growing polymer is demonstrated.

Identical solutions of 32 mg of VAZO®-88 and 4 mg Co(II)(DPG-BF₂)₂ in 7.7 mL of butyl acrylate (BA), 1.5 mL MMA and 8 mL of 1,2-dichloroethane were degassed and kept in a 90 °C oil bath. The samples were removed from the temperature bath at various times shown in Table 5.1. Then each reaction mixture was chilled and evaporated in high vacuum till constant weight. The results, shown in Table 5.1, indicates that MW increases sharply at the end of the polymerization process. Because most of the monomer had been consumed before the increase in molecular weight, the only way that it could occur is through reincorporation of the macromonomers formed at the beginning of the reaction. GPC and KIDS data are consistent.
Table 5.1

<table>
<thead>
<tr>
<th>Conversion</th>
<th>$M_n$</th>
<th>$M_n/M_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12%</td>
<td>540</td>
<td>2.08</td>
</tr>
<tr>
<td>20%</td>
<td>640</td>
<td>2.08</td>
</tr>
<tr>
<td>55%</td>
<td>890</td>
<td>2.06</td>
</tr>
<tr>
<td>93%</td>
<td>2270</td>
<td>2.84</td>
</tr>
</tbody>
</table>

The catalyst remained active during the course of the polymerization. Sudden inactivation of the catalyst at conversion >60% cannot account for an increase of the Mn from 890 at 55% conversion to 2270 at 93% conversion. Less than doubling of the conversion (93% vs 55%) cannot provide a 2.6 fold increase of the Mn (2270 vs 890) maintaining a unimodal distribution.

The linear macromonomers formed at 55% conversion were incorporated into the polymer at higher conversions. The incorporation of macromonomer into growing polymer chains provides branched polymer. With continuous termination of polymeric radicals by the cobalt catalyst, such an incorporation leads to polymer with a structure containing “branches-on-branches” - in the extreme, it is hyperbranched.

Confirmation of the macromonomer reincorporation into the polymer back-bone was provided by MALDI mass spectroscopy. As seen on the MALDI spectra, at conversions <50% the polymer contains from 1 to 5 MMA units per chain. For $M_n \approx 900$, it means that the polymer is enriched with MMA vs composition of the initial monomer solution. As a result, the concentration of unreacted MMA monomer in the solution decreases faster than that of BA. At 55% conversion, more than 70% of the original MMA is consumed.

Fewer MMA units are available to be incorporated into the high molecular weight polymer formed at conversions >60% than at lower conversions if polymer that forms at high conversion does not incorporate previously formed macromonomer. Incorporation of the previously-formed macromonomer would provide MMA to the high molecular weight polymer. The MALDI spectrum of the polymer at 93% conversion demonstrated this clearly. The MALDI spectrum of the polymer at 93% conversion becomes unresolved at masses >2500 due to the high levels of MMA incorporation.
EXAMPLE 138

A reaction mixture containing 4 mg of the CTC-catalyst (COBF), 32 mg of VAZO®-88, 2 ml of butyl acrylate, 6 ml MMA-trimer, 0.2 ml of methyl methacrylate and 4 ml of 1,2-dichloroethane was degassed by three freeze-pump-thaw cycles and put into an oil bath at 90°C. Samples of the reaction mixture were taken after 1.5 hours, 3 hours, 7 hours and 22 hours. Initial GPC analysis shows that molecular weight of the polymeric product increases with time. Comparision of GPC data with that of KIDS and MALDI shows that in the first case the average measured MW are lower than expected in case of higher conversion samples. The first samples had readily observable quantities of vinylene protons (1H NMR spectra), indicating the formation of methacrylate-terminated polymer at the beginning of the CTC process. All of these observations are consistent with the proposed scheme.
WHAT IS CLAIMED IS:

1. In a process for the free-radical polymerization of at least two unsaturated monomers to form a polymer whose molecular architecture comprises properties of molecular weight, branching, and vinyl-terminated end groups, the monomers having the formula

\[ \text{CH}_2=\text{CXY} \]

wherein

- X is selected from the group consisting of H, CH₃, and CH₂OH;
- Y is selected from the group consisting of OR, O₂CR, halogen, CO₂H, COR, CO₂R, CN, CONH₂, CONHR, CONR₂, and R’;
- R is selected from the group consisting of substituted and unsubstituted alkyl, substituted and unsubstituted aryl, substituted and unsubstituted heteroaryl, substituted and unsubstituted aralkyl, substituted and unsubstituted alkaryl, and substituted and unsubstituted organosilyl, the substituents being the same or different and selected from the group consisting of carboxylic acid, carboxylic ester, epoxy, hydroxyl, alkoxy, primary amino, secondary amino, tertiary amino, isocyanato, sulfonic acid and halogen; and the number of carbons in said alkyl groups is from 1 to 12; and
- R’ is selected from the aromatic group consisting of substituted and unsubstituted aryl, substituted and unsubstituted heteroaryl, the substituents being the same or different and selected from the group consisting of carboxylic acid, carboxylic ester, epoxy, hydroxyl, alkoxy, primary amino, secondary amino, tertiary amino, isocyanato, sulfonic acid, substituted and unsubstituted alkyl, substituted and unsubstituted aryl, substituted and unsubstituted olefin and halogen;

by contacting said monomers with a cobalt-containing chain transfer agent and a free radical initiator at a temperature from about 80° to 170°C;

the improvement which comprises controlling polymer architecture by introducing into the presence of the chain transfer agent at least one each of monomers A and B in the molar ratio of A:B, said molar ratio lying in the range of about 1,000:1 to 2:1, wherein for monomer A X is H and for monomer B X is methyl or hydroxymethyl; by one or more of the following steps:

I decreasing the ratio of A:B from about 1,000:1 toward 2:1;
II increasing the temperature from above 80°C toward 170°C;
III increasing the conversion of monomer to polymer toward 100% from less than about 50%;
IV decreasing the ratio of the chain transfer constant of A:B to below 1; and
V increasing the concentration of cobalt chain transfer agent;
whereby:

to effect lower molecular weight, employ at least one of steps I, II, IV and V;

to effect a higher degree of vinyl-terminated end groups, employ at least one of steps I, II, IV, and V; and
to effect increased branching, employ at least one of steps I, II, IV, and V with step III.

2. A process according to Claim 1 wherein the improvement comprises:
controlling molecular weight of the polymer by introducing into the presence of the chain transfer agent at least one each of monomers C and D in the molar ratio of C:D lying in the range of about 1,000:1 to 2:1, in which for monomer C, X is H, and Y=R' and for monomer D, X is H, and Y=R' by:
decreasing the ratio of C:D from about 1,000:1 toward 2:1; or
increasing the temperature from above 80°C toward 170 °C.

3. A process according to Claim 1 wherein the improvement comprises polymerizing monomer(s) in the presence of an excess of a nonpolymerizable olefin, \( Y^1 Y^2 C = CY^3 Y^4 \). The product in the initial stages of the polymerization will be composed primarily of

\[
\begin{align*}
\text{H} & \quad \text{Y}^1 \quad \text{Y}^3 \\
\text{C} & \quad \text{C} \quad \text{C} \\
\text{Y}^2 & \quad \text{Y}^4
\end{align*}
\]

wherein:

\( Y^1 \) and \( Y^3 \), and optionally \( Y^2 \) and \( Y^4 \), are each independently selected from the group consisting of -\( \text{CH}(O) \), -\( \text{CN} \), -\( \text{C}(O)\text{OR} \), -\( \text{C}(O)\text{NR}^6 \text{R}^7 \), -\( \text{CR}^8 \text{(O)} \), alkyl, aryl, substituted alkyl, substituted aryl; or

where \( Y^1 \) and \( Y^3 \) or \( Y^2 \) and \( Y^4 \) are combined in a cyclic structure

which includes any of the above functionalities, or can be -\( \text{C}(O)-(\text{CH}_2)_x \text{-} \), -\( \text{C}(O)-\text{O}(\text{CH}_2)_x \text{-} \), -\( \text{C}(O)-(\text{CH}_2)_x \text{-} \), -\( \text{C}(O)-(\text{CH}_2)_x \text{-} \), -\( \text{C}(O)-\text{NR}^9 \text{-}(\text{CH}_2)_x \text{-} \), where \( x = 1-12, \)

\( R^5, R^6, R^7, R^8 \), or \( R^9 \) are hydrogen, alkyl, aryl, substituted alkyl, or substituted aryl; and where at least one of \( Y^1 \) and \( Y^3 \) is selected from the group consisting of -\( \text{CH}(O) \), -\( \text{CN} \), -\( \text{C}(O)\text{OR} \), -\( \text{C}(O)\text{NR}^6 \text{R}^7 \), -\( \text{CR}^8 \text{(O)} \), aryl, substituted aryl; and the remaining of \( Y^2 \) and \( Y^4 \) are -H.
4. A process according to Claim 1 comprising selecting A and B so the ratio of their chain transfer constants is less than 1, whereby functionality derived from monomer B will be located on the vinyl-terminated end of the polymer.

5. The process according to Claim 1 in which monomer A is at least one member selected from the group substituted and unsubstituted alkyl acrylates, substituted and unsubstituted acrylamides, acrylonitrile, and vinyl esters; and monomer B is at least one of:

a) substituted and unsubstituted α-methyl styrenes;
b) alkyl methacrylates
c) methacrylonitrile;
d) substituted or unsubstituted methacrylamide;
e) 2-chloropropene,

f) 2-fluoropropene,
g) 2-bromopropene
h) methacrylic acid,
i) itaconic acid,
j) itaconic anhydride,
k) substituted and unsubstituted styrenics, and
l) isopropenyl esters;
alkyl being C\textsubscript{1} to C\textsubscript{12} and substituents being selected from the group carboxylic acid, carboxylic ester, epoxy, hydroxyl, alkoxy, primary amino, secondary amino, tertiary amino, isocyananto, sulfonic acid and hydrogen.

6. A process according to Claim 5 in which monomer A is at least one member selected from the group alkyl acrylate, acrylamide, acrylonitrile and vinyl ester.

7. A process according to Claim 2 in which monomer A is at least one member selected from the group substituted and unsubstituted alkyl acrylates substituted and unsubstituted acrylamides, acrylonitrile, and vinyl esters; and monomer B is at least one of:

a) substituted and unsubstituted α-methyl styrenes;
b) alkyl methacrylates
c) methacrylonitrile;
d) substituted and unsubstituted methacrylamide;
e) 2-chloropropene,
f) 2-fluoropropene,
g) 2-bromopropene
h) methacrylic acid,
i) itaconic acid,
j) itaconic anhydride,
k) substituted and unsubstituted styrenics, and
l) isopropenyl esters;

alkyl being C₁ to C₁₂ and substituents being selected from the group carboxylic acid, carboxylic ester, epoxy, hydroxyl, alkoxy, primary amino, secondary amino, tertiary amino, isocyananto, sulfonic acid and hydrogen.

8. A polymer having the formula:

![Polymer Structure](image)

Y is selected from the group consisting of OR, O₂CR, halogen, CO₂H, COR, CO₂R, CN, CONH₂, CONHR, CONR₂ and R;  
n = 1-20, m = 1-5, p=1-20, and n + m + p ≥ 3, and

Z is selected from the group CH₂CHYCH₃, CH₂CMeYCH₃, and, optionally,

![Polymer Structure](image)

m' = 0-5, p' = 0-20; n + m' + p' ≥ 2;

and if m or m' > 1, the m or m' insertions respectively are not consecutive.

9. A polymer having the formula:

![Polymer Structure](image)

where Z = H, CH₃, CH₂CHYCH₃, CH₂CMeYCH₃, or
wherein:

- $k = 0$ or $1$, $n = 0-20$, $m = 0-5$, $p = 0-20$; and $k + n + m + p \geq 2$; if $m > 1$,
- the $m$ insertions are consecutive;

5

- $Y$ is selected from the group consisting of OR, O$_2$CR, halogen, CO$_2$H,
- COR, CO$_2$R, CN, CONH$_2$, CONHR, CONR$_2$ and R; and

- $Y^1$ and $Y^3$, and optionally $Y^2$ and $Y^4$, are each independently selected
from the group consisting of -CH(O), -CN, -C(O)OR$^5$, -C(O)NR$^6$, -R$^7$, -CR$^8$(O),
aleryl, aryl, substituted alkyl, substituted aryl; or

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- where $Y^1$ and $Y^3$ or $Y^2$ and $Y^4$ are combined in a cyclic structure
which includes any of the above functionalities, or can be -C(O)-(CH$_2$)$_x$-C(O)-
- O-(CH$_2$)$_x$-, -C(O)O-CH$_2$-C(O)-, -C(O)(CH$_2$)$_x$-, -C(O)NR$^9$-(CH$_2$)$_x$-, wherein $x = 1-12$,
- R$^5$, R$^6$, R$^7$, R$^8$, or R$^9$ are hydrogen, alkyl, aryl, substituted alkyl, or substituted
aryl; and where at least one of $Y^1$ and $Y^3$ is selected from the group consisting of

15

- CH(O), -CN, -C(O)OR$^5$, -C(O)NR$^6$R$^7$, -CR$^8$(O), aryl, substituted aryl; and the
remaining of $Y^2$ and $Y^4$ are -H;

- R is selected from the group consisting of substituted and
unsubstituted alkyl, substituted and unsubstituted aryl, substituted and
unsubstituted heteroaryl, substituted and unsubstituted aralkyl, substituted and
unsubstituted alkaryl, and substituted and unsubstituted organosilyl, the
substituents being the same or different and selected from the group consisting of
carboxylic acid, carboxylic ester, epoxy, hydroxyl, alkoxy, primary amino,
secondary amino, tertiary amino, isocyanato, sulfonic acid and halogen; and the
number of carbons in said alkyl groups is from 1 to 12; and

20

- R' is selected from the aromatic group consisting of substituted and
unsubstituted aryl, substituted and unsubstituted heteroaryl, the substituents being
the same or different and selected from the group consisting of carboxylic acid,
carboxylic ester, epoxy, hydroxyl, alkoxy, primary amino, secondary amino,
tertiary amino, isocyanato, sulfonic acid, substituted and unsubstituted alkyl,
substituted and unsubstituted aryl, substituted and unsubstituted olefin and
halogen.
10. A polymer having the formula:

\[
\begin{array}{c}
\text{H} \\
\text{CH}_2 \\
\text{CH}_2 \equiv \\
\text{C} \\
\text{R}^1
\end{array}
\]

where \( Y \neq R^1 \) and \( n \geq 1 \); in which

\( Y \) is selected from the group consisting of \( \text{OR}, \text{O}_2\text{CR}, \text{halogen}, \text{CO}_2\text{H}, \text{COR}, \text{CO}_2\text{R}, \text{CN}, \text{CONH}_2, \text{CONHR} \) and \( \text{CONR}_2 \); and

\( R^1 \) is selected from the aromatic group consisting of substituted and unsubstituted aryl, substituted and unsubstituted heteroaryl, the substituents being the same or different and selected from the group consisting of carboxylic acid, carboxylic ester, epoxy, hydroxyl, alkoxy, primary amino, secondary amino, tertiary amino, isocyanato, sulfonic acid, substituted and unsubstituted alkyl, substituted and unsubstituted aryl, substituted and unsubstituted olefin and halogen.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F2/38 C08F290/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>MACROMOLECULES, vol. 28, no. 15, 1995, pages 5381-5385, X000515367 J. KRSTINA ET AL.: &quot;narrow polydispersity block copolymers by free-radical polymerization in the presence of macromonomers&quot; see the whole document</td>
<td>8,9</td>
</tr>
<tr>
<td>X</td>
<td>US 5 362 813 A (J. ANTONELLI ET AL.) 8 November 1994 see example 2</td>
<td>9</td>
</tr>
<tr>
<td>X</td>
<td>US 4 680 354 A (JU-CHUI LIN ET AL.) 14 July 1987 cited in the application see examples 3A,3B,3C,5A-B</td>
<td>9</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of box C.

Patient family members are listed in annex.

* Special categories of cited documents:
  'A' document defining the general state of the art which is not considered to be of particular relevance
  'E' earlier document but published on or after the international filing date
  'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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Date of the actual completion of the international search
9 June 1997

Date of mailing of the international search report
26.06.97

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