

明 細 書

ビニル系重合体の製造方法、ビニル系単量体重合用開始剤及び
スチレン系樹脂組成物

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技術分野

本発明は、ビニル系重合体の製造方法及びビニル系単量体重合用開始剤及びスチレン系樹脂組成物に関する。本発明の製造方法によれば、従来のアニオン重合法に比べて高単量体濃度かつ高温の反応条件下であるにもかかわらず、重合反応時に発生する熱による自己加速反応や移動反応・停止反応を起こすことなく、制御可能な温度範囲でリビング重合を進行させることができる。

背景技術

ポリスチレンに代表されるスチレン系重合体は、古くからラジカル重合法により工業的に生産されてきた。しかし、ラジカル重合法は周知の通り、成長ラジカルの再結合反応等による停止反応又は溶媒や単量体へのラジカルの移動反応が起こるため、ポリマーの構造制御、例えば分子量分布やポリマー末端構造の制御が困難であった。また、ラジカル重合法はリビング重合でないため、ブロックポリマーや星型ポリマーを製造することもできなかった。

これらの不都合を解決する手法としては、スチレンやブタジエンに代表される単量体のリビングアニオン重合法がある。例えば、汎用的な開始剤であるブチルリチウムを使って行うスチレンのアニオン重合においては、移動反応及び停止反応のないいわゆるリビング重合が進行するので、極めて単分散性のポリマーが得られる。また、リビングポリマーの生長末端の反応性を利用することにより、ブタジエンとのブロックポリマーを始め、本来ラジカル重合法では得られない構造制御された様々なポリマーを得ることができる。しかし、スチレンのリビングアニオン重合法は、このように非常に魅力的な樹脂材料が得られるにもかかわらず、特殊な例を除いて、これまで工業的に利用されなかった。この理由の一つとして、リビングアニオン重合が溶液重合であるため、生産収率が低いこと、及び大掛かりな溶媒回収プロセスが必要となることから製造コストが従来のラジカル重合法

に比べ高くなってしまい、工業的利用価値がほとんど無かったことが挙げられる。したがって、スチレンとブタジエンとのブロックポリマーのようなポリマーは、従来の溶液重合法に頼らざるを得なかった。

- リビングアニオン重合法の製造コストを下げるためには、重合時に使用する溶媒の量を少なくし、生産性を向上させ、かつ溶媒回収の負荷を極力抑える必要がある。しかし、溶媒の使用量を少なくすると、重合系の粘度が極度に上昇するため、重合温度は従来の溶液重合よりかなり高温にしなければならない。

このような条件下で従来のように、例えばブチルリチウムを用いてスチレンを重合すると、次の問題点が生じるので、そのような重合は実用的ではない。

- 10 ① 重合開始反応及び成長反応が極めて速く起こるため急激に重合反応熱が生じ、それにより多くの場合、十分な除熱ができず重合系内の温度が急上昇し、自己加速反応、いわゆる暴走反応（反応速度の制御が不可能な状態）が起こる。
- ② 例えば100℃以上の高温では、成長末端の炭素アニオンが不安定となり、溶媒やポリマー主鎖への移動反応、β位の水素引き抜き反応による停止反応等が多発してリビングポリマーの活性が極度に低下する。

- 従来のように、ブチルリチウム等の有機アルカリ金属を開始剤に用いる重合では、開始剤の量を少なくすることによって重合速度を抑制して上記①の問題を解決することはできるが、得られるポリマーの分子量が大きくなるという問題が生じる。有機アルキル金属を用いるアニオン重合で得られるポリマーの数平均分子量M_nは、次式

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$$M_n = [\text{単量体}] / [\text{有機アルキル金属}] \times (\text{単量体の分子量})$$
（[] : モル濃度）で表されるように、単量体とアルキル金属との量比で決まるため、少量の開始剤ではポリマーが高分子量化し、低分子量のポリマーを得たいときは多くの開始剤が必要となる。従って、暴走反応を抑制しなければならないという操作上の制約のために、目的の分子量のポリマーを自由自在に得ることは困難であった。

また、従来の有機アルキル金属を用いると、開始反応が成長反応に対して極めて速く進行するため、多くの場合得られるポリマーの分子量分布は極めて単分散である。しかし、樹脂材料の観点から、分子量分布が単分散であることが成形加工性と物性のバランスに対して不都合となる場合がある。したがって、分子量分

布を多分散化するためには開始剤を徐々に添加するか、又は滞留時間分布のある連続リアクター内で重合を行わざるを得ず、重合反応を行うだけで分子量分布を自由にコントロールできるリビングアニオン重合系の発見が望まれていた。

発明の開示

- 5 本発明は、高単量体濃度かつ高温の条件下においてビニル系単量体のアニオン重合を、自己反応熱による暴走反応を引き起こすことなく制御可能な重合速度で進行させ、高温下でも移動反応や停止反応のない、従来技術では達成できなかったリビング重合が可能となり、分子量分布の制御されたビニル系重合体を与える新規な製造方法を提供することを目的とする。本発明はまた、成形加工性に優れ、
- 10 熱分解によるスチレン系単量体の発生量の少ないスチレン系樹脂組成物を提供することを目的とする。

- 本発明者は、かかる目的を達成すべく鋭意検討を重ねた結果、スチレン、ブタジエンに代表されるビニル系単量体のアニオン重合を、有機マグネシウム化合物と特定のアルキル金属化合物とからなる開始剤を用いて行くと、極めて驚くべき
- 15 ことに高単量体濃度かつ高温の条件下においても、重合反応が暴走を起こすことなく、また極端に重合速度が遅くなることもなく、除熱制御が十分可能な反応速度でリビング重合が進行し、分子量分布の制御が可能となることを見出し、この知見に基づき本発明を完成した。さらに、得られるスチレン系樹脂組成物は、従来のアニオン重合開始剤を使って得られた樹脂組成物よりも、熱滞留下での分解
- 20 速度が小さく単量体の生成が少ないことを見出し、本発明を完成させた。

- 本発明は、重合成長末端の炭素アニオンと対になっているカチオンの金属がMgであるか、又はMg及びM' (M' は、Li, Na及びKからなる群から選ばれる少なくとも1種類のアルカリ金属であり、MgとM' の金属モル濃度が
- [Mg] / [M'] $\geq$ 4なる関係を満たす) であるアニオン重合を、重合温度 4
- 25 5℃以上250℃以下、ビニル系単量体の重合溶媒に対する濃度が45wt%～100wt%の条件下で行うことからなるビニル系重合体の製造方法に関する。

本発明はまた、重合開始剤として(R²)₂Mg (R² は炭化水素基) を単独で用いる上記ビニル系重合体の製造方法に関する。

本発明はまた、重合開始剤として(R²)₂Mg及びR¹M' 及び／又はR¹

OM' (R¹、R²は炭化水素基、Oは酸素原子、M'は、Li、Na及びKからなる群から選ばれる少なくとも1種類のアルカリ金属)で表される有機金属化合物であって、MgとM'の金属モル濃度が[Mg]/[M'] ≥ 4なる関係を満たす有機金属化合物を用いる上記ビニル系重合体の製造方法に関する。

- 5 本発明はまた、上記金属モル濃度が[Mg]/[M'] = 10～100なる関係を満たす上記ビニル系重合体の製造方法に関する。

本発明はまた、(R²)₂Mg及びR¹M'及びR³OH及び/又は(R³)₂NH(R¹、R²、R³は炭化水素基、Oは酸素原子、Nは窒素原子、M'は、Li、Na及びKからなる群から選ばれる少なくとも1種類のアルカリ

- 10 金属)で表される化合物を、

[Mg] > [M'] 及び

2x[Mg] + [M'] > [R³OH] + [(R³)₂NH]なる関係を満たすように混合して用いる上記ビニル系重合体の製造方法に関する。

- 本発明はまた、ビニル系単量体の重合率(転換率)が0～70%の領域において重合温度が45℃以上200℃以下である上記ビニル系重合体の製造方法に関する。
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- 本発明はまた、(R²)₂Mg及びR¹M'の有機金属化合物において、R¹及びR²の炭化水素基の金属に結合している炭素の少なくとも1つが2級炭素及び/又は3級炭素であり、しかも2級炭素及び/又は3級炭素のR¹及びR²の総量[R^{1,2}]が[R^{1,2}] ≥ [Mg]である上記ビニル系重合体の製造方法に関する。
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本発明はまた、(R²)₂Mg及びR¹M'の有機金属化合物において、R¹及びR²の炭化水素基の少なくとも1つがポリマー炭素アニオンである上記ビニル系重合体の製造方法に関する。

- 25 本発明はまた、(R²)₂Mg及びR³OH及び/又は(R³)₂NH(R²、R³は炭化水素基、Oは酸素原子、Nは窒素原子)で表される化合物を
- 2x[Mg] > [R³OH] + [(R³)₂NH]なる関係を満たすように混合して用いる上記ビニル系重合体の製造方法に関する。

本発明はまた、重合溶媒が炭化水素系化合物である上記ビニル系重合体の製造

方法；実質的にビニル系単量体の重合溶媒に対する濃度が100wt%である上記ビニル系重合体の製造方法；重合反応を押出機中で行う上記ビニル系重合体の製造方法に関する。

本発明はさらにまた、 $(R^2)_2Mg$ (R^2 は炭化水素基)を含むビニル系単
5 量体重合用開始剤に関する。

本発明はまた、 $(R^2)_2Mg$ 及び R^1M^1 及び／又は R^1OM^1 (R^1 、
 R^2 は炭化水素基、Oは酸素原子、 M^1 は、Li、Na及びKからなる群から選
ばれる少なくとも1種類のアルカリ金属)で表される有機金属化合物を含み、金
属モル濃度比が $[Mg] / [M^1] \geq 4$ なる関係を満たすビニル系単量体重合用
10 開始剤に関する。

本発明はまた、 $(R^2)_2Mg$ 及び R^1M^1 及び／又は R^1OM^1 (R^1 、
 R^2 は炭化水素基、Oは酸素原子、 M^1 は、Li、Na及びKからなる群から選
ばれる少なくとも1種類のアルカリ金属)で表される有機金属化合物を含み、金
属モル濃度比が $[Mg] / [M^1] = 10 \sim 100$ なる関係を満たすビニル系単
15 量体重合用開始剤に関する。

本発明はまた、 $(R^2)_2Mg$ 及び R^1M^1 及び R^3OH 及び／又は
 $(R^3)_2NH$ (R^1 、 R^2 、 R^3 は炭化水素基、Oは酸素原子、Nは窒素原子、
 M^1 は、Li、Na及びKからなる群から選ばれる少なくとも1種類のアルカリ
金属)で表される化合物を含み、 $[Mg] > [M^1]$ 及び $2x[Mg] + [M^1]$
20 $> [R^3OH] + [(R^3)_2NH]$ なる関係を満たすビニル系単量体重合用開
始剤に関する。

本発明はまた、 $(R^2)_2Mg$ 及び R^3OH 及び／又は $(R^3)_2NH$ (R^2 、
 R^3 は炭化水素基、Oは酸素原子、Nは窒素原子)で表される化合物を含み、
 $2x[Mg] > [R^3OH] + [(R^3)_2NH]$ なる関係を満たすビニル系単
25 量体重合用開始剤に関する。

本発明はさらにまた、上記記載の製造方法によって得られ得るビニル系重合体
に関する。

本発明はさらにまた、スチレン系単量体のアニオン重合によって得られるスチ
レン系重合体であって、その分子量分布 Mw/Mn が2.0～10.0であり、

かつスチレン系単量体由来のトリマーの含有量が250ppm以下である上記スチレン系樹脂組成物に関する。

本発明はさらにまた、上記スチレン系樹脂組成物を射出成形又は押出成形して得られる成形体に関する。

5 図面の簡単な説明

図1、図4及び図10は、実施例及び比較例で得られた高分子量体の重合率(Con v.)と数平均分子量(Mn)との関係を示すグラフである。

図2、図3及び図9は、実施例及び比較例で得られた高分子量体の重合時間(Time)と重合率(Con v.)との関係を示すグラフである。

10 図5は、実施例で得られた高分子量体のGPC曲線である。

図6は、実施例、比較例で得られた高分子量体の数平均分子量(Mn)と重合初期条件である単量体とBu₂Mgの濃度比([SM] / [Mg])との関係を示すグラフである。

図7は、実施例、比較例で得られた高分子量体の数平均分子量(Mn)と重合
15 初期条件であるBu₂MgとBuLiとの濃度比([Mg] / [Li])との関係を示すグラフである。

図8は、実施例、比較例で得られた高分子量体の重量平均分子量(Mw)と数平均分子量(Mn)との比(Mw/Mn)と、重合初期条件であるBu₂MgとBuLiとの濃度比([Mg] / [Li])との関係を示すグラフである。

20 発明を実施するための最良の形態

本発明で用いられるビニル系単量体とは、スチレン系単量体及び共役ジエン系単量体を包含する。

スチレン系単量体としては、スチレン、 α -アルキル置換スチレン、核アルキル置換スチレン等が挙げられる。それらの具体例としては、 α -メチルスチレン、
25 α -メチルー-p-メチルスチレン、p-メチルスチレン、m-メチルスチレン、
o-メチルスチレン、p-エチルスチレン、2,4-ジメチルスチレン、2,5-
ジメチルスチレン、p-イソプロピルスチレン、2,4,6-トリメチルスチレン等が挙げられる。

共役ジエン系単量体としては、1,3-ブタジエン、イソプレン、2,3-ジ

メチルブタジエン、2-エチル-1,3-ブタジエン、1,3-ペンタジエン等が挙げられる。

これらのビニル系単量体は、一種類で、又は共重合体を得る目的で2種類以上の組み合わせで使用してもよい。

- 5 重合温度は45℃以上250℃以下、好ましくは50℃以上240℃以下、更に好ましくは60℃以上230℃以下である。重合温度の下限は、少なくとも目標とする重合時間内に重合が完結する重合速度をある程度保持する温度でなければならない。45℃より低い温度でも重合は進行するが、本発明に係る重合系においてはその重合が極めて遅く進行するため、工業生産的見地からは、好ましく
- 10 ないと判断される。重合温度が250℃以上になると移動反応や停止反応等の副反応が頻繁に起こり、高分子量のポリマーを得ることが困難となるとともにポリマーが着色する。

- 本発明において重合温度は、重合反応中一定である必要はなく、重合反応の進行に従い任意の速度で上昇させてもかまわない。特に、単量体の濃度が高い重合
- 15 反応の初期段階においては、反応速度が速く発生する熱量が多いため低い温度から重合反応を始め、単量体の濃度が低くなるにつれて徐々に温度を上昇させる方法でもよい。ビニル単量体の重合率が0~70%の領域では、45℃~200℃の温度範囲で重合を行うことが好ましく、単量体が少なくなった重合率70%以上の領域では、200℃以上250℃以下の温度領域で重合を行うことが好まし
- 20 い。ただし、重合反応系の粘度が低く、重合温度を必要以上に上げる必要がなければ、重合率70%~100%の領域での重合を200℃以下で行ってもかまわない。

- ビニル系単量体の重合溶媒に対する濃度は、45wt%以上100wt%以下、好ましくは50wt%以上100wt%以下である。溶媒の回収を考えれば、単
- 25 量体の濃度は高いほど好ましいが、得られる重合体の種類によっては温度と重合系の粘性との関係から、ある程度の溶媒量が必要となる場合がある。しかし、必要以上に濃度が希薄になれば、重合反応が遅くなるばかりでなく、高温時に溶媒への移動反応が起こり易くなるため、リビング重合性の効率の観点から濃度は少なくとも45wt%である。

実質的にビニル系単量体の重合溶媒に対する濃度が100wt%であるとは、開始剤溶液由来の溶媒以外に使用する溶媒が存在しないことをいう。重合溶媒を使用しない単量体濃度100%の重合は、溶媒への移動・停止反応がなく、開始剤の使用効率が高いこと、生産性が高いこと、さらに重合停止後の工程での溶媒
5 回収プロセスが不要となることから、工業的には最も理想的な重合条件である。

本発明でいう重合溶媒とは、重合反応に関与せず、かつ重合体と相溶性のある溶媒をいい、一般的にリビングアニオン重合に使われるものであれば何でもよく、その種類は特に制限はない。好ましい重合溶媒としては、移動反応、停止反応の起こりにくい比較的極性の低い芳香族系炭化水素化合物又は脂環式炭化水素化合物
10 物である。それらの例として、例えば、エチルベンゼン、トルエン、イソプロピルベンゼン、ベンゼン、シクロヘキサン等が挙げられる。また、これらの溶媒中に本発明の目的を超えない範囲で、テトラヒドロフラン、ジオキサン、トリオキサン等のエーテル系化合物、テトラメチルエチレンジアミン等の3級アミンやピリジン等の窒素系化合物、ペンタン、n-ヘキサン、ヘプタン、オクタン、ノナ
15 ン、デカン等の脂肪族飽和炭化水素化合物、トリエチルアルミニウム、ジエチル亜鉛等の弱ルイス酸を少量含有させてもよい。

本発明で用いられる、 $(R^2)_2Mg$ で表される有機マグネシウム化合物とは、Mgに炭化水素基が結合している化合物である。炭化水素基としては、例えば、メチル基、エチル基、プロピル基、イソプロピル基、n-ブチル基、t-ブチル
20 基、sec-ブチル基、アミル基、ヘキシル基等の CH_3 、 $(CH_2)_n$ で表される(直鎖又は分枝)アルキル基が好ましい。具体的なマグネシウム化合物としては、ジ-n-ブチルマグネシウム、ジ-t-ブチルマグネシウム、ジ-sec-ブチルマグネシウム、n-ブチル-sec-ブチルマグネシウム、n-ブチルエチルマグネシウム、n-アミルマグネシウム等が好ましい。これらの化合物は1種類
25 で、又は2種類以上の併用で用いてもよい。

従来から、 R^2Mg (Rはアルキル基)単独では、ビニル系単量体の重合が開始しないこと、さらにヘキサメチルホスホルアミド(HMPA)等の極性化合物を添加しない限り重合が開始しないことが知られている。しかし本発明者は、極性化合物を添加せず、 R^2Mg 化合物単独で、しかも無極性の炭化水素系溶媒中

においても、特定の温度条件下ではビニル系単量体の重合が開始し、さらにその重合がリビング重合であることを見出した。

$R^2 Mg$ を単独で開始剤として使用する場合の重合下限温度は $100^{\circ}C$ 以上、好ましくは $110^{\circ}C$ 以上、更に好ましくは $120^{\circ}C$ 以上である。 $100^{\circ}C$ 以下で

5 は重合が極めて遅く進行するか、又は重合が開始しない。

$R^2 Mg$ 単独による重合よりも効率的に重合開始反応及び成長反応を促進するためには、 $R^2 Mg$ に $R^1 M^1$ 及び／又は $R^1 OM^1$ (R^1 、 R^2 は炭化水素基、 O は酸素原子、 M^1 は、 Li 、 Na 及び K からなる群からなる少なくとも1種類のアルカリ金属)で表される有機金属化合物を添加することが好ましい。

10 $R^2 Mg$ 及び $R^1 M^1$ 及び／又は $R^1 OM^1$ の組み合わせからなる開始剤は従来から知られてはいたが、下記に示すような問題点があり、満足のいくものではなかった。

Macromolecules, vol. 19, p. 299 (1986) 及び
US-A-3, 716, 495には、本発明と同様にジブチルマグネシウム及び
15 ブチルリチウム、ジアミルマグネシウム及びブチルリチウムからなる重合開始剤を使って $50^{\circ}C$ 又は $70^{\circ}C$ でスチレンの重合、ブタジエンの重合、スチレンとブタジエンとの共重合の例が開示されている。しかし、重合溶媒であるシクロヘキサンに対する単量体の濃度が約11%と低く、しかも金属濃度比が $[Mg] <$

$[Li]$ の領域である。本発明者の知見によれば、 $[Mg] < [Li]$ なる領域
20 では、重合成長末端の金属が Mg にはならず、重合速度、ポリマーの分子量、分子量分布をそれぞれ独立に制御することができない。また、上記の引例の開始剤を用いると、単量体の濃度が11%と低い領域では、 $50^{\circ}C$ 又は $70^{\circ}C$ で暴走反応を起こさずにリビング重合を行うことはできるが、本発明のような単量体の濃度及び温度領域では、暴走反応を起こしてしまい重合速度の制御ができない。

25 US-A-4, 225, 690には、ジブチルマグネシウムとアミルカリウム又はアミロキシカリウムからなる重合開始剤が開示されている。しかし、この重合開始剤についても $[Mg] < [K]$ の領域であり、単量体濃度も約10%~25%と低く、同様に重合成長末端が Mg にはならず、重合速度、ポリマーの分子量、分子量分布をそれぞれ独立に制御することができない。しかも、本発明のよ

うな濃度及び温度領域では暴走反応を起こして重合速度の制御ができない。

EP-A-234,512には、スチレンとブタジエンのブロック共重合体を製造する方法が開示されている。その実施例34には、ジブチルマグネシウム及びブチルリチウムからなる重合開始剤を $[Mg] / [Li] = 2.5$ なる金属濃度比で使って、65℃でスチレンを重合し、次いでブタジエンをブロックさせている例が開示されている。しかし、重合溶媒であるシクロヘキサンに対する単量体濃度が20%と低く、暴走反応はしないがリビングポリマーの活性が低下し、そのため後段のブタジエンのブロック重合において未反応のポリスチレンが残り、しかも得られる分子量 M_n も8,900と低い。

10 本発明者は、 R_2Mg と $R'M'$ 及び／又は $R'OM'$ からなる重合開始剤が、特定の金属モル濃度比 $[Mg] / [M'] \geq 4$ ($[]$ はモル濃度) なる関係を満たすと、高温かつ高単量体濃度の重合条件下でも暴走反応を起こすことなく、しかもリビング重合が進行し、分子量、重合速度及び分子量分布を独立に制御することができることを見出した。

15 従来のアニオン重合法では、1ポットの重合で分子量、重合速度及び分子量分布をそれぞれ独立に制御することができなかったので、本発見は極めて驚くべきことであり、本発明は従来の技術からは到底予測できなかったものである。

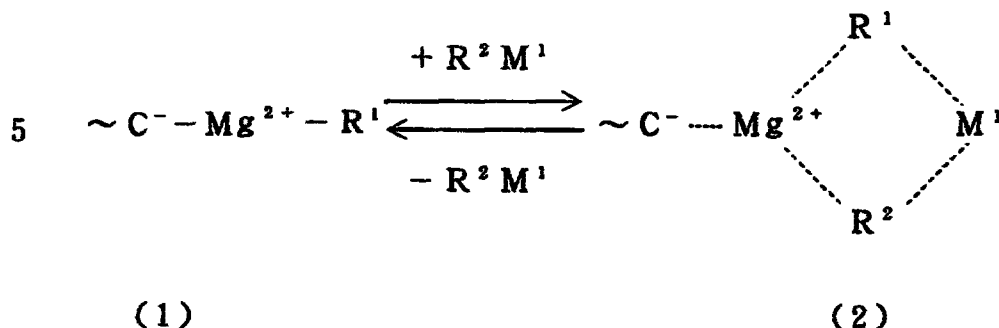
かかる本発明の効果は下記の作用により生じると推定される。

本発明においては、従来の汎用的なブチルリチウムによる重合では高温下において不安定となる炭素アニオンが、安定な結合を形成する金属で下式(1)のようにキャッピングされ、さらに式(1)の構造と相互作用しうる化合物が炭素アニオンと対カチオン金属との結合力を弱めて炭素アニオンを活性化すると考えられる(式(2)参照)。さらに重合温度下において式(1)の構造が休止状態(dormant)、式(2)の構造が活性(active)となり、式(1)と式(2)の構造は平衡状態にある。このような反応機構をとる重合系においては、高温状態になる程平衡を左側に偏らせて(dormant状態を増やして)安定状態を増やせば、リビング重合系を形成しやすいと推定される。また、Mgが重合の成長末端に必ず存在することからポリマーの分子量はMg量に支配され、M'が活性化して重合を進行させることから重合速度は $[Mg] / [M']$ 比に

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支配され、さらに、平衡の偏りと RM^1 の他の dormant 末端への交換速度から分子量分布も $[Mg] / [M^1]$ 比に支配されると推定される。



本発明における重合開始剤の活性化剤（本明細書ではこの活性化剤をも含めて
 10 重合開始剤ということもある）としては、 $R^1 M^1$ 及び／又は $R^1 OM^1$ （ R^1 、 R^2 は炭化水素基、Oは酸素原子、 M^1 は、Li、Na及びKからなる群から選ばれる少なくとも1種類のアルカリ金属）で表される有機金属化合物を用いることが好ましい。具体的には、 $R^1 M^1$ の R^1 は炭化水素基であり、例えば、メチル基、エチル基、プロピル基、イソプロピル基、n-ブチル基、t-ブチル基、
 15 sec-ブチル基、アミル基、ヘキシル基等の $CH_3 (CH_2)_n$ で記述される直鎖状又は分枝状アルキル基が好ましい。具体的な $R^1 M^1$ の例としては、メチルリチウム、n-ブチルリチウム、sec-ブチルリチウム、t-ブチルリチウム、iso-プロピルリチウム、n-プロピルリチウム、iso-プロピルリチウム、ベンジルリチウム、フェニルリチウム、ヘキシルリチウム、ブチルナトリウム、ブ
 20 チルカリウム、クミルカリウム等が挙げられる。これらの化合物は1種類で、又は2種類以上の併用で用いてもよい。

$R^1 OM^1$ の R^1 は炭化水素基であり、例えば、メチル基、エチル基、プロピル基、イソプロピル基、n-ブチル基、t-ブチル基、sec-ブチル基、アミル基、ヘキシル基等の $CH_3 (CH_2)_n$ で記述される直鎖状又は分枝状アルキ
 25 ル基、フェニル基、アルキル置換フェニル基が好ましい。具体的な $R^1 OM^1$ の例としては、メトキシリチウム、メトキシナトリウム、メトキシカリウム、エトキシリチウム、エトキシナトリウム、エトキシカリウム、プロポキシリチウム、プロポキシナトリウム、プロポキシカリウム、イソプロポキシリチウム、イソプロポキシナトリウム、イソプロポキシカリウム、n-ブトキシリチウム、n-ブ

トキシナトリウム、n-ブトキシカリウム、sec-ブトキシリチウム、sec-ブ
 トキシナトリウム、sec-ブトキシカリウム、tert-ブトキシリチウム、tert-
 ブトキシナトリウム、tert-ブトキシカリウム、アミロキシリチウム、アミロキ
 シナトリウム、アミロキシカリウム、tert-アミロキシリチウム、tert-アミロ
 5 キシナトリウム、tert-アミロキシカリウム、ヘキシロキシリチウム、ヘキシロ
 キシナトリウム、ヘキシロキシカリウム、フェノキシリチウム、フェノキシナ
 リウム、フェノキシカリウム、2, 4-ジ-tert-ブチルフェノキシリチウム、
 2, 4-ジ-tert-ブチルフェノキシナトリウム、2, 4-ジ-tert-ブチル
 フェノキシカリウム、2, 6-ジ-tert-ブチルフェノキシリチウム、2, 6-ジ
 10 -tert-ブチルフェノキシナトリウム、2, 6-ジ-tert-ブチルフェノキシカ
 リウム、3, 5-ジ-tert-ブチルフェノキシリチウム、3, 5-ジ-tert-ブ
 チルフェノキシナトリウム、3, 5-ジ-tert-ブチルフェノキシカリウム、2,
 6-ジ-tert-ブチル-4-メチルフェノキシリチウム、2, 6-ジ-tert-ブ
 チル-4-メチルフェノキシナトリウム、2, 6-ジ-tert-ブチル-4-メチ
 15 ルフェノキシカリウム等が挙げられる。これらの化合物は1種類で、又は2種類
 以上の併用で用いてもよい。

$R^1 M^1$ と $R^1 OM^1$ は、それぞれ単独で使用してもよく、又は併用して使用
 してもかまわない。

$R^1 M^1$ 及び/又は $R^1 OM^1$ は、 Mg と M^1 とのモル濃度比が $[Mg] /$
 20 $[M^1] \geq 4$ ($[]$ はモル濃度) なる関係を満たすように使用する。好ましく
 は $[Mg] / [M^1] \geq 4.5$ 、さらに好ましくは $[Mg] / [M^1] \geq 5$ であ
 る。 $[Mg] / [M^1]$ が1より小さいと重合物に生じるリビングポリマーの重
 合成長末端の炭素アニオンと対になっているカチオン金属の一部が M^1 金属単独
 となってしまう、 Mg の存在により反応性を制御することができなくなる。した
 25 がって、本発明の重合温度及び単量体濃度の範囲では暴走反応を起こし、安定な
 リビング重合系を形成しなくなる。 $1 \leq [Mg] / [M^1] < 4$ の領域では、本
 発明における重合濃度と温度領域の下限付近で暴走反応を起こさせずにリビング
 重合が進行するが、重合溶媒をほとんど使用しない極めて高濃度の条件下でしか
 も100℃以上の高温で重合を行った場合は、暴走反応を引き起こしてしまい

ビングポリマーの活性も低下する。また、その場合、分子量分布が単分散に近いポリマーしか得られない。成形樹脂材料には、その成形時の流動性と機械物性とのバランスから、ある程度の割合で低分子量成分と高分子量成分が混在しているポリマー、即ち分子量分布が単分散性より多分散性のポリマーの方が好ましい用途がある。

本発明者は、ある一定の重合時間内に重合を完結する条件下において、 $[Mg] / [M']$ の比率を変えてビニル系単量体を重合すると驚くべきことに、 $[Mg] / [M'] \geq 4$ の領域で分子量分布が急激に広がることを見出した。これは、単量体濃度が高い領域では重合の進行につれて反応系の粘度が上昇し、重合開始剤の活性化剤の交換反応速度が見かけ上低下するためと推定される。

高濃度溶液の反応系の粘度を下げるためには100℃以上の高温下での重合が好ましく、その領域で暴走反応を起こさずにリビング重合を進行させるためには、 $[Mg] / [M'] \geq 10$ であることが好ましい。また、本発明者はその比率をさらに増大させるにつれて分子量分布が連続的に広がることも見出した。しかし、必要以上にこの比率を増大させると分子量分布が広くなりすぎて、低分子量成分、例えばダイマーやトリマーを含むオリゴマー成分の存在量が増大し、好ましくない。従って、 $10 \leq [Mg] / [M'] \leq 100$ の領域が最も好ましい。

本発明者は、 $(R^3)_2Mg$ 及び R^3M' からなる開始剤 ($[Mg] > [M']$) に、本来アニオン重合停止剤となり得る R^3OH 及び/又は $(R^3)_2NH$ (R^3 は炭化水素基、 O は酸素原子、 N は窒素原子) で表される化合物を、ある特定の比率で添加すると、驚くべきことにビニル系単量体の重合が開始し、しかも高温、高濃度の重合条件下でリビング重合が進行することを見出した。

本発明で用いられる R^3OH 及び $(R^3)_2NH$ の R^3 は炭化水素基であり、例えば、メチル基、エチル基、プロピル基、イソプロピル基、*n*-ブチル基、*t*-ブチル基、*sec*-ブチル基、アミル基、ヘキシル基等の CH_3 、 $(CH_2)_n$ で記述される直鎖状又は分枝状アルキル基、フェニル基、アルキル置換フェニル基、 $CH_3(OCH_2CH_2)_n$ で記述される炭化水素系のエーテル化合物基、 $(CH_3)_2N(CH_2CH_2)_n$ が好ましい。具体的な R^3OH の例として

は、メタノール、エタノール、プロパノール、イソプロパノール、*n*-ブチルアルコール、*sec*-ブチルアルコール、*tert*-ブチルアルコール、アミルアルコール、ヘキシルアルコール、フェノール、2, 4-ジ-*tert*-ブチルフェノール、2, 6-ジ-*tert*-ブチルフェノール、3, 5-ジ-*tert*-ブチルフェノール、
 5 2, 6-ジ-*tert*-ブチル-4-メチルフェノール、2-メトキシエタノール、2-(2-メトキシエトキシ)エタノール等が挙げられる。具体的な
 (R^3)₂NHの例としてはN、N-ジメチルエタノールアミン、ジメチルアミン、N-エチルメチルアミン、ジエチルアミン、ジプロピルアミン、ジブチルアミン、ジヘキシルアミン、ジオクチルアミン、ジデシルアミン、N, N, N'-
 10 トリメチルエチレンジアミン、N, N, N', N'-テトラメチルジエチレントリアミン等が挙げられる。これらの化合物は1種類で、又は2種類以上の併用系で用いてもよい。

R^3 OH及び(R^3)₂NHの添加量は、 $2 \times [Mg] + [M^1] >$

$[R^3 OH] + [(R^3)_2 NH]$ となる関係を満たすことが必要である。逆に、
 15 $2 \times [Mg] + [M^1] < [R^3 OH] + [(R^3)_2 NH]$ とすれば重合が開始しない。

本発明者は、さらに(R^2)₂Mg及び $R^1 M^1$ からなる有機金属化合物について鋭意研究を重ねた結果、 R^1 及び R^2 の炭化水素基の金属に結合している炭素の少なくとも1つが2級炭素及び／又は3級炭素であり、しかも2級炭素及び
 20 /又は3級炭素の R^1 及び R^2 の総量 $[R^{1,2}]$ が $[R^{1,2}] \geq [Mg]$ の関係を満たす有機金属化合物をビニル系単量体の重合に用いると、(R^2)₂Mgの重合開始剤効率が高くなり(開始反応点が増加し)、しかも重合速度が遅くなることを見出した。これは、1級炭素の R^1 、 R^2 よりも2級炭素及び3級炭素有する R^1 、 R^2 からの重合の方が開始しやすいため、 $[R^{1,2}] \geq [Mg]$ の
 25 とき、Mgは $[R^{1,2}] - [Mg]$ に相当する量だけ2官能性開始剤となり、開始剤効率が上昇するものと推定される。従って、1級炭素及び2級炭素及び／又は3級炭素有する R^1 、 R^2 が混在していれば、必ずポリマーの開始末端には2級炭素及び／又は3級炭素の R^1 、 R^2 のみが結合していて、分子量も単量体と2級炭素及び／又は3級炭素の R^1 、 R^2 の量比で決まる。また、重合成長末

端は2種類の構造、(A) $\sim$ ポリマー $\sim$ —Mg—R²、と(B) $\sim$ ポリマー $\sim$ —Mg— $\sim$ ポリマー $\sim$ が混在し、(B)の方が重合反応性が低い、すなわち重合速度が遅いと推定される。したがって、(A)と(B)の存在比率により重合速度を制御することが可能となる。

- 5 本発明においては、(R²)₂Mg及びR¹M¹からなる有機金属化合物において、R¹及びR²の炭化水素系化合物の少なくとも1つがポリマー炭素アニオンであってもよい。ポリマー炭素アニオンとは、ビニル系単量体のリビング重合により得られるリビングポリマーアニオンのことを言い、その重合度は1以上であれば特に制限はない。
- 10 本発明においては、(R²)₂Mg化合物を用いると、高温、高単量体濃度下でビニル系単量体の重合が開始し、しかもリビング重合が進行するが、さらにR¹M¹、R¹OM¹を添加する代わりにR³OH及び／又は(R³)₂NH (R²、R³は炭化水素基、Oは酸素原子、Nは窒素原子)で表される化合物を混合することによっても、高温・高濃度下で暴走反応を起こさずにリビング重合
- 15 が進行することを見出した。R³OH及び／又は(R³)₂NHの添加効果は、(R²)₂Mg単独添加の場合の重合速度を増大させることであり、その添加量を増加することによって重合速度は増大する。ただし添加量は、 $2 \times [\text{Mg}] > [\text{R}^3 \text{OH}] + [(\text{R}^3)_2 \text{NH}]$ なる関係を満たす領域に限られる。逆に、 $2 \times [\text{Mg}] + [\text{M}^1] \leq [\text{R}^3 \text{OH}] + [(\text{R}^3)_2 \text{NH}]$ とすれば重合が
- 20 進行しない。

本発明の開始剤によるビニル系単量体の重合は、高単量体濃度領域で進行することから重合系の粘度はかなり高くなることが予想され、そのため重合反応の均一性を考えて重合反応器は押出機であることが好ましい。押出機とは、スクリュウ及び／又はニーディングディスクのついた単軸又は2軸の押出機をいう。

- 25 本発明の開始剤による押出機内の重合法は、溶媒量が極めて少ない領域でもリビング重合が起こるため、重合終了後の溶媒回収プロセスが不要となり、押出機途中の脱気工程だけで溶媒を除去できるという極めて経済的なプロセスとなり得る。

本発明において、重合の停止方法としては特に制限はなく、一般的なアニオン

重合法の停止方法を用いればよい。例えば、水、アルコール、カルボン酸等のプロトン酸化合物や二酸化炭素などを重合溶液に添加することで重合を停止する。

ラジカル重合で得られるスチレン系重合体中には、少量の単量体が存在することが知られており、スチレン系重合体の成形品が親油性化合物雰囲気下にあると、

- 5 その単量体がブリードアウトして問題となる場合がある。

単量体は、主として重合時の未反応単量体としてポリマー中に残留する場合と、成形加工時のポリマー、オリゴマーの分解により生成して成形品中に混在する場合とが考えられる。重合時の未反応単量体は、高真空下で脱気処理すれば、かなり低減させることは可能であるが、成形時に熱的及び剪断的負荷を受けた場合、

- 10 ポリマー及びオリゴマーがさらに分解して単量体を生成させる。特に、ダイマーやトリマー等のオリゴマーからの熱分解による単量体の生成量が多く、しかもこのオリゴマーは脱気処理でポリマー中から除去することが困難である。

一般的にポリマーの熱滞留によって生成するオリゴマーのうち、トリマーの方がダイマーより多いことが知られており (J. POLYMER SCI. :

- 15 Symposium No. 57, 81-88 (1976))、実際ラジカル重合によるスチレン系重合体中のトリマー量もダイマー量に比べて約10倍程多く存在している。したがって、ポリマー中に存在するトリマーの生成量を抑制し、さらに成形加工時に生成する単量体量が極めて少ないスチレン系樹脂を提供することが最重要課題である。

- 20 本発明者は、かかる課題に対し鋭意研究を重ねた結果、特定のアニオン重合法を用いると重合時に生成するトリマーの量が少なく、さらにその製法によって得られるポリマーの熱滞留下における単量体の生成量が極めて少ないことを見出し本発明を完成させた。すなわち、本発明の製造方法によって得られるスチレン系重合体は、熱滞留下における単量体の生成量が少ない。

- 25 また、本発明の製造方法で得られたスチレン系重合体は、重合開始剤由来の金属残渣がポリマー中に少量残存していても、熱滞留下で単量体の生成量が大きくならない。従来のアニオン重合では開始剤由来の金属残渣がポリマー中に残り、それが成形加工時の熱分解を加速することが知られており、水等で金属残渣を抽出除去することが一般的であるが、完全に金属残渣を取り除くことはできず、実

質的にポリマー中に金属を少量残存してしまう。本発明のスチレン系重合体では少量のMgとM' 金属が残存していても、特にトリマーの生成が促進されることもないので、特に少量の開始剤で重合可能な高分子量体の製造や連鎖移動剤による重合については、金属残渣の抽出工程を特に必要としない非常に経済的な工業

5 プロセスを採用することができる。

本発明の製造方法で得られるスチレン系樹脂の分子量は、 $10^3 \sim 10^7$ であり、このとき使用されるMgの量は、約3～2,400ppmではあるが、Mgが100ppm以下の含有量となる分子量領域で特に好ましい効果が発現される。

本発明のスチレン系重合体に残存し得るMgとM' は、重合開始剤として用い
10 たMgとM' 化合物が失活して生成するMg及びM' 化合物のことをいう。そのモル比は、好ましくは $[Mg] / [M'] = 4 \sim 10$ 、より好ましくは $[Mg] / [M'] = 5 \sim 90$ 、更に好ましくは $[Mg] / [M'] = 6 \sim 80$ である。

本発明者は、さらに研究を重ねた結果、スチレン系重合体の熱分解性、成形加工性、特に発泡特性のすぐれたスチレン系樹脂組成物を見出した。その組成物と
15 は、アニオン重合で得られるスチレン系樹脂の組成物であって、その分子量分布 Mw/Mn が $2.0 \sim 10.0$ であり、かつスチレン系由来のトリマーの含有量が250ppm以下のスチレン系樹脂組成物である。

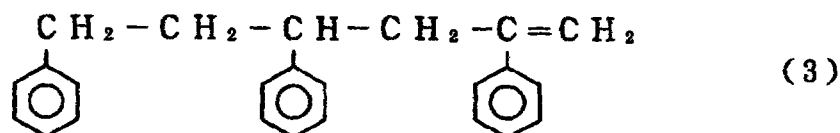
成形機や押出機中での熱的負荷によるポリスチレンからのスチレンの生成を阻止する方法が、JP-A-7-292188に開示されている。しかし、ポリマ
20 ーとしてラジカル重合で得られたポリスチレンを使用しているため、熱的負荷によるスチレンの生成抑制効果は十分でない。また、アニオン重合により得られたポリスチレンを使用すればスチレンの生成抑制効果は若干改善されるが、トリマー存在量及び発泡特性の効果は開示されていない。

本発明者は、発泡特性が特定の分子量分布領域にあると向上し、さらに熱的に
25 極めて安定で分解による単量体の生成量の少ないスチレン系樹脂組成物を見出して本発明を完成させた。

本発明でいうスチレン系樹脂とは、アニオン重合によって得られるスチレン系重合体のことをいい、しかもその重合体の分子量分布 Mw/Mn (重量平均分子量/数平均分子量) は、 $2.0 \sim 10.0$ 、好ましくは $2.1 \sim 9.5$ 、さらに

好ましくは2.2～9.0である。Mw/Mnが2.0より小さいと発泡特性が悪くなり、また、10.0を超えると低分子量成分が増えるため、射出発泡成形や押し出し発泡等の2次加工時においてポリマーの分解によるスチレン系単量体の生成量が多くなる。

- 5 本発明で言うトリマーとは、下式(3)で表される構造を有するものをいう。スチレン系重合体中に存在するトリマーの量は、250ppm以下、好ましくは230ppm以下、更に好ましくは200ppm以下である。250ppmより多いと熱滞留下で生成するスチレン系単量体量が多くなり、成形品が例えば食品包装材として使用された場合、脂肪含有の食料品等へのマイグレーション量が無視できなくなる。



- 15 本発明のスチレン系樹脂組成物は、熱分解によるスチレン系単量体の生成が少なく、かつ発泡特性の良いスチレン系樹脂組成物であり、射出成形用材料及び押し出し成形用材料として極めて好適な材料である。

本発明のスチレン系樹脂組成物には、発明を超えない範囲で滑剤、離型剤、可塑剤、着色剤、難燃剤、発泡剤等を含有させてもかまわない。

- 20 次に本発明を実施例及び比較例により詳細に説明するが、本発明はそれら実施例により制限されるものではない。

本発明に用いた単量体及び溶媒は次の方法で精製して使用した。また、使用した有機金属化合物、アルコール、2級アミン、及びその他の試薬は、以下の通りである。

- 25 (1) スチレン(SM)：旭化成工業(株)社製。CaH₂下でスチレンを1回減圧蒸留し、脱気処理後乾燥窒素下に封入した。

(2) エチルベンゼン(EB)、シクロヘキサン：和光純薬工業社製、特級試薬をCaH₂下で1回減圧蒸留し、脱気処理後モレキュラーシーブスを入れ乾燥窒素下に封入した。

- (3) *n*-ブチルリチウム (*n*BuLi) : 関東化学社製 1. 6 Mの*n*-ヘキサン溶液
- (4) *sec*-ブチルリチウム (*s*BuLi) : 関東化学社製 1. 0 Mのシクロヘキサン溶液
- 5 (5) *tert*-ブチルリチウム (*t*BuLi) : 関東化学社製 1. 6 Mの*n*-ヘプタン溶液
- (6) ジブチルマグネシウム (*Bu*₂Mg) : Aldrich社製 1. 0 Mのヘプタン溶液、*n*-ジブチルマグネシウムと*sec*-ジブチルマグネシウムの1 : 1混合溶液
- 10 (7) *n*-ブチルアルコール (*n*BuOH)、*sec*-ブチルアルコール (*s*BuOH)、*tert*-ブチルアルコール (*t*BuOH)、ジ-*n*-ブチルアミン (*Bu*₂NH) : 関東化学社製、特級試薬、CaH₂ 下で蒸留精製後脱気処理後、モレキュラーシーブスを入れ乾燥窒素下に封入した。
- (8) *tert*-ブトキシナトリウム (*t*BuONa)、*tert*-ブトキシカリウム (*t*BuOK) : Aldrich社製
- 15 (9) 重合停止剤 : テトラヒドロフラン (THF) とメタノール (MeOH) を90 / 10 (vol比) で混合したものを使用した。
- 重合終了して得られたポリマーの重合率、分子量、分子量分布は次の方法で測定した。
- 20 (10) 重合率の測定 : 未反応のSMをガスクロマトグラフィー (GC) により条件1で測定し、次式により重合率 (転換率) を求めた。
- $$\text{重合率 (\%)} = ([\text{仕込みSM濃度}] - [\text{未反応SM濃度}]) / [\text{仕込みSM濃度}] \times 100$$
- (11) 数平均分子量 (*M_n*)、重量平均分子量 (*M_w*) 及び*M_w*/*M_n*の測定
- 25 は、ゲルパーミエーションクロマトグラフィー (GPC) を用いて測定した。
- (12) トリマーの測定条件 : 条件2で求めた。
- [GCの測定条件]
- (条件1)
- 測定器 : 島津製作所 GC14B

カラム：PEG 20M (ϕ 3 mm $\times$ 3 m)

キャリアーガス：窒素、流量 50 ml/min

検出器：FID

カラム温度：125℃で10分保持し、その後35℃/minで230℃まで昇

5 温インジェクション及びディテクター温度：230℃

内部標準試薬：EB

(条件2)

測定器：島津製作所 GC14B

カラム：TC-1 (内径0.25 mm、厚み0.25 μ m、長さ30 m：GLサ

10 イエンス社製)

キャリアーガス：窒素、流量 50 ml/min

検出器：FID

カラム温度：50℃で5分保持、20℃/minで320℃まで昇温

インジェクション温度：260℃

15 ディテクター温度：330℃

内部標準試薬：アントラセン

[GPCの測定条件]

測定器：東ソー HLC-8020 (示差屈折率検出器内蔵)

カラム：東ソー TSK gel-GMH_{XL}を2本使用

20 温度：38℃

溶媒：テトラヒドロフラン (THF)

サンプル濃度：0.1 wt/v%

サンプリングピッチ：1/0.4 (回/秒)

分子量計算：東ソー TSK 標準ポリスチレンの分子量と溶出時間の関係を3次回

25 帰曲線として検量線を作成し、算出した。

以下の実施例及び比較例の記載において特に断りのない限りすべての重合操作法は次の手順で行った。

[重合操作法] 140℃に加熱乾燥したガラス容器及び注射器と単量体、溶媒、試薬を窒素グローブ内に入れた。窒素グローブは、(有)栄興商会社製のVDB

—S A—Q型を使用した。窒素グローブ内は、モレキュラーシーブスで脱水乾燥した窒素で充分置換された環境下にある。50 mlの耐圧ガラス瓶に単量体、溶媒を注射器で所定量入れ、さらに所定量の重合開始剤を添加した。重合開始剤の濃度が高い場合は、あらかじめエチルベンゼンで希釈後単量体溶液に添加した。

- 5 重合溶液はすべて10 mlとした。仕込み終了後、耐圧瓶にニトリルゴムで栓をし、その後窒素グローブから取り出して金属の王冠で打栓した。耐圧瓶を所定温度のオイルバス中に入れ、入れた時間を0時間とした。適宜耐圧瓶を振って反応溶液を攪拌した。所定の時間が経過したら耐圧瓶をオイルバスから取り出し、直ちに水中に入れ室温まで冷却した。冷却後空気が入らないよう停止剤を5 ml打ち込み、素早く耐圧瓶を振って停止剤を均一分散させた。重合溶液をTHFで希釈し、その溶液をGC及びGPCの測定溶液とした。

実施例1～3

- 窒素グローブ内でEB 9 ml、 Bu_2Mg 1 mlを30 mlのビーカーに入れ
15 Bu_2Mg を希釈した。SMとEBの混合溶液を表1に記載の濃度になるよう耐圧瓶に仕込み、その後希釈した開始剤溶液を所定量の濃度になるよう添加し、重合溶液をよく振り混ぜた。全く同一の重合溶液を3本作り、表1に示す重合時間に到達したら停止剤を添加し重合を止めた。各ポリマーの分析結果を表1に示す。

- 一般にリビング重合系であれば、ポリマーの分子量 M_n は重合率(Con v.)に比例して直線的に増加する。本発明の重合系における実施例1～3の M_n 対
20 Con v. のグラフを図1に示す。実施例に示した重合系は、いずれも直線的に M_n がCon v. に比例して増加し、リビング重合系であることを示した。また、図2に示すように実施例1～3の重合速度は、暴走反応を引き起こすことなく、適度な速度で進行した。

比較例1

- 25 Bu_2Mg の代わりに $n\text{BuLi}$ 溶液を、添加量が2.56 mMとなるように用い、開始剤を入れた耐圧瓶を液体窒素内に入れ重合が開始しないようにし、窒素グローブから取り出した後、120℃のオイルバスに入れた以外は実施例1と同様の操作を行った。数分で重合溶液が突沸し重合が完結した(暴走反応した)。

比較例 2

表 2 記載の重合濃度で重合を行った以外は実施例 1 と同様の操作を行った。重合は暴走反応を行わずに進行したが、図 1 の結果から、Conv. の増加に伴い、Mn の増加傾向は直線性からはずれリビング重合活性が低下した。

5 比較例 3

Bu₂Mg の開始剤溶液を添加せずに 150℃ で重合を行った以外は実施例 1 と同様の操作を行った。

図 1 に示した Mn 対 Conv. のプロットから分かるように、この重合系（従来の熱ラジカル重合系である）は重合の進行に関係なく分子量は一定であった。

- 10 しかも、Mw/Mn が 2.2 の広い分子量分布を有するポリマーしか得られなかった。

実施例 1～3 の重合条件は 120～150℃ で 6 時間の重合であり、本来熱ラジカル重合が起こる条件である。しかし、GPC の分析結果から比較例 3 に示されているような分子量のピークは全く観測されなかった。すなわち、熱ラジカル

- 15 重合は実施例 1～3 では起こっておらず、アニオン重合のみ起こっていると判断される。

実施例 4～8

窒素グローブ内で予め Bu₂Mg と nBuLi の希釈溶液を表 3 に示した混合比率になるようそれぞれ作った。SM と EB を混ぜた溶液に希釈開始剤溶液を表
20 3 の濃度になるように入れ、よくかき混ぜた。その溶液を各 10 ml ずつ耐圧瓶に分け、表 3 に示した温度及び時間で重合に付した。

図 3 に示すように、高温、高単量体濃度の条件にも関わらず、暴走反応なしに重合が進行した。

- 25 図 4 に示した Mn 対 Conv. から重合の進行とともに分子量が増加し、リビング重合が進行したことが分かる。Conv. の増加とともに分子量分布が増加しているが、これはリビング性が低下して広がったのではなく、重合系の粘度の上昇及び成長速度と重合活性点 (Mg) 及び重合活性化剤 (Li) の交換反応速度の比率の上昇などで分子量分布が広がっていったものと考えられる。図 5 に実施例 8-1 と 8-2 の分子量分布を示す。重合の進行に伴い分子量分布は全

体的にシフトしていて失活したポリマーが存在しないことが分かる。

比較例 4

$\text{Bu}_2\text{Mg}/\text{nBuLi} = 4$ で、SMのEBに対する濃度の低い領域で重合を行った。重合は暴走反応せずに進行したが、重合の進行とともに分子量分布が広
5 くなった。GPC測定結果から、重合の進行とともに低分子両側に大きくテーリングした分子量分布が得られ、重合中に活性点が徐々に失活した（リビング重合活性の低下）と考えられる。

比較例 5

表 7 に示した条件で重合を行った。重合は極めて遅く進行した。

10 実施例 9 ～ 12

重合溶媒をシクロヘキサンにして、 Bu_2Mg と nBuLi の開始剤で表 4 に示す方法で同様に重合を行った。Conv. が 70 % 以下の領域で 80 °C で 4 時間重合を行い、その後 120 °C に上げて 30 分後に重合を停止した重合はすでに終了していた。ただし、実施例 12 だけは重合時間 4 時間で重合が完結していた。
15 得られたポリマーの Mn と $[\text{SM}] / [\text{Mg}]$ 比の関係を図 6 に示す。

比較例 6 ～ 8

重合溶媒をシクロヘキサンにして、 Bu_2Mg と nBuLi の開始剤で表 7 に示す方法で同様に重合を行った。Conv. が 70 % 以下の領域で 50 °C で重合を行い、その後 80 °C に上げて重合を完結させた。ただし、比較例 8 は重合初期
20 に若干内部温度がオイルバスの温度より高めになって重合が進行した。得られたポリマーの Mn と $[\text{SM}] / [\text{Mg}]$ 比の関係を図 6 に示す。

図 6 の結果から、 $[\text{Mg}] \geq [\text{Li}]$ の領域ではポリマーの Mn は、 $[\text{SM}] / [\text{Mg}]$ 比で決まることが明らかである。

図 7 に Mn と $[\text{Mg}] / [\text{Li}]$ 比の関係を示す。 $[\text{Mg}] \geq [\text{Li}]$ の領域
25 ではポリマーの Mn は、 $[\text{Mg}] / [\text{Li}]$ 比に関係せずに一定値を示すが、 $[\text{Mg}] < [\text{Li}]$ の領域では逆に分子量が低下する。

$[\text{Mg}] \geq [\text{Li}]$ の領域で得られたポリマーの ^1H 及び ^{13}C の NMR を測定した結果、ポリマーの末端に結合しているブチル基が sec - ブチル基であり、その数が重合停止末端のベンジルプロトン量と同量であること及び sec - ブチル基

の量から計算した M_n の値がGPCで求めた M_n とほぼ一致することを確認した。このことから重合活性点の炭素アニオンと対になっている金属カチオンはMgであることが確認できた。

実施例13～14及び比較例9～10

- 5 重合溶媒をEBにして、 Bu_2Mg と $nBuLi$ の開始剤で表4及び表7に示す条件で重合を行った。いずれも240分で重合が完結する条件で重合を行った。

図8に240分の重合で得られたポリマー（ただし、Conv. が95%以上のポリマー）の分子量分布と $[Mg]/[Li]$ 比の関係を示す。 $[Mg]/[Li]$ 比 ≤ 2 では分子量分布が狭いが、 $[Mg]/[Li] \geq 4$ から大きく分

- 10 子量分布が増大した。

実施例15及び17

- EB中で Bu_2Mg と $nBuOH$ 又は $sBuOH$ をそのモル比が1:1になるように混ぜた。その溶液に表5に示す $[Mg]/[Li]$ 比となるように $nBuLi$ を添加し、これを重合開始剤として用いて重合を行った。重合溶媒はEBである。

実施例16、18及び19

- EB中で $nBuLi$ と $nBuOH$ 又は $sBuOH$ 又は $tBuOH$ をそのモル比が1:1になるように混ぜた。その溶液に表5に示す $[Mg]/[Li]$ 比となるように $nBuLi$ を添加し、これを重合開始剤として用いて重合を行った。重合溶媒はEBである。

実施例20

- EB中で $nBuLi$ と $nBuOH$ をそのモル比が1:1になるように混ぜた。さらに別の容器にEB中、 Bu_2Mg と $nBuOH$ をそのモル比が1:1になるように混ぜた。それぞれの溶液を表6に示す $[Mg]/[Li]$ 比となるように混ぜて、これを重合開始剤として用いて重合を行った。重合溶媒はEBである。

実施例21

EB中で Bu_2Mg と Bu_2NH をそのモル比が1:1になるように混ぜた。その溶液に表6に示す $[Mg]/[Li]$ 比となるように $nBuLi$ を添加し、これを重合開始剤として用いて重合を行った。重合溶媒はEBである。

実施例 22 及び 23

EB中に $t\text{BuONa}$ 又は $t\text{BuOK}$ 粉末を入れ、さらにそこへ Bu_2Mg を表 6 に示す $[\text{Mg}] / [\text{M}^1]$ 比となるように混ぜた。これを重合開始剤として用いて重合を行った。重合溶媒は EB である。

- 5 実施例 15 ~ 23 の重合結果を表 6 に示す。いずれも $\text{Bu}_2\text{Mg} / \text{BuLi}$ の開始剤と同様に、暴走反応を起こすことなくリビング重合が進行した。

また、それぞれの開始剤で $\{ [\text{R}^3\text{OH}] + [(\text{R}^3)_2\text{NH}] \} / \{ 2x[\text{Mg}] + [\text{M}^1] \}$ 比が 5 倍になるように入れた混合物を調製したが、いずれも重合は開始しなかった。

10 実施例 24 及び 25

窒素グローブ内で予め Bu_2Mg と $s\text{BuLi}$ 又は $t\text{BuLi}$ の希釈溶液を表 8 に示した混合比率になるようにそれぞれ作った。重合溶媒は EB である。表 8 の条件で重合を行った。

- 15 実施例 4 と同一の条件で重合を行ったが、重合速度は遅くなり、しかも得られる分子量は若干低くなった。 $s\text{BuLi}$ と $t\text{BuLi}$ は全く同一の重合挙動を示した。図 9 と図 10 にそれぞれの重合結果を示す。

実施例 26

- EBに $n\text{BuLi}$ を入れ、更に SM を $[\text{SM}] / [\text{Li}] = 2$ なる比率で添加した。しばらくすると褐色に変化した。その後、 Bu_2Mg を $[\text{Mg}] / [\text{Li}]$ 20 $= 4$ になるよう添加して開始剤溶液を作った。表 8 に示す条件で重合を行った。重合結果は $\text{Bu}_2\text{Mg} / n\text{BuLi}$ で開始したものと全く同一であった。

実施例 27

- EB中で Bu_2Mg と $s\text{BuOH}$ をそのモル比が 1 : 1 になるように混ぜた。これを重合開始剤に用いて表 8 に示す条件で重合を行った。暴走反応することなく 25 Bu_2Mg と $s\text{BuOH}$ をそのモル比が 1 : 1 になるように混ぜた。これを重合開始剤に用いて表 8 に示す条件で重合を行った。暴走反応することなくリビング重合が進行した。

実施例 28

EB中で Bu_2Mg と $(\text{Bu})_2\text{NH}$ を、そのモル比が 1 : 1 になるように混ぜた。これを重合開始剤に用いて表 8 に示す条件で重合を行った。暴走反応することなくリビング重合が進行した。

また、実施例27と実施例2.8の開始剤溶液の調製の際、 $[\text{sBuOH}] / [\text{Bu}_2\text{Mg}] = 10$ 、 $[(\text{Bu})_2\text{NH}] / [\text{Bu}_2\text{Mg}] = 10$ になるように入れた混合物も同時に調製し、重合を試みたが、いずれも重合は開始しなかった。

- 5 本発明の実施例1～28の重合では、いずれも高温で重合反応しているにもかかわらず、全くラジカル重合由来の分子量ピークは観測されなかった。

実施例29

本発明の重合開始剤 $\text{Bu}_2\text{Mg}/\text{nBuLi}$ (10/1)を用いてSMの高温、バルク重合を押出機内で行った。押出機はWerner社製、ZSK25 (L/

- 10 D=47)を使用した。

押出機は、11ブロックから成っており、それぞれの温度を次のように設定した。ブロック1 (室温)、ブロック2 (120℃)、ブロック3、4 (140℃)、ブロック5及び6 (160℃)、ブロック7及び8 (200℃)、ブロック9～11 (220℃)。ブロック8と9の間に液体添加装置があり、そこから

- 15 重合停止剤 (BuOHとEBの混合液) を圧入した。精製脱水したSM、EBとEBで希釈した $\text{Bu}_2\text{Mg}/\text{nBuLi}$ (10/1)の開始剤をそれぞれ密閉窒素雰囲気下の容器に貯蔵した。各容器からはギアポンプで3Lの攪拌翼の付いたタンクにフィードでき、さらにそこからギアポンプで押出機のゾーン1にフィードできる構造となっている。押出機内を乾燥窒素で充分置換しておき、そこへE
20 Bと開始剤の混合溶液をまずフィードして押出機内を洗浄した。その後徐々にSM濃度を上げていき、最終的にはSM濃度を100にした。SMのフィード量は100ml/minとした。開始剤の量は $[\text{SM}] / [\text{Mg}] = 1,000$ なる比率になるようにフィードした。ダイスから出てきたポリマーは、直ちに水中下で冷却し、ペレットとして得た。得られたポリマーの分子量及び分子量分布は、
25 $M_n = 91000$ 、 $M_w/M_n = 3.5$ であった。

実施例30、比較例11及び比較例12

表9に示す条件でポリマーを得た。ポリマーをEBに約20%濃度になるように溶解し、蒸留水で金属残渣の一部を抽出した。それぞれの金属含有量を表9に示す。洗浄後のポリマー溶液にメタノールを入れてポリマーを析出させた後、8

- 0℃で真空乾燥した。得られたポリマーをガラス管に0.2g入れ、真空下で封管した。ガラス管を280℃のオイルバスに入れ10分、20分、40分で取り出した。取り出したガラス管は水中に入れ冷却した。ガラス管を粉碎し、それをTHFに入れ溶解させた。アントラセンを一定量入れ内部標準としてガスクロで
- 5 単量体の生成速度を求めた。

結果を表10に示す。

実施例31

- 実施例29で得られたポリマーを、フレオン12を使って押出發泡実験を行った。得られた発泡体の連続気泡率をASTM-2856に準拠して求めた。また、
- 10 得られた発泡体に含有している単量体も測定した。結果を表11、12に示す。

比較例13

- 100Lのオートクレーブ内で、nBuLi開始剤を用い、EBを溶媒にしてSM濃度50vol%で重合を行った。重合温度は、145℃まで上昇した。得られたポリマー溶液をドラムドライヤーで溶媒を除去した。ポリマーをさらにシリ
- 15 ダー温度220℃の押出機内に入れ、残りのEBをベントから除去した。ポリマーはペレット状で回収した。結果を表11、12に示す。

比較例14

- ラジカル重合で得られたポリマーを実施例31と同様に押出發泡させ、得られた発泡体の連続気泡率と単量体含有量を調べた。結果を表11、12に示す。
- 20 本願は1996年3月14日に日本で出願された日本国特許出願第8-084474号、1996年10月30日に日本で出願された日本国特許出願第8-303483号及び1996年10月30日に日本で出願された日本国特許出願第8-303484号に基づいており、それらの内容は全て本明細書中に参照することにより導入されている。

表 1

	[SM] (vol%)	[Bu ₂ Mg] (mM)	重合温度* (°C)	重合時間 (min)	Conv. (%)	Mn (x10 ⁻³)	Mw (x10 ⁻³)	Mw/Mn
実施例1-1	50	5.16	150	60	19	12	19	1.62
実施例1-2	50	5.16	150	120	27	18	30	1.65
実施例1-3	50	5.16	150	240	42	25	42	1.68
実施例2-1	80	2.58	150	60	22	42	63	1.51
実施例2-2	80	2.58	150	120	36	83	134	1.62
実施例2-3	80	2.58	150	240	58	125	210	1.68
実施例3-1	80	2.58	120	120	10	20	27	1.40
実施例3-2	80	2.58	120	240	20	38	56	1.48
実施例3-3	80	2.58	120	480	33	61	92	1.50

* 溶媒は、EBを使用。

表 2

	[SM] (vol%)	[Bu ₂ Mg] (mM)	重合温度* (°C)	重合時間 (min)	Conv. (%)	Mn (x10 ⁻³)	Mw (x10 ⁻³)	Mw/Mn
比較例1	50	* 1	120	* 2	100	183	198	1.08
比較例2-1	20	2.06	150	60	15	10	17	1.71
比較例2-2	20	2.06	150	120	23	14	25	1.82
比較例2-3	20	2.06	150	240	38	18	38	2.10
比較例3-1	50	0	150	120	29	92	212	2.30
比較例3-2	50	0	150	240	43	92	207	2.25

* 溶媒はEBを使用。

* 1 : Bu₂Mgの代わりにBuLiを2.56mM添加した。

* 2 : 重合系は暴走反応し、1分以内に重合は完結した。

表 3

	[SM] (vol%)	[Bu ₂ Mg] (mM)	$\frac{[\text{Bu}_2\text{Mg}]}{[\text{BuLi}]}$	重合温度 (℃)	重合時間 (min)	Conv. (%)	Mn ($\times 10^{-3}$)	Mw ($\times 10^{-3}$)	Mw/Mn
実施例4-1	80	6.9	4	80	60	60	70	82	1.17
実施例4-2	80	6.9	4	80	120	82	82	101	1.23
実施例4-3	80	6.9	4	80	240	96	91	114	1.25
実施例5-1	90	7.8	6	90	60	59	62	73	1.18
実施例5-2	90	7.8	6	90	120	80	77	95	1.24
実施例5-3	90	7.8	6	90	240	95	90	126	1.40
実施例6-1	90	7.8	10	100	60	38	35	43	1.23
実施例6-2	90	7.8	10	100	120	60	55	74	1.35
実施例6-3	90	7.8	10	100	240	85	79	130	1.65
実施例7-1	100	8.6	20	110	60	36	31	43	1.40
実施例7-2	100	8.6	20	110	120	60	51	77	1.51
実施例7-3	100	8.6	20	110	240	83	57	98	1.72
実施例8-1	100	8.6	30	120	60	33	25	44	1.76
実施例8-2	100	8.6	30	120	120	61	48	85	1.78
実施例8-3	100	8.6	30	120	240	80	55	104	1.90

表 4

	[SM] (vol%)	[Bu ₂ Mg] (mM)	$\frac{[Bu_2Mg]}{[BuLi]}$	重合温度* (°C)	重合時間 (min)	Conv. (%)	Mn ($\times 10^{-3}$)	Mw ($\times 10^{-3}$)	Mw/Mn
実施例9-1	80	69	6	80	240	72	7.5	8.8	1.18
実施例9-2	80	69	6	80→120	240+30	100	11	13	1.17
実施例10-1	80	35	6	80	240	65	14	16	1.17
実施例10-2	80	35	6	80→120	240+30	100	21	24	1.17
実施例11-1	80	23	6	80	240	60	17	20	1.17
実施例11-2	80	23	6	80→120	240+30	100	29	34	1.16
実施例12	80	35	4	80	240	100	20	23	1.17
実施例13	100	6.9	10	100	240	100	88	150	1.70
実施例14	100	6.9	20	120	240	100	70	127	1.81

* 溶媒はシクロヘキサン

表 5

	開始剤	開始剤 比率	[SM] (vol%)	[Mg] (mM)	$\frac{[Mg]}{[Li]}$	重合温度 (°C)	重合時間 (min)	Conv. (%)	Mn ($\times 10^{-3}$)	Mw ($\times 10^{-3}$)	Mw/Mn
実施例15-1	nBuLi/Bu ₂ Mg/nBuOH	1/6/6	90	7.8	6	90	60	53	49	58	1.19
実施例15-2	nBuLi/Bu ₂ Mg/nBuOH	1/6/6	90	7.8	6	90	120	78	74	90	1.22
実施例15-3	nBuLi/Bu ₂ Mg/nBuOH	1/6/6	90	7.8	6	90	240	93	89	117	1.32
実施例16-1	nBuLi/Bu ₂ Mg/nBuOH	1/6/1	90	7.8	6	90	60	44	42	48	1.15
実施例16-2	nBuLi/Bu ₂ Mg/nBuOH	1/6/1	90	7.8	6	90	120	71	68	82	1.20
実施例16-3	nBuLi/Bu ₂ Mg/nBuOH	1/6/1	90	7.8	6	90	240	90	85	107	1.26
実施例17-1	nBuLi/Bu ₂ Mg/sBuOH	1/10/10	90	7.8	10	100	60	68	63	88	1.40
実施例17-2	nBuLi/Bu ₂ Mg/sBuOH	1/10/10	90	7.8	10	100	120	90	80	131	1.64
実施例17-3	nBuLi/Bu ₂ Mg/sBuOH	1/10/10	90	7.8	10	100	240	10	90	154	1.71
実施例18-1	nBuLi/Bu ₂ Mg/sBuOH	1/6/1	90	7.8	6	100	60	63	56	76	1.36
実施例18-2	nBuLi/Bu ₂ Mg/sBuOH	1/6/1	90	7.8	6	100	120	85	79	130	1.64
実施例18-3	nBuLi/Bu ₂ Mg/sBuOH	1/6/1	90	7.8	6	100	240	99	90	153	1.70
実施例19-1	nBuLi/Bu ₂ Mg/tBuOH	1/6/1	90	7.8	6	100	60	90	81	133	1.64
実施例19-2	nBuLi/Bu ₂ Mg/tBuOH	1/6/1	90	7.8	6	100	120	10	90	153	1.70

表 6

	開始劑	開始劑 比率	[SM] (vol%)	[Mg] (mM)	[Mg] [Li]	重合溫度 (°C)	重合時間 (min)	Conv. (%)	Mn ($\times 10^{-3}$)	Mw ($\times 10^{-3}$)	Mw/Mn
実施例20-1	nBuLi/Bu ₂ Mg/nBuOH	1/10/11	90	7.8	10	100	60	37	34	42	1.23
実施例20-2	nBuLi/Bu ₂ Mg/nBuOH	1/10/11	90	7.8	10	100	120	59	54	73	1.36
実施例20-3	nBuLi/Bu ₂ Mg/nBuOH	1/10/11	90	7.8	10	100	240	84	79	131	1.66
実施例21-1	nBuLi/Bu ₂ Mg/Bu ₂ NH	1/10/10	90	7.8	10	100	60	70	65	92	1.42
実施例21-2	nBuLi/Bu ₂ Mg/Bu ₂ NH	1/10/10	90	7.8	10	100	120	91	81	134	1.66
實施例21-3	nBuLi/Bu ₂ Mg/Bu ₂ NH	1/10/10	90	7.8	10	100	240	100	90	156	1.73
實施例22-1	tBuONa/Bu ₂ Mg	1/6	90	7.8	6	80	60	60	59	67	1.14
實施例22-2	tBuONa/Bu ₂ Mg	1/6	90	7.8	6	80	120	82	79	95	1.20
實施例22-3	tBuONa/Bu ₂ Mg	1/6	90	7.8	6	80	240	98	95	121	1.27
實施例23-1	tBuOK/Bu ₂ Mg	1/10	90	7.8	10	80	60	62	60	82	1.36
實施例23-2	tBuOK/Bu ₂ Mg	1/10	90	7.8	10	80	120	83	80	132	1.65
實施例23-3	tBuOK/Bu ₂ Mg	1/10	90	7.8	10	80	240	99	91	156	1.71

表 7

	[SM] (vol%)	[Bu ₂ Mg] (mM)	$\frac{[Bu_2Mg]}{[BuLi]}$	重合温度 (°C)	重合時間 (min)	Conv. (%)	Mn ($\times 10^{-3}$)	Mw ($\times 10^{-3}$)	Mw/Mn
比較例4-1	10	0.9	4	80	60	19	18	22	1.21
比較例4-2	10	0.9	4	80	120	38	33	43	1.30
比較例4-3	10	0.9	4	80	240	62	45	70	1.55
比較例5-1	50	4.3	6	25	120	1	ND	ND	ND
比較例5-2	50	4.3	6	25	240	3	ND	ND	ND
比較例5-3	50	4.3	6	25	480	6	0.7	0.8	1.17
比較例6-1	50	22	2	50	240	71	16	17	1.09
比較例6-2	50	22	2	50→80	240→60	100	20	22	1.10
比較例7-1	50	22	1	50	240	62	13	14	1.07
比較例7-2	50	22	1	50→80	240→60	100	20	22	1.08
比較例 8	30	13	0.5	30	60	100	14	16	1.14
比較例 9	80	6.9	2	80	240	95	105	114	1.09
比較例10	80	6.9	1	25	240	100	110	118	1.07

表 8

	開始剤	[SM] (vol%)	[Mg] (mM)	$\frac{[Mg]}{[Li]}$	重合温度 ($^{\circ}C$)	重合時間 (min)	Conv. (%)	Mn ($\times 10^{-3}$)	Mw ($\times 10^{-3}$)	Mw/Mn
実施例24-1	Bu ₂ Mg/sBuLi	80	6.9	4	80	60	40	32	36	1.13
実施例24-2	Bu ₂ Mg/sBuLi	80	6.9	4	80	120	63	47	55	1.16
実施例24-3	Bu ₂ Mg/sBuLi	80	6.9	4	80	240	89	68	84	1.24
実施例25-1	Bu ₂ Mg/tBuLi	80	6.9	4	80	60	40	32	36	1.13
実施例25-2	Bu ₂ Mg/tBuLi	80	6.9	4	80	120	63	47	55	1.16
実施例25-3	Bu ₂ Mg/tBuLi	80	6.9	4	80	240	89	68	84	1.24
実施例26-1	Bu ₂ Mg/StLi	80	6.9	4	80	60	60	70	82	1.17
実施例26-2	Bu ₂ Mg/StLi	80	6.9	4	80	120	82	82	101	1.23
実施例26-3	Bu ₂ Mg/StLi	80	6.9	4	80	240	96	91	114	1.25
実施例27-1	Bu ₂ Mg/sBuOH(1/1)	100	8.6	--	150	60	50	47	66	1.40
実施例27-2	Bu ₂ Mg/sBuOH(1/1)	100	8.6	--	150	120	76	74	104	1.41
実施例27-3	Bu ₂ Mg/sBuOH(1/1)	100	8.6	--	150	240	90	85	120	1.41
実施例28-1	Bu ₂ Mg/Bu ₂ NH(1/1)	100	8.6	--	150	60	40	37	55	1.50
実施例28-2	Bu ₂ Mg/Bu ₂ NH(1/1)	100	8.6	--	150	120	58	55	82	1.50
実施例28-3	Bu ₂ Mg/Bu ₂ NH(1/1)	100	8.6	--	150	240	83	39	59	1.51

表 9

	開始剤	[SM] (vol%)	[Mg] (mM)	[Mg] (Li)	給電 (℃)	給電 (min)	Conv (%)	Mn ($\times 10^{-3}$)	Mw ($\times 10^{-3}$)	Mw/Mn
実施例30	Bu ₂ Mg/nBuLi(6/1)	100	8.6	6	80→120	120→30	100	95	103	1.09
比較例11	nBuLi	50	4.3	0	80	～1	100	94	127	1.35
比較例12	無	100	—	—	120	240	21	250	437	1.75

*実施例30は、80℃で120分重合した後120分で30分重合した。実施例30と比較例11の重合溶媒はEBである。

*比較例11は、暴走反応して最終的には内温が150～160℃に上昇した。

*比較例12は、ラジカル重合。未反応モノマーはポリマーをメタノール中に再沈精製して除去した。

	ポリマー洗浄後の金属量		
	Mg	Li	Mg/Li
実施例30	25	4	6.3
比較例11	----	30	----

表 10

	熱滞留試験後のポリマー中SM濃度*		
	滞留時間(分)		
	10	20	40
実施例30	38	95	200
比較例11	90	190	410
比較例12	140	265	530

*単位はppm

表 11

	ポリマー特性			ポリマー中 含有量(ppm)	
	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n	SM	トリマー
実施例31	91	319	3.5	10	52
比較例13	254	305	1.2	16	75
比較例14	96	328	3.4	450	1810

表 12

	発泡体中 存在する SM量	発泡体の特性		
		発泡倍率	発泡径 (mm)	連続気泡率
実施例31	21	16	22	94
比較例13	28	12	21	38
比較例14	558	15	22	93

請求の範囲

1. 重合成長末端の炭素アニオンと対になっているカチオンの金属がMgであるか、又はMg及びM' (M' は、Li、Na及びKからなる群から選ばれる少なくとも1種類のアルカリ金属であり、MgとM' の金属モル濃度が $[Mg] / [M'] \geq 4$ なる関係を満たす) であるアニオン重合を、重合温度45℃以上250℃以下、ビニル系単量体の重合溶媒に対する濃度が45wt%～100wt%の条件下で行うことからなるビニル系重合体の製造方法。
2. 重合開始剤として $(R^2)_2Mg$ (R^2 は炭化水素基) を単独で用いる請求項1記載のビニル系重合体の製造方法。
3. 重合開始剤として、 $(R^2)_2Mg$ 及び R^1M' 及び/又は R^1OM' (R^1 、 R^2 は炭化水素基、Oは酸素原子、M' は、Li、Na及びKからなる群から選ばれる少なくとも1種類のアルカリ金属) で表される有機金属化合物であって、MgとM' の金属モル濃度が $[Mg] / [M'] \geq 4$ なる関係を満たす有機金属化合物を用いる請求項1記載のビニル系重合体の製造方法。
4. 前記金属モル濃度が $[Mg] / [M'] = 10 \sim 100$ なる関係を満たす請求項1又は3記載のビニル系重合体の製造方法。
5. 重合開始剤として、 $(R^2)_2Mg$ 及び R^1M' 及び R^3OH 及び/又は $(R^3)_2NH$ (R^1 、 R^2 、 R^3 は炭化水素基、Oは酸素原子、Nは窒素原子、M' は、Li、Na及びKからなる群から選ばれる少なくとも1種類のアルカリ金属) で表される化合物を、 $[Mg] > [M']$ 及び $2x[Mg] + [M'] > [R^3OH] + [(R^3)_2NH]$ なる関係を満たすように混合して用いる請求項1記載のビニル系重合体の製造方法。
6. ビニル系単量体の重合率(転換率)が0～70%の領域において重合温度が45℃以上200℃以下である請求項1に記載のビニル系重合体の製造方法。
7. $(R^2)_2Mg$ 及び R^1M' の有機金属化合物において、 R^1 及び R^2 の炭化水素基の金属に結合している炭素の少なくとも1つが2級炭素及び/又は3級炭素であり、しかも2級炭素及び/又は3級炭素の R^1 及び R^2 の総量 $[R^{1,2}]$ が $[R^{1,2}] \geq [Mg]$ である請求項3～5のいずれか1項に記載の





ビニル系重合体の製造方法。

8. $(R^2)_2Mg$ 及び R^1M^1 の有機金属化合物において、 R^1 及び R^2 の炭化水素基の少なくとも1つがポリマー炭素アニオンである請求項7記載のビニル系重合体の製造方法。

5 9. 重合開始剤として、 $(R^2)_2Mg$ 及び R^3OH 及び／又は $(R^3)_2NH$ (R^2 、 R^3 は炭化水素基、Oは酸素原子、Nは窒素原子) で表される化合物を $2x[Mg] > [R^3OH] + [(R^3)_2NH]$ なる関係を満たすように混合して用いる請求項1に記載のビニル系重合体の製造方法。

10 10. 重合溶媒が炭化水素系化合物である請求項1記載のビニル系重合体の製造方法。

11. 実質的にビニル系単量体の重合溶媒に対する濃度が100wt%である請求項1記載のビニル系重合体の製造方法。

12. 重合反応を押出機中で行う請求項1記載のビニル系重合体の製造方法。

13. $(R^2)_2Mg$ (R^2 は炭化水素基) を含むビニル系単量体重合開始剤。

15 14. $(R^2)_2Mg$ 及び R^1M^1 及び／又は R^1OM^1 (R^1 、 R^2 は炭化水素基、Oは酸素原子、 M^1 は、Li、Na及びKからなる群から選ばれる少なくとも1種類のアルカリ金属) で表される有機金属化合物を含み、金属モル濃度が $[Mg] / [M^1] \geq 4$ なる関係を満たすビニル系単量体重合開始剤。

20 15. $(R^2)_2Mg$ 及び R^1M^1 及び／又は R^1OM^1 (R^1 、 R^2 は炭化水素基、Oは酸素原子、 M^1 は、Li、Na及びKからなる群から選ばれる少なくとも1種類のアルカリ金属) で表される有機金属化合物を含み、金属モル濃度比が $[Mg] / [M^1] = 10 \sim 100$ なる関係を満たすビニル系単量体重合開始剤。

16. $(R^2)_2Mg$ 及び R^1M^1 及び R^3OH 及び／又は $(R^3)_2NH$

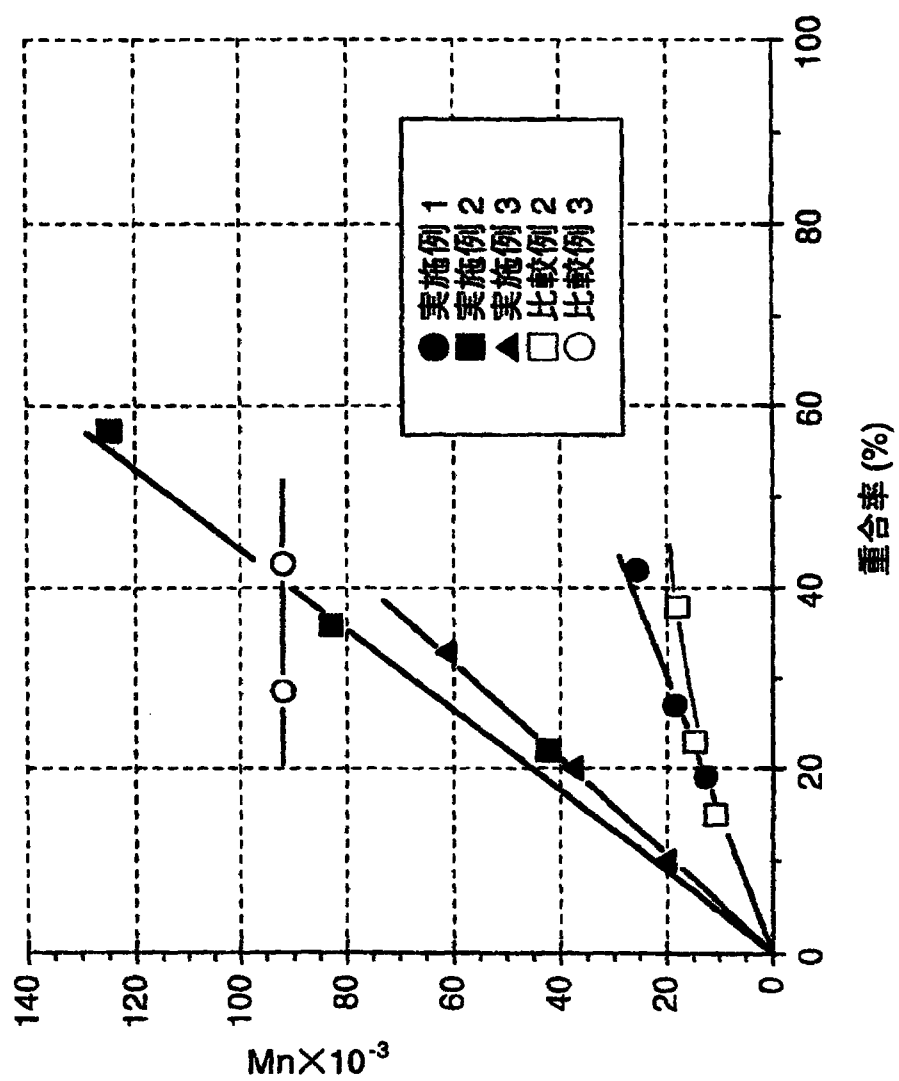
25 (R^1 、 R^2 、 R^3 は炭化水素基、Oは酸素原子、Nは窒素原子、 M^1 は、Li、Na及びKからなる群から選ばれる少なくとも1種類のアルカリ金属) で表される化合物を含み、 $[Mg] > [M^1]$ 及び $2x[Mg] + [M^1] > [R^3OH] + [(R^3)_2NH]$ なる関係を満たすビニル系単量体重合開始剤。



17. $(R^2)_2Mg$ 及び R^3OH 及び／又は $(R^3)_2NH$ (R^2 、 R^3 は炭化水素基、Oは酸素原子、Nは窒素原子) で表される化合物を含み、
 $2 \times [Mg] > [R^3OH] + [(R^3)_2NH]$ なる関係を満たすビニル系単量体重合用開始剤。
- 5 18. 請求項1～12記載の製造方法によって得られ得るビニル系重合体。
19. アニオン重合によって得られるスチレン系重合体であって、その分子量分布 Mw/Mn が2.0～10.0であり、かつスチレン系単量体由来のトリマーの含有量が250ppm以下であるスチレン系樹脂組成物。
20. 請求項18又は請求項19に記載のスチレン系樹脂組成物を射出成形又は
- 10 押出成形して得られる成形体。

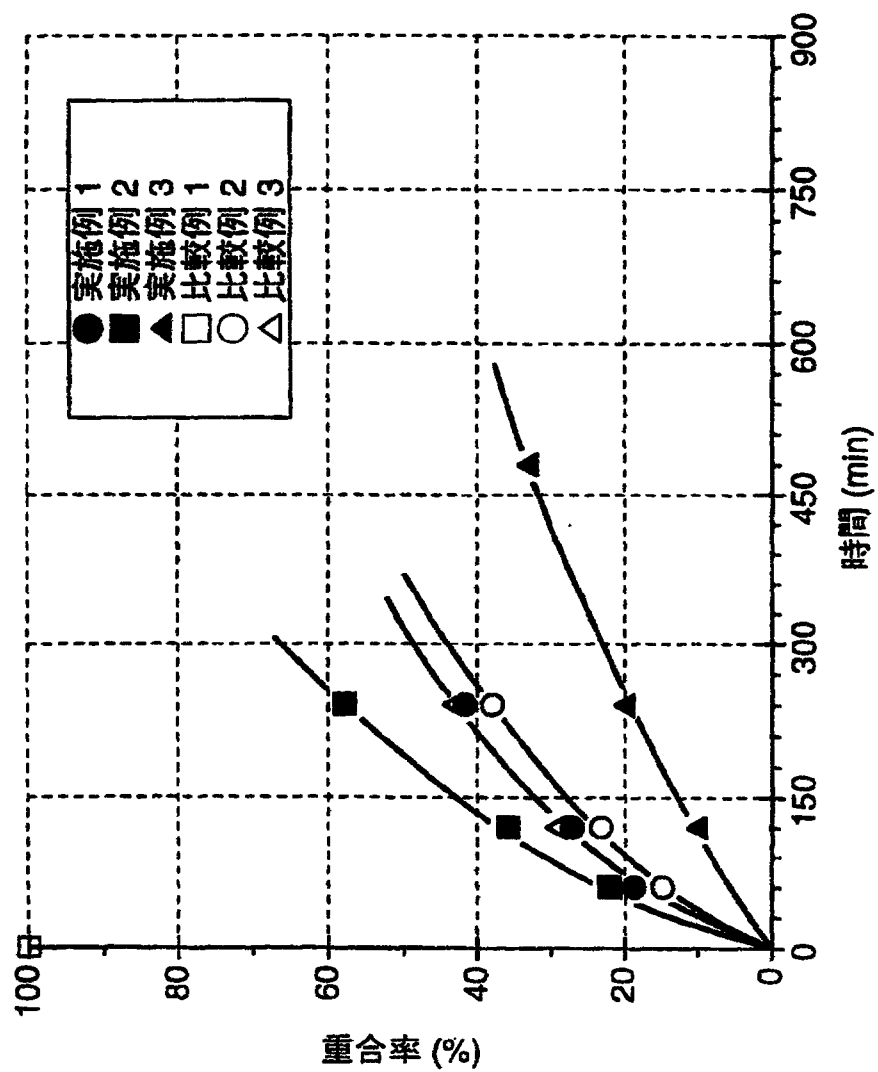
1/10

FIG. 1



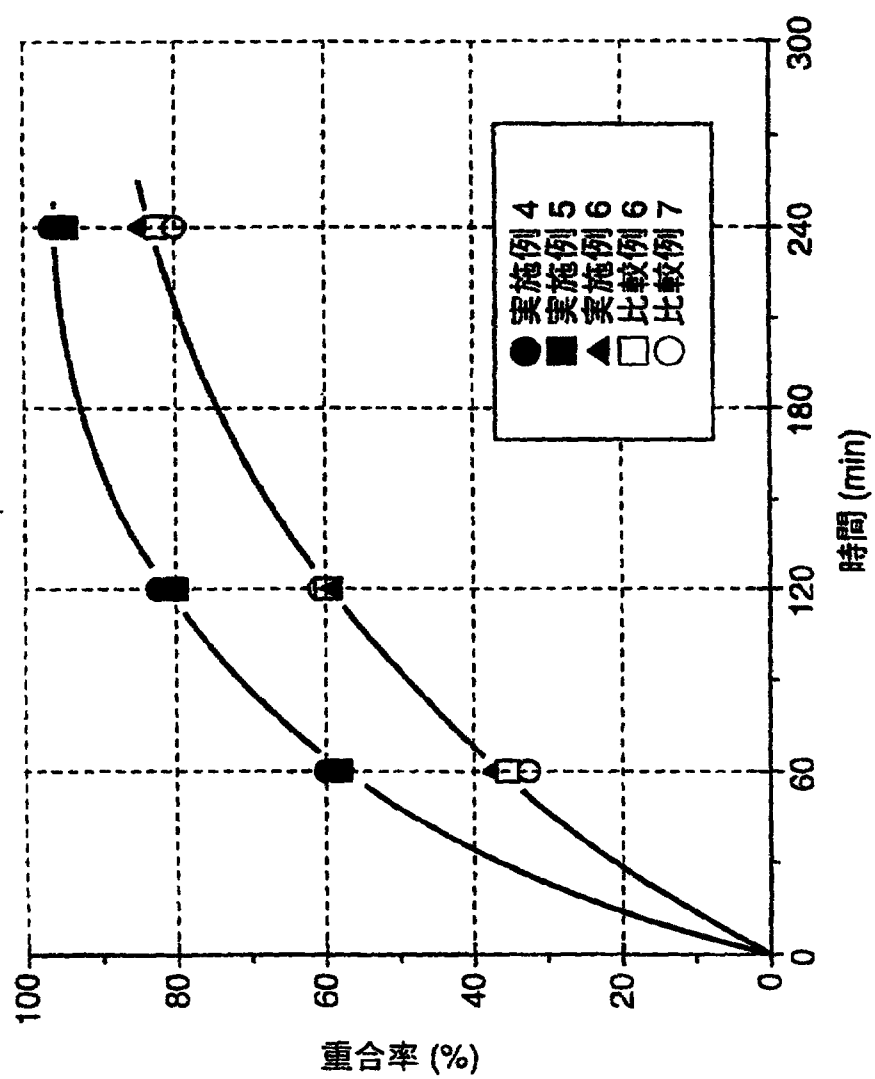
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FIG. 2



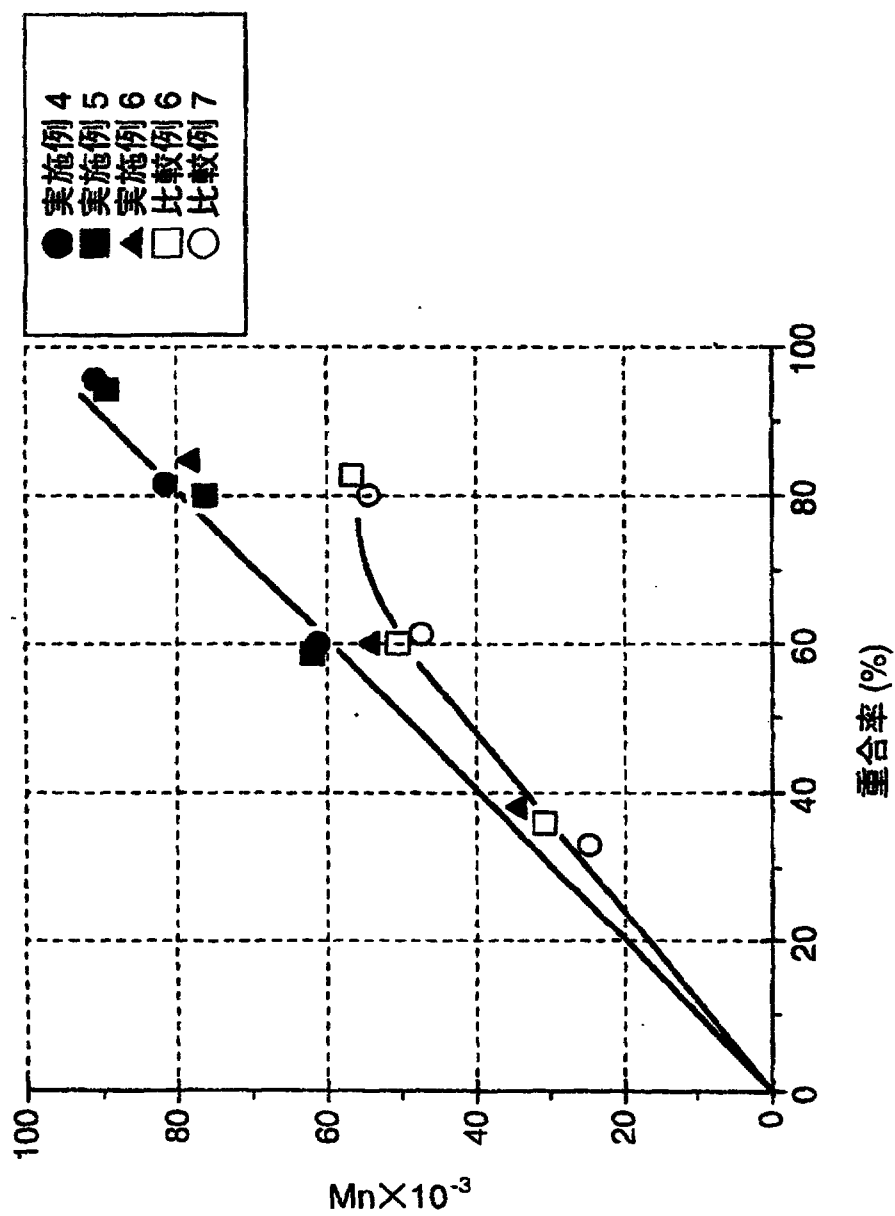
3/10

FIG. 3



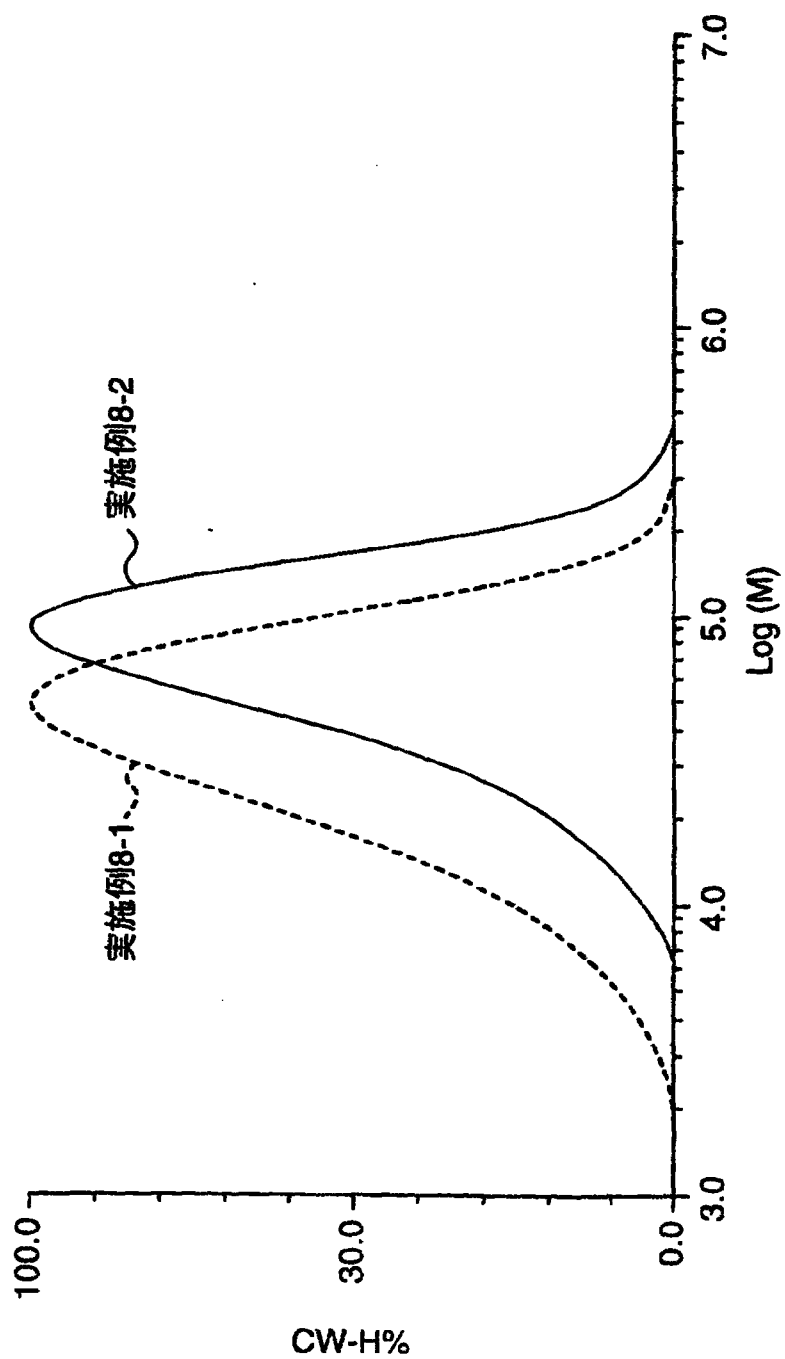
4/10

FIG. 4



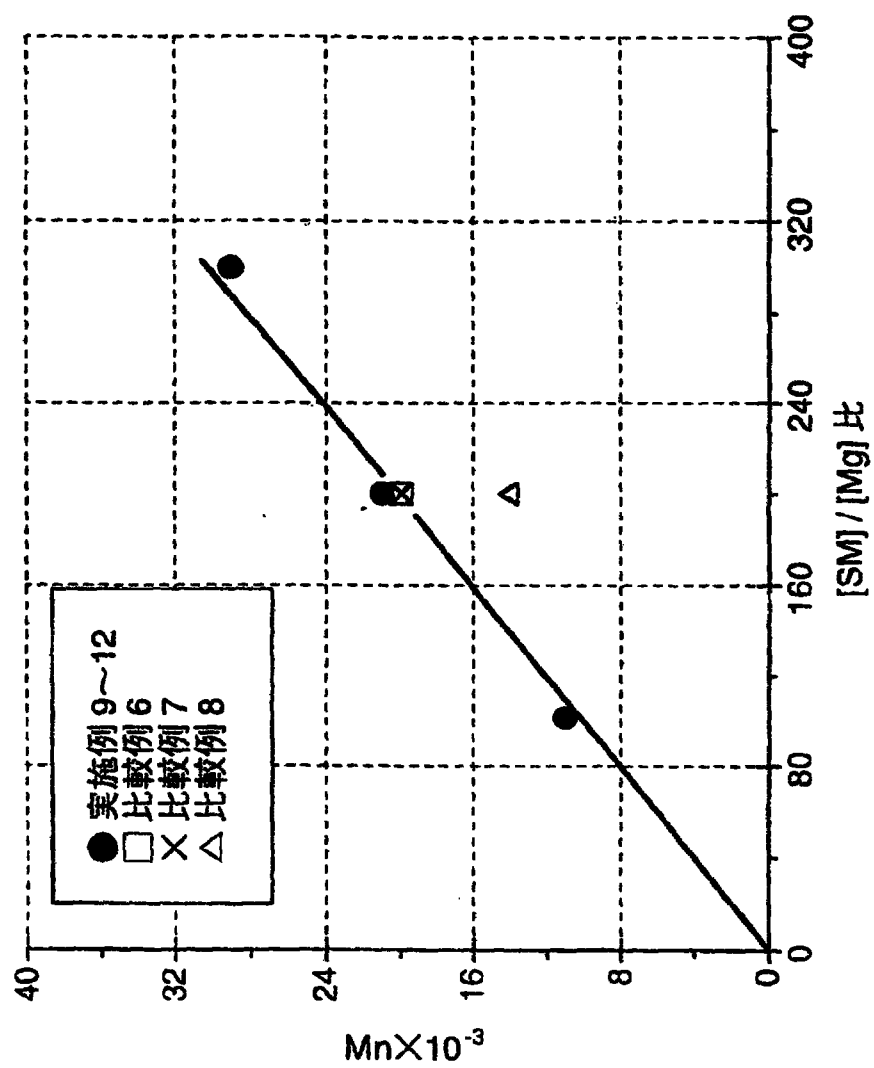
5/10

FIG. 5



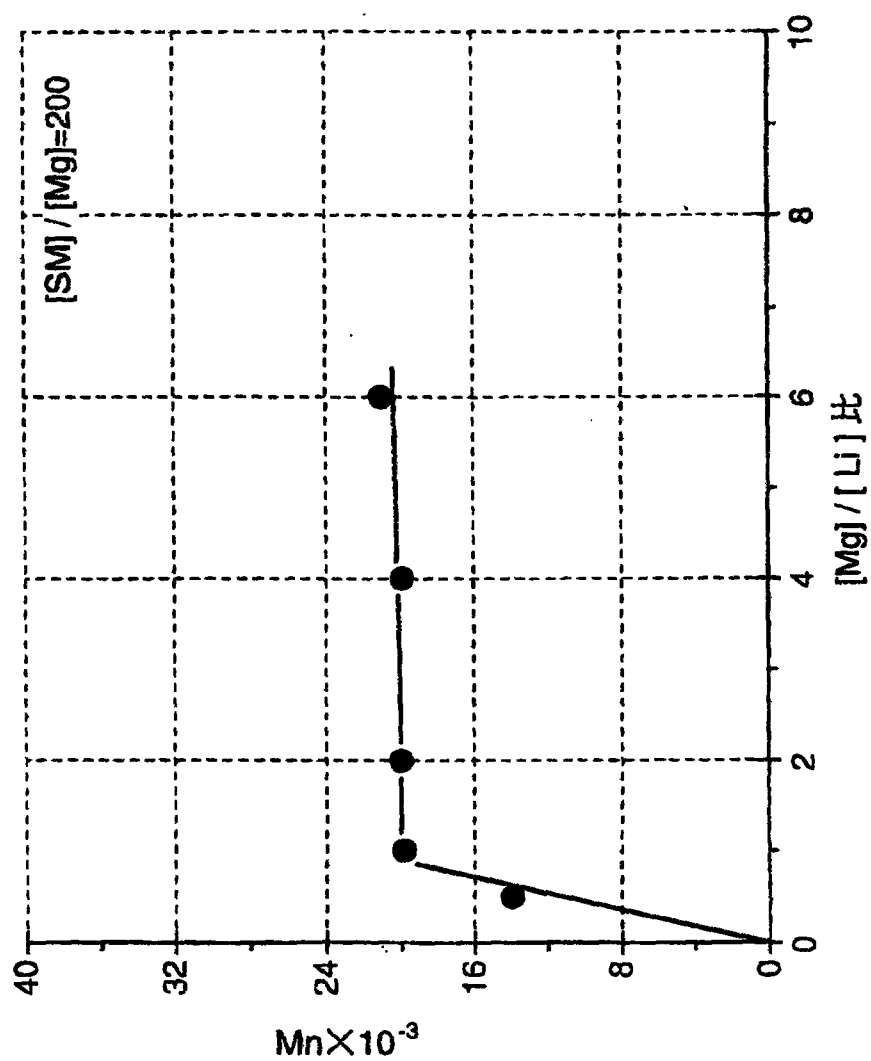
6/10

FIG. 6



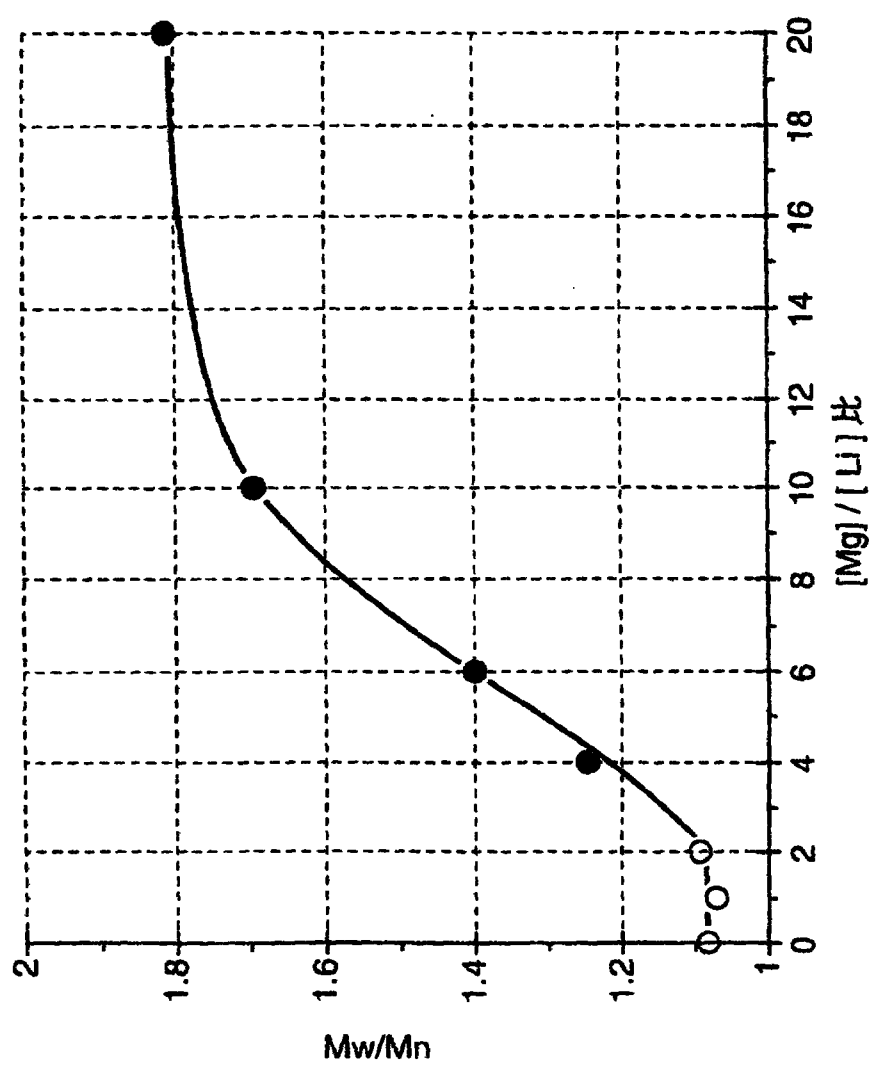
7/10

FIG. 7



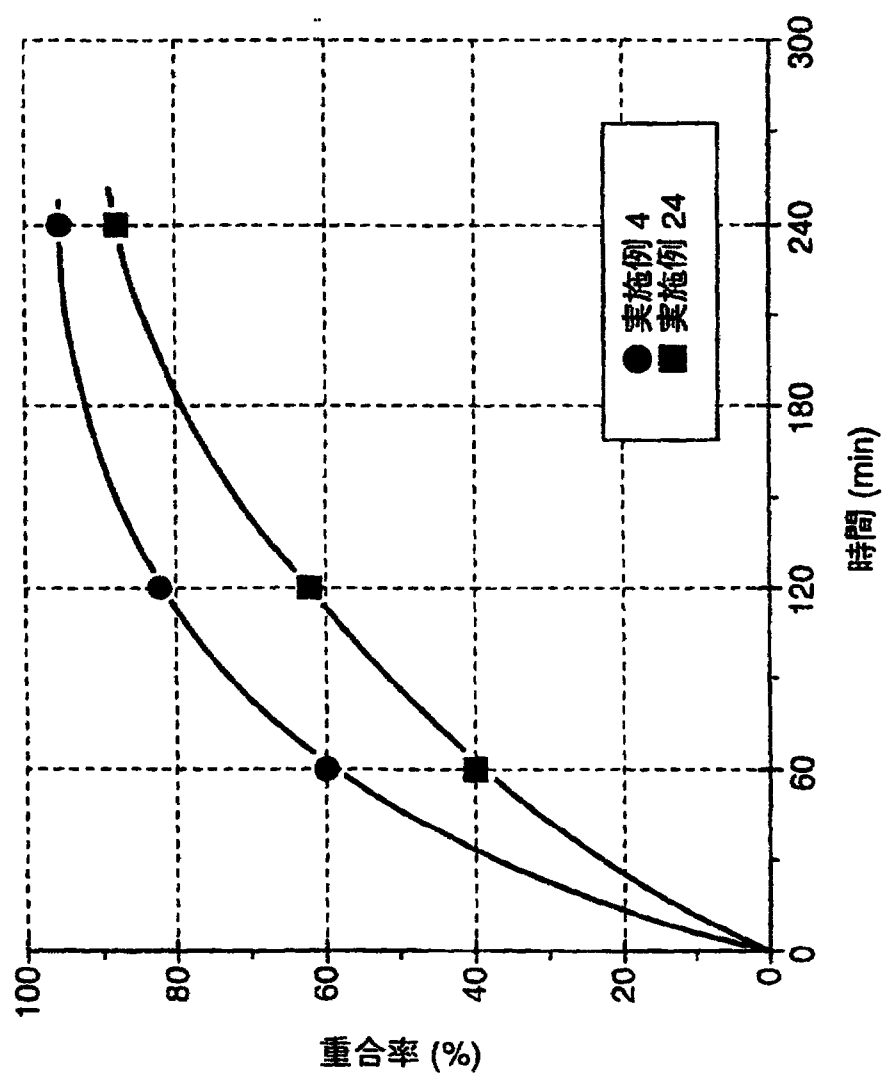
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FIG. 8



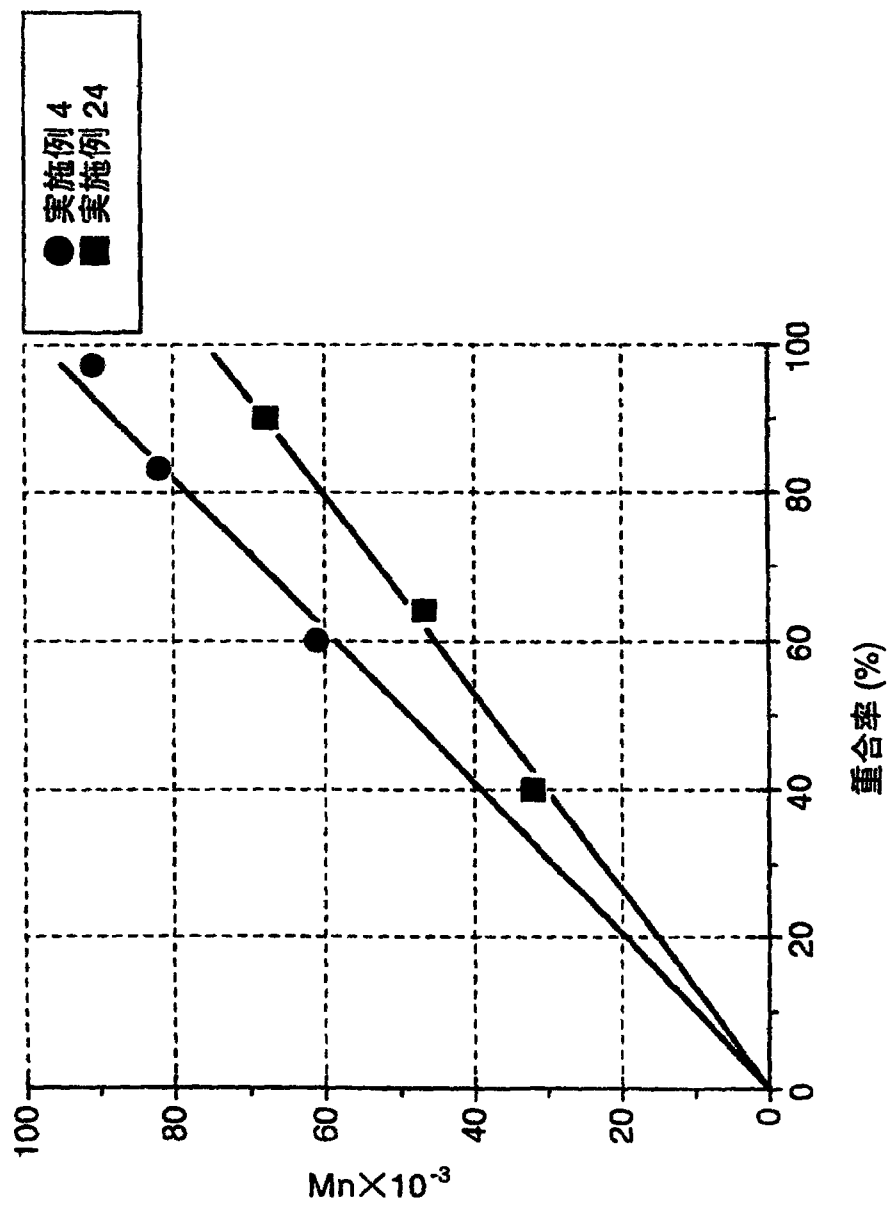
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FIG. 9



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FIG. 10



DESCRIPTION

-1

VINYL POLYMER PREPARATION PROCESS, VINYL MONOMER

5 POLYMERIZATION INITIATOR AND STYRENE RESIN COMPOSITIONS

Technical Field

The present invention relates to a vinyl polymer preparation process, vinyl monomer polymerization initia-
10 tor and styrene resin compositions. According to the process of the present invention, living polymerization can be carried out in a controllable temperature range without causing self-accelerated reaction due to genera-
tion of heat in the polymerization reaction, transfer
15 reaction and termination despite high monomer concentration and high temperature reaction conditions in comparison with the conventional anionic polymerization.

Background Art

20 Styrene polymers, a typical example of which is polystyrene, have been industrially produced for a long time by means of radical polymerization. However, radical polymerization, as is well known, causes reaction termination due to recombinations of growing radicals, etc. or
25 radical transfer reactions to the solvent or monomer, so that it was difficult to achieve structural control of the polymer, such as control of molecular weight distribution or the structures of the polymer chain ends. Also, since

radical polymerization is not living polymerization, it was not possible to produce block polymers or radial polymers.

Living anionic polymerization of monomers such as styrene and butadiene has been proposed as a solution to the above problems. For instance, in anionic polymerization of styrene using butyl lithium which is a general-purpose initiator, there can be obtained a polymer with very narrow molecular weight distribution since, in this case, living polymerization free of transfer reactions and reaction termination can proceed. Also, by taking advantage of reactivity of the propagating species of the living polymer, it is possible to obtain various well-defined polymers which have been unobtainable with the conventional radical polymerization, such as styrene/butadiene block polymers. However, the living anionic polymerization of styrene, despite its potential in producing very attractive resin materials, has not been industrially utilized except for some specific cases. This is attributable, for one thing, to low production yield because living anionic polymerization is a type of solution polymerization and to high production cost as compared with conventional radical polymerization, resulting in little industrial utilization, because of the necessity of a large-scale solvent recovery process. Therefore, there has been no other way but to resort to the conventional solution polymerization techniques for the production of specific polymers such as styrene/

butadiene block polymers.

For reducing the production cost in living anionic polymerization, it is necessary to decrease the amount of the solvent used for the polymerization, to enhance productivity and to minimize the load for solvent recovery. However, reduction of the amount of the solvent invites a sharp rise of viscosity of the polymerization solution, necessitating elevation of the polymerization temperature to a remarkably higher level than required in conventional solution polymerization.

When styrene is polymerized by using, for example, butyl lithium under these conditions according to the conventional art, there arise the following problems, which make such polymerization impractical.

① Since the polymerization initiation reaction and propagation reaction take place very rapidly, polymerization reaction heat is generated quickly, often resulting in unsatisfactory release of heat from the polymerization system to cause a steep rise of temperature in the system, which tends to initiate a self-accelerated reaction, the so-called "runaway" reaction (a situation where control of the reaction rate is impossible).

② At a high temperature such as 100°C or more, carbonic anions at the propagating species of the polymer become unstable to cause frequent occurrence of transfer reactions to the solvent or polymer backbone or reaction termination due to the β -elimination, resulting in a remarkable reduction of activity of the living polymer.

In the conventional polymerization using an organic alkali metal such as butyl lithium as initiator, the above problem ① can be solved by controlling the polymerization rate by decreasing the amount of the initiator, but this gives rise to the problem that a polymer having a high molecular weight is only obtained. The number-average molecular weight M_n of a polymer obtained by anionic polymerization using an organic alkali metal depends upon the ratio of the monomer to the alkali metal according to the following equation:

$$M_n = [\text{monomer}] / [\text{organic alkali metal}] \times (\text{molecular weight of monomer})$$

([] : molar concentration)

15

Therefore, when the amount of the initiator is small, the produced polymer is correspondingly high in molecular weight, which means that a large amount of initiator is necessary for obtaining a polymer of low molecular weight. It has thus been difficult with the prior art to freely obtain a polymer of a desired molecular weight because of the operational restrictions required for preventing the runaway reaction.

It is also notable that when a conventional organic alkali metal is used, the initiation reaction proceeds very rapidly as against the propagation reaction, so that in many cases the produced polymer has a very narrow molecular weight distribution. However, the narrow

molecular weight distribution is sometimes detrimental to the balance of moldability and physical properties of the resin material. Therefore, in order to have a broad molecular weight distribution, it has been essential to add an initiator gradually or to carry out polymerization in a continuous reactor having a specific retention time profile. Thus, discovery of a living anionic polymerization system capable of freely controlling the molecular weight distribution without a complicated polymerization reaction has been desired.

Disclosure of the Invention

An object of the present invention is to provide a novel process for producing vinyl polymers with a controlled molecular weight distribution, according to which anionic polymerization of vinyl monomers is carried out under the high monomer concentration and high temperature conditions to allow the polymerization reaction to proceed at a controllable rate without causing a runaway reaction due to self-induced reaction heat, making it possible to conduct living polymerization free of transfer reactions and reaction termination even when conducted at a high temperature, which has never been achievable with the prior art. Another object of the present invention is to provide a styrene resin composition having excellent moldability and minimized in production of styrene monomers due to thermal decomposition.

In the course of studies aimed at these objects, the present inventor found that when anionic polymerization of a vinyl monomer such as styrene or butadiene is carried out using an initiator comprising an organic magnesium compound and a specific alkyl metal compound, quite surprisingly living polymerization proceeds at a reaction rate which enables control of heat release without causing a runaway reaction or extremely slow polymerization rate even under the conditions of high monomer concentration and high temperature. As a result, control of the molecular weight distribution is made possible. It was further found that the thus obtained styrene resin composition is lower in decomposition rate under heat retention and less in monomer formation than the resin compositions obtained by using the conventional anionic polymerization initiators. The present invention has been attained on the basis of these findings.

The present invention relates to a vinyl polymer preparation process which comprises carrying out anionic polymerization under the condition in which the polymerization temperature is not lower than 45°C and not higher than 250°C and the concentration of the vinyl monomer based on the polymerization solvent is 45-100% by weight, in which anionic polymerization the metal of the cation forming a counterpart to the carbonic anion at the polymerization propagating species comprises Mg, or Mg and M^1 (wherein M^1 is at least one alkali metal selected from the group consisting of Li, Na and K, and the molar

concentrations of Mg and M^1 satisfy the relation of
 $[Mg]/[M^1] \geq 4$).

The present invention also relates to the vinyl
 polymer preparation process wherein $(R^2)_2Mg$ (R^2 :
 5 hydrocarbon group) is used singly as the polymerization
 initiator.

The present invention also relates to the vinyl
 polymer preparation process wherein organic compounds
 represented by $(R^2)_2Mg$ and R^1M^1 and/or R^1OM^1 (R^1 and R^2 : a
 10 hydrocarbon group; O: an oxygen atom; M^1 : at least one
 alkali metal selected from the group consisting of Li, Na
 and K) are used as polymerization initiator, and the molar
 concentrations of Mg and M^1 satisfy the relation of
 $[Mg]/[M^1] \geq 4$.

15 The present invention further relates to the
 vinyl polymer preparation process wherein the above molar
 concentrations satisfy the relation of $[Mg]/[M^1] = 10-100$.

The present invention also relates to the vinyl
 polymer preparation process wherein compounds represented
 20 by $(R^2)_2Mg$ and R^1M^1 and R^3OH and/or $(R^3)_2NH$ (R^1, R^2 and R^3 : a
 hydrocarbon group; O: an oxygen atom; N: a nitrogen atom;
 M^1 : at least one alkali metal selected from the group
 consisting of Li, Na and K) are used by mixing them so as
 to satisfy the relations of $[Mg] > [M^1]$ and $2 \times [Mg] +$
 25 $[M^1] > [R^3OH] + [(R^3)_2NH]$.

The present invention also relates to the vinyl
 polymer preparation process wherein the polymerization
 temperature is not lower than 45°C and not higher than

200°C in the region of conversion of the vinyl monomer of 0-70%.

The present invention further relates to the vinyl polymer preparation process wherein in organic metal compounds represented by $(R^2)_2Mg$ and R^1M^1 , at least one of the carbons attached to the metals of the hydrocarbon groups R^1 and R^2 is secondary carbon and/or tertiary carbon, and the total amount $[R^{1,2}]$ of R^1 and R^2 of the secondary carbon and/or tertiary carbon satisfies the relation of $[R^{1,2}] \geq [Mg]$.

The present invention also relates to the vinyl polymer preparation process wherein in organic metal compounds represented by $(R^2)_2Mg$ and R^1M^1 , at least one of the hydrocarbon groups of R^1 and R^2 is a polymer carbonic anion.

The present invention further relates to the vinyl polymer preparation process wherein compounds represented by $(R^2)_2Mg$ and R^3OH and/or $(R^3)_2NH$ (R^2 and R^3 : a hydrocarbon group; O: an oxygen atom; N: a nitrogen atom) are used by mixing them so as to satisfy the relation of $2 \times [Mg] > [R^3OH] + [(R^3)_2NH]$.

The present invention also relates to the vinyl polymer preparation process wherein the polymerization solvent is a hydrocarbon compound; the vinyl polymer preparation process wherein the concentration of the vinyl monomer based on the polymerization solvent is substantially 100% by weight; and the vinyl polymer preparation process wherein the polymerization reaction is

carried out in an extruder.

The present invention further relates to a vinyl monomer polymerization initiator containing $(R^2)_2Mg$ (R^2 : a hydrocarbon group).

5 The present invention also relates to a vinyl monomer polymerization initiator containing organic metal compounds represented by $(R^2)_2Mg$ and R^1M^1 and/or R^1OM^1 (R^1 and R^2 : a hydrocarbon group; O: an oxygen atom; M^1 : at least one alkali metal selected from the group consisting
10 of Li, Na and K), wherein the molar concentrations of the metals satisfies the relation of $[Mg]/[M^1] \geq 4$.

 The present invention also relates to a vinyl monomer polymerization initiator containing organic metal compounds represented by $(R^2)_2Mg$ and R^1M^1 and/or R^1OM^1 (R^1
15 and R^2 : a hydrocarbon group; O: an oxygen atom; M^1 : at least one alkali metal selected from the group consisting of Li, Na and K), wherein the molar concentrations of the metals satisfies the relation of $[Mg]/[M^1] = 10-100$.

 The present invention also relates to a vinyl
20 monomer polymerization initiator containing compounds represented by $(R^2)_2Mg$ and R^1M^1 and R^3OH and/or $(R^3)_2NH$ (R^1 , R^2 and R^3 : a hydrocarbon group; O: an oxygen atom; N: a nitrogen atom; M^1 : at least one alkali metal selected from the group consisting of Li, Na and K), wherein the
25 compounds satisfy the relations of $[Mg] > [M^1]$ and $2 \times [Mg] + [M^1] > [R^3OH] + [(R^3)_2NH]$.

The present invention further relates to a vinyl monomer polymerization initiator containing compounds

represented by $(R^2)_2Mg$ and R^3OH and/or $(R^3)_2NH$ (R^2 and R^3 : a hydrocarbon group; O: an oxygen atom; N: a nitrogen atom), wherein the compounds satisfy the relation of $2 \times [Mg] > [R^3OH] + [(R^3)_2NH]$.

5 The present invention also relates to a vinyl polymer obtainable by the above-described preparation process.

 The present invention further relates to the styrene resin compositions obtainable by anionic
10 polymerization of styrene monomers, wherein their molecular weight distribution M_w/M_n is 2.0-10.0 and the content of trimers derived from the styrene monomers is 250 ppm or less.

 The present invention further relates to a
15 molded product obtainable by injection molding or extrusion molding of the above styrene resin compositions.

Brief Description of the Drawings

 Figs. 1, 4 and 10 are graphs showing the
20 relation between conversion (Conv.) and number-average molecular weight (M_n) of the polymers obtained in the Examples and Comparative Examples.

 Figs. 2, 3 and 9 are graphs showing the relation
between polymerization time (Time) and conversion of the
25 polymers obtained in the Examples and Comparative Examples.

 Fig. 5 shows GPC curves of the polymers obtained in the Examples.

 Fig. 6 is a graph showing the relation between

the number-average molecular weight (M_n) of the polymers obtained in the Examples and Comparative Examples and the concentration ratio of the monomer and Bu_2Mg ($[SM]/[Mg]$), which is the initial polymerization condition.

5 Fig. 7 is a graph showing the relation between the number-average molecular weight (M_n) of the polymers obtained in the Examples and Comparative Examples and the concentration ratio of Bu_2Mg and $BuLi$ ($[Mg]/[Li]$), which is the initial polymerization condition.

10 Fig. 8 is a graph showing the relation between the ratio (M_w/M_n) of weight-average molecular weight (M_w) and number-average molecular weight (M_n) of the polymers obtained in the Examples and Comparative Examples and the concentration ratio of Bu_2Mg and $BuLi$ ($[Mg]/[Li]$), which is
15 the initial polymerization condition.

Best Mode for Carrying Out the Invention

The "vinyl monomers" used in the present invention include styrene monomers and conjugated diene
20 monomers.

The styrene monomers include styrene, α -alkyl-substituted styrene, nuclear alkyl-substituted styrene and the like. More specifically, they include α -methyl-styrene, α -methyl-p-methylstyrene, p-methylstyrene, m-methylstyrene, 25 o-methylstyrene, p-ethylstyrene, 2,4-dimethylstyrene, 2,5-dimethylstyrene, p-isopropyl-styrene, 2,4,6-trimethylstyrene, etc.

The conjugated diene monomers include 1,3-

butadiene, isoprene, 2,3-dimethylbutadiene, 2-ethyl-1,3-butadiene, 1,3-pentadiene, etc.

These vinyl monomers may be used either singly or in combinations of two or more of them for the purpose
5 of obtaining a copolymer.

The polymerization temperature is not lower than 45°C and not higher than 250°C, preferably not lower than 50°C and not higher than 240°C, more preferably not lower than 60°C and not higher than 230°C. The lower limit of
10 the polymerization temperature should be a temperature which is at least capable of maintaining the polymerization rate at which the polymerization can be completed within the prescribed period of time. The polymerization can proceed at a low temperature below 45°C,
15 but in the polymerization solution according to the present invention, the polymerization rate is very slow at such a low temperature, so that use of a temperature below 45°C is disadvantageous from the viewpoint of industrial production of the polymers. When the polymerization
20 temperature is 250°C or higher, side reactions such as transfer reactions and reaction termination may take place frequently, making it difficult to obtain a polymer of a high molecular weight while causing coloration of the produced polymer.

25 In the present invention, the polymerization temperature need not be kept constant throughout the reaction; it may be raised at any desired rate in accordance with the progress of the polymerization

reaction. In view of the fact that the reaction rate is high and the volume of heat generated is large in the initial stage of the polymerization reaction when the monomer concentration is high, it is recommended to
5 initiate the polymer-ization reaction at a low temperature and gradually raise the temperature as the monomer concentration lowers with the progress of the reaction. Polymerization is preferably carried out in the temperature range of 45-200°C when the conversion of the
10 vinyl monomer is in the range of 0-70%, and a polymerization temperature in the range of not lower than 200°C and not higher than 250°C is preferred when the conversion is in the range of 70% or higher. In case the viscosity of the polymerization reaction solution is low
15 and there is no need of raising the polymerization temperature more than necessary, polymerization may be conducted at a temperature of 200°C or lower in the 70-100% conversion region.

The concentration of the vinyl monomer based on
20 the polymerization solvent is not lower than 45% by weight and not higher than 100% by weight, preferably not lower than 50% by weight and not higher than 100% by weight. The higher the monomer concentration, the more desirable for the recovery of solvent, but there are the cases,
25 depending on the type of the polymer produced, where a solvent is required to some extent from the relation between temperature and viscosity of the polymerization solution. However, since an extremely low monomer



concentration is responsible not only for slow polymerization rate but also for occurrence of a transfer reaction under a high temperature condition, it is essential that the monomer concentration be at least 45% by weight in view of living polymerization efficiency.

That the concentration of the vinyl monomer based on the polymerization solvent is substantially 100% by weight means that there exists no solvent to be used other than the one derived from the initiator solution.

10 Polymerization with 100% monomer concentration, where no polymerization solvent is used, is the most ideal form of polymerization for the industrial practice since no transfer reaction of monomer to solvent nor any reaction termination takes place. This assures high use efficiency

15 of the initiator as well as high productivity. Also, a process for solvent recovery after termination of the polymerization is unnecessary.

The "polymerization solvent" referred to in the present invention means a solvent which takes no part in

20 the polymerization reaction and has compatibility with the polymers. Any type of solvent generally employed for living anionic polymerization can be used, but the aromatic or alicyclic hydrocarbon compounds which are suppressive against transfer reaction and reaction

25 termination are preferably used as polymerization solvent. Typical examples of such solvents include ethylbenzene, toluene, isopropylbenzene, benzene, cyclohexane and the like. If necessary, small quantities of other substances,

for example, an ether compound such as tetrahydrofuran, dioxane, trioxane, etc., a tertiary amine such as tetramethylethylenediamine, a nitrogen compound such as pyridine, an aliphatic saturated hydrocarbon compound such as pentane, n-hexane, heptane, octane, nonane, decane, etc., and a weak Lewis acid such as triethylaluminum, diethyl zinc, etc., may be contained in the solvent within limits which do not jeopardize the effect of the present invention.

10 The "organic magnesium compounds represented by $(R^2)_2Mg$ " used in the present invention are the compounds in which a hydrocarbon group is attached to Mg. The hydrocarbon group is preferably a (linear or branched) alkyl group represented by $CH_3(CH_2)_n$ - such as methyl, ethyl, propyl, isopropyl, n-butyl, t-butyl, sec-butyl, amyl and hexyl. Preferred examples of the magnesium compounds include di-n-butylmagnesium, di-t-butylmagnesium, di-sec-butylmagnesium, n-butyl-sec-butylmagnesium, n-butylethylmagnesium and n-amylmagnesium. These compounds may be used either singly or in combination.

 It has been known that no polymerization of a vinyl monomer is initiated when R^2Mg (R: alkyl) is used singly, and that no polymerization is initiated unless a polar compound such as hexamethylformamide (HMPA) is added. 25 The present inventor found, however, that even if an R^2Mg compound is used singly, with no polar compound added, and even in a non-polar hydrocarbon solvent, the polymerization of a vinyl monomer is initiated under a specific



temperature condition, and the manner of the polymerization is living polymerization.

The lower limit of polymerization temperature when using R^2Mg singly as the initiator is $100^{\circ}C$ or higher, preferably $110^{\circ}C$ or higher, more preferably $120^{\circ}C$ or higher. At $100^{\circ}C$ or lower, polymerization proceeds very slowly or is not initiated.

For conducting the polymerization initiating reaction or propagation reaction more efficiently than in polymerization using R^2Mg alone as initiator, it is recommended to add to R^2Mg an organic metal compound(s) represented by R^1M^1 and/or R^1OM^1 (R^1 , R^2 : a hydrocarbon group; O: an oxygen atom; M^1 : at least one alkali metal selected from the group consisting of Li, Na and K).

Some initiators comprising a combination of R^2Mg and R^1M^1 and/or R^1OM^1 have been known, but they were impractical because of the problems such as mentioned below.

Macromolecules, Vol. 19, p. 299 (1986) and US-A-3,716,495 show the examples of styrene polymerization, butadiene polymerization, and styrene and butadiene copolymerization at $50^{\circ}C$ or $70^{\circ}C$ using a polymerization initiator consisting of dibutyl magnesium and butyl lithium, or diamyl magnesium and butyl lithium as in the present invention. In these cases of polymerization, however, the concentration of the monomer based on the polymerization solvent cyclohexane is as low as about 11%, and further the metal concentration ratio is in the region

of $[Mg] < [Li]$. To the knowledge of the present inventor, in the region of $[Mg] < [Li]$, the metal at the polymerization propagating species does not have Mg, and it is impossible to control the polymerization rate, molecular weight of the polymer and molecular weight distribution independently of each other. Also, when the initiators cited in the above references are used, although it is possible to carry out living polymerization without causing a runaway reaction at 50°C or 70°C with a low monomer concentration such as 11%, a runaway reaction does take place with the monomer concentrations and temperature ranges specified in the present invention, thus making it unable to control the polymerization rate.

US-A-4,225,690 discloses a polymerization initiator comprising dibutyl magnesium and amyl potassium or amyl oxypotassium. However, in this polymer initiator, too, the metal concentrations are in the region of $[Mg] < [K]$, the monomer concentration is as low as about 10-25%, the polymerization propagating species does not have Mg, and it is impossible to independently control the polymerization rate, molecular weight of the polymer produced and its molecular weight distribution. Also, a runaway reaction occurs with the concentration and temperature ranges specified in the present invention, making it impossible to control the polymerization rate.

EP-A-234,512 discloses a process for producing styrene/butadiene block copolymers. Example 34 thereof describes a procedure where styrene is polymerized at 65°C

using a polymerization initiator composed of dibutyl magnesium and butyl lithium at a concentration ratio ($[Mg]/[Li]$) of 2.5, and then butadiene is blocked with styrene. In this case, however, the monomer concentration
5 based on the polymerization solvent (cyclohexane) is as low as 20%, and although no runaway reaction occurs, the activity of the living polymer lowers, so that unreacted polystyrene remains in the ensuing step of block polymerization of butadiene. In addition, the molecular
10 weight M_n of the obtained copolymer is as low as 8,900.

The present inventor found that if the polymerization initiator composed of R^2Mg and R^1M^1 and/or R^1OM^1 satisfies the particular relation of $[Mg]/[M^1] \geq 4$ ($[]$: molar concentration) for the molar concentration ratio of
15 metals, living polymerization proceeds without causing a runaway reaction even under the high temperature and high monomer concentration conditions. Thus, it is possible to the control molecular weight, polymerization rate and molecular weight distribution independently of each other.

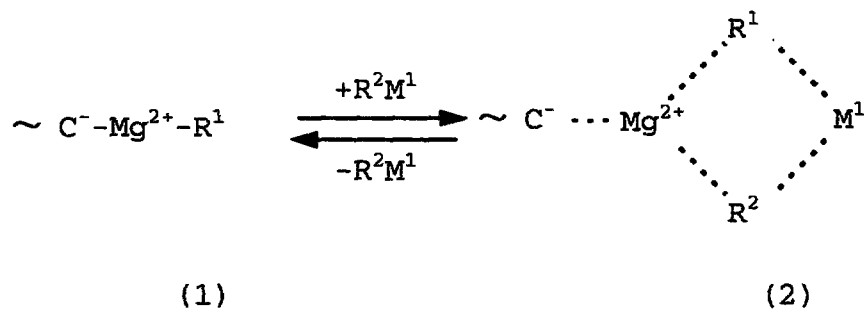
20 It has never been possible with the conventional anionic polymerization techniques to control molecular weight, polymerization rate and molecular weight distribution independently of each other in one pot of polymerization, so that this finding is quite surprising
25 and the present invention could have never been predicted from the prior art.

Such effect of the present invention is speculated to be attributable to the following mechanism.

This Sheet Has Been Replaced



It is considered that in the present invention, the carbonic anions which become unstable under high temperatures in polymerization with a conventional general-purpose initiator such as butyl lithium are capped with a metal forming a stable bond as shown in the following formula (1), and further a compound which can interact structurally with the compound of the formula (1) weakens the bonding force of the carbonic anions and their counter cations to thereby activate the carbonic anions (see the formula (2)). Further, under the polymerization temperature, the structure of the formula (1) is brought into a dormant state while the structure of the formula (2) becomes active, thus producing an equilibrium state between the structure of the formula (1) and that of the formula (2).



It is speculated that in a polymerization system having such a reaction mechanism, it will become easier to establish a living polymerization system if the equilibrium is biased to the left side (growing the dormant state) with rise of temperature to accordingly expand the stable state. It is also speculated that the molecular weight of the polymer is governed by the amount

of Mg since Mg always exists at the propagating species of polymerization, the polymerization rate is governed by the $[Mg]/[M^1]$ ratio since M^1 is activated to permit the polymerization to advance, and the molecular weight distribution is also governed by the $[Mg]/[M^1]$ ratio because of the bias of equilibrium and exchange rate to the other dormant terminals of RM^1 .

As the activator of the polymerization initiator in the present invention (when the term "polymerization initiator" is used in this specification, it may include its activator), the organic metal compounds represented by R^1M^1 and/or R^1OM^1 (R^1 and R^2 : a hydrocarbon group; O: an oxygen atom; M^1 is at least one alkali metal selected from the group consisting of Li, Na and K) are preferably used. Specifically, R^1 in the formula R^1M^1 represents a hydrocarbon group, preferably a linear or branched alkyl group represented by $CH_3(CH_2)_n$ - such as methyl, ethyl, propyl, isopropyl, n-butyl, t-butyl, sec-butyl, amyl or hexyl. Typical examples of R^1M^1 include methyl lithium, n-butyl lithium, sec-butyl lithium, t-butyl lithium, isopropyl lithium, n-propyl lithium, iso-propyl lithium, benzyl lithium, phenyl lithium, hexyl lithium, butyl sodium, butyl calcium, and cumyl potassium. These compounds may be used either singly or in combination.

R^1 in the formula R^1OM^1 represents a hydrocarbon group, preferably a linear or branched alkyl group represented by $CH_3(CH_2)_n$ - such as methyl, ethyl, propyl, isopropyl, n-butyl, t-butyl, sec-butyl, amyl or hexyl, a



phenyl group or an alkyl-substituted phenyl group.

Examples of R^1OM^1 include methoxylithium, methoxysodium, methoxypotassium, ethoxylithium, ethoxysodium, ethoxypotassium, propoxylithium, propoxysodium, 5 propoxypotassium, isopropoxylithium, isopropoxysodium, isopropoxypotassium, n-butoxylithium, n-butoxysodium, n-butoxypotassium, sec-butoxylithium, sec-butoxysodium, sec-butoxypotassium, tert-butoxy-lithium, tert-butoxysodium, tert-butoxypotassium, amyloxylithium, amyloxysodium, 10 amyloxypotassium, tert-amyloxylithium, tert-amyloxysodium, tert-amyloxy-potassium, hexyloxylithium, hexyloxysodium, hexyloxy-potassium, phenoxylithium, phenoxysodium, phenoxy-potassium, 2,4-di-tert-butylphenoxylithium, 2,4-di-tert-butylphenoxysodium, 2,4-di-tert-butylphenoxy- 15 potassium, 2,6-di-tert-butylphenoxylithium, 2,6-di-tert-butyl-phenoxy-sodium, 2,6-di-tert-butylphenoxypotassium, 3,5-di-tert-butylphenoxylithium, 3,5-di-tert-butyl-phenoxy-sodium, 3,5-di-tert-butylphenoxypotassium, 2,6-di-tert-butyl-4-methylphenoxylithium, 2,6-di-tert-butyl-4- 20 methylphenoxysodium, and 2,6-di-tert-butyl-4-methylphenoxypotassium. These compounds may be used either singly or in a combination of two or more of them.

R^1M^1 and R^1OM^1 may be used either singly or in combination.

25 R^1M^1 and/or R^1OM^1 are used so that the Mg to M^1 molar concentration ratio will satisfy the relation of $[Mg]/[M^1] \geq 4$ ([]: molar concentration), preferably $[Mg]/[M^1] \geq 4.5$, more preferably $[Mg]/[M^1] \geq 5$. When

[Mg]/[M¹] is less than 1, part of the cationic metal forming a counterpart to the carbonic anion at the polymerization propagating species of the living polymer produced during polymerization is constituted by the M¹ metal alone, and it is not possible to control the reactivity due to the presence of Mg. Consequently, a runaway reaction may take place with the polymerization temperature and monomer concentration ranges specified in the present invention, and no stable living polymerization system can be formed. In the region of $1 \leq [\text{Mg}]/[\text{M}^1] < 4$, living polymerization proceeds without causing a runaway reaction under a condition close to the lower limit of the polymerization concentration and temperature ranges in the present invention. In case polymerization is carried out under a condition of extremely high concentration, where almost no polymerization solvent is used, and at a high temperature of 100°C or more, a runaway reaction is induced and the living polymer activity is lowered. Further, in this case, there can be obtained only those polymers whose molecular weight distribution is substantially narrow. As for the molding resin material, it is desirable for certain uses of the product to use a polymer in which the low-molecular weight component and the high-molecular weight component are mixed with each other in a certain ratio, that is, a polymer whose molecular weight distribution is broad rather than narrow, from the standpoint of offering a good balance of fluidity and mechanical properties at the time of molding.

The present inventor found that when a vinyl monomer is polymerized by varying the $[Mg]/[M^1]$ ratio under conditions for completing polymerization in a certain prescribed period of time, quite surprisingly the

5 molecular weight distribution widens sharply in the region of $[Mg]/[M^1] \geq 4$. This is probably because the viscosity of the reaction system rises up with progress of polymerization in the high monomer concentration range, causing an apparent drop of exchange reaction rate of the

10 activator for the polymerization initiator.

For reducing the viscosity of the high concentration solution in the reaction system, it is recommended to carry out polymerization at a high temperature of 100 C or more, and to set the Mg and M^1

15 molar concentration rate at $[Mg]/[M^1] \geq 10$ for allowing progress of living polymerization without causing a runaway reaction in such a situation. The present inventor also found that the molecular weight distribution widens consistently as the $[Mg]/[M^1]$ ratio increases. However,

20 excessive increase of the $[Mg]/[M^1]$ ratio is undesirable as it causes too much widening of the molecular weight distribution and also increases the amount of the low molecular weight components, for example, oligomer moieties including dimers and trimers. The most preferred

25 range of molar concentration ratio is $10 \leq [Mg]/[M^1] \leq 100$.

The present inventor further found that when a compound or compounds represented by R^3OH and/or $(R^3)_2NH$ (R^3 : a hydrocarbon group; O: an oxygen atom; N: a nitrogen



atom), which normally can serve as an anionic polymerization terminator, is added to an initiator consisting of $(R^2)_2Mg$ and R^1M^1 ($[Mg] > [M^1]$) at a specific ratio, quite surprisingly polymerization of vinyl monomers is initiated and further living polymerization proceeds under the high-temperature and high-concentration conditions.

R^3OH and $(R^3)_2NH$ used in the present invention are the hydrocarbon groups, which are preferably linear or branched alkyl groups represented by $CH_3(CH_2)_n-$, such as methyl, ethyl, propyl, isopropyl, n-butyl, t-butyl, sec-butyl, amyl and hexyl, phenyl groups, alkyl-substituted phenyl groups, hydrocarbon-based ether compound groups represented by $CH_3(OCH_2CH_2)_n-$, and the groups represented by $(CH_3)_2N(CH_2CH_2)_n-$. Typical examples of R^3OH are methanol, ethanol, propanol, isopropanol, n-butyl alcohol, sec-butyl alcohol, tert-butyl alcohol, amyl alcohol, hexyl alcohol, phenol, 2,4-di-tert-butylphenol, 2,6-di-tert-butylphenol, 3,5-di-tert-butylphenol, 2,6-di-tert-butyl-4-methylphenol, 2-methoxyethanol, and 2-(2-di-tert-methoxyethoxy)ethanol. Examples of $(R^3)_2NH$ are N,N-dimethylethanolamine, dimethylamine, N-ethylmethylaniline, diethylamine, dipropylamine, dibutylamine, dihexylamine, dioctylamine, didecylamine, N,N,N'-trimethylethylenediamine, N,N,N',N'-tetramethyldiethylenetriamine and the like. These compounds may be used either singly or in combinations of two or more.

R^3OH and $(R^3)_2NH$ added must be in an amount that



satisfies the relation of $2 \times [\text{Mg}] + [\text{M}^1] > [\text{R}^3\text{OH}] + [(\text{R}^3)_2\text{NH}]$.
 Otherwise, if $2 \times [\text{Mg}] + [\text{M}^1] < [\text{R}^3\text{OH}] + [(\text{R}^3)_2\text{NH}]$,
 polymerization will not be initiated.

As a result of further research on the organic
 5 metal compounds composed of $(\text{R}^2)_2\text{Mg}$ and R^1M^1 , the present
 inventor found that at least one of the carbons attached
 to the metal of the hydrocarbon group of R^1 and R^2 is a
 secondary carbon and/or tertiary carbon, and when an
 organic metal compound satisfying the relation of $[\text{R}^{1,2}] \geq$
 10 $[\text{Mg}]$ ($[\text{R}^{1,2}]$: the total amount of R^1 and R^2 of secondary
 carbon and/or tertiary carbon) is used for polymerization
 of a vinyl monomer, the polymerization initiator
 efficiency of $(\text{R}^2)_2\text{Mg}$ is enhanced (the initiating reaction
 points are increased) and yet the polymerization rate is
 15 lowered. This is probably for the reason that since it is
 easier to initiate polymerization with R^1 and R^2 having a
 secondary carbon and/or tertiary carbon than with R^1 and R^2
 having a primary carbon, when $[\text{R}^{1,2}] \geq [\text{Mg}]$, Mg serves as a
 bifunctional initiator in an amount which corresponds to
 20 $[\text{R}^{1,2}] - [\text{Mg}]$, inviting a corresponding rise of initiator
 efficiency. Therefore, if R^1 and R^2 having a primary
 carbon and secondary and/or tertiary carbon are present in
 a mixed state, R^1 and R^2 having a secondary carbon and/or
 tertiary carbon alone are necessarily attached to the
 25 initiating terminal of the polymer, and the molecular
 weight is determined by the ratio amount of the monomer to
 R^1 and R^2 of secondary carbon and/or tertiary carbon. At
 the polymerization propagating species, there exist mixed

with each other two different structures: (A) ~ polymer ~
 -Mg-R² and (B) ~ polymer ~ Mg- ~ polymer ~, and it is
 supposed that (B) is lower in polymerization reactivity,
 that is, lower in polymerization rate. Therefore, it is
 5 possible to control the polymerization rate by adjusting
 the (A)/(B) ratio.

In the present invention, in the organic metal
 compounds composed of (R²)₂Mg and R¹M¹, at least one of the
 hydrocarbon compounds of R¹ and R² may be a polymer
 10 carbonic anion. "Polymer carbonic anion" is an anion of
 the living polymer obtained by living polymerization of a
 vinyl monomer, with its polymerization degree being not
 less than 1.

In the present invention, when a (R²)₂Mg compound
 15 is used, polymerization of a vinyl monomer is initiated
 even under a high-temperature and high-monomer-
 concentration condition, and living polymerization
 proceeds. It was further found that living polymerization
 is also allowed to proceed without causing a runaway
 20 reaction even under a high-temperature and high-
 concentration condition when a compound represented by R³OH
 and/or (R³)₂NH (R² and R³: a hydrocarbon group; O: an oxygen
 atom; N: a nitrogen atom) is mixed instead of adding R¹M¹
 and R¹OM¹. The effect of addition of R³OH and/or (R³)₂NH is
 25 to elevate the polymerization rate more than the addition
 of (R²)₂Mg alone. The polymerization rate is elevated as
 the amount of said compound(s) is increased. However, the
 amount of said compound(s) to be added is limited to such

a range that satisfies the relation of $2 \times [\text{Mg}] > [\text{R}^3\text{OH}] + [(\text{R}^3)_2\text{NH}]$. If $2 \times [\text{Mg}] + [\text{M}^1] \leq [\text{R}^3\text{OH}] + [(\text{R}^3)_2\text{NH}]$, polymerization will not proceed.

Since the polymerization of vinyl monomer using
5 an initiator of the present invention proceeds in the region of high monomer concentration, it is expected that the viscosity of the polymerization solution will become fairly high, so that it is desirable to use an extruder as the polymerization reactor in view of the uniformity of
10 the polymerization reaction. "Extruder" means here a single-screw or double-screw extruder which has a screw and/or a kneading disc.

Polymerization in the extruder by use of an initiator of the present invention can dispense with the
15 solvent recovery operation after completion of polymerization since living polymerization occurs even with a very small quantity of solvent, so that there can be realized a very economical process in which the solvent can be removed only by a deaeration treatment in the
20 extruder.

The method for termination of polymerization is not critical in the present invention; generally known termination methods of anionic polymerization can be used. For example, polymerization can be terminated by adding
25 water, an alcohol, a protonic acid compound such as carboxylic acids, carbon dioxide or the like to the polymerization solution.

It is known that a small quantity of monomer(s)

exists in the styrene polymers obtained by radical polymerization, and if a molded product of the styrene polymer is placed in an oleophilic compound atmosphere, the monomer(s) in the molded product may bleed out to give
5 rise to problems.

There are considered principally two patterns in which the monomers remain in the polymer: the monomers which have not been reacted during the polymerization operation being left in the polymer; or the monomers which
10 have been produced by decomposition of polymers or oligomers during the molding operation being present in the molded product. Monomers which remain unreacted during the polymerization can be significantly reduced by a deaeration treatment under high vacuum, but the polymer
15 and oligomer are further decomposed upon encountering thermal and shearing loads during molding so as to produce monomers. Monomers are produced in large quantities by thermal decomposition of the oligomers such as dimers and trimers, and it is difficult to remove these oligomers
20 from the polymer by a deaeration treatment.

It is known that, with oligomers produced by heat retention of a polymer, generally, the trimer exists in greater amount than the dimer (J. Polymer Sci.: Symposium No. 57, 81-88, (1976)). In fact, the amount of
25 trimer in a styrene polymer produced by radical polymerization is approximately ten times the amount of dimer. Therefore, it has been an important subject to control the formation of trimer in the polymer and to

provide a styrene resin which is minimized in the amount of monomer produced during the molding operation.

The present inventor has pursued research on this subject and found that the amount of trimer produced during polymerization can be significantly lessened by using a specific anionic polymerization technique, and that the polymer obtained by this process is minimized in the amount of monomer formed under heat retention. This finding constitutes a basis for the present invention.

Thus, the styrene polymers produced according to the process of the present invention are minimized in the amount of monomers formed under heat retention.

Also, the styrene polymers produced by the process of the present invention can function to arrest formation of monomers under heat retention even if metal residues originating in the polymerization initiator exist in small quantities in the polymer. In the conventional anionic polymerization, metal residues originating in the polymerization initiator are inevitably left in the produced polymer, and it is considered that these metal residues accelerate thermal decomposition of the polymer in molding thereof. It is generally practiced to remove these metal residues by extraction with water, but this method is incapable of perfectly removing the metal residues, and thus small quantities of metal residues are substantially left in the produced polymer. In the case of the styrene polymers of this invention, even if small quantities of Mg and M¹ metals are left in the polymer,

there is insignificant formation of trimer. Thus, in accordance with this invention, a very economical industrial process requiring no step for extraction removal of metal residues can be employed for the
5 production of polymers obtainable with a small amount of initiator or for polymerization using a chain transfer agent.

The molecular weight of styrene resin obtained according to the process of the present invention is in
10 the range of 10^3 to 10^7 , and the amount of Mg used in this process is about 3 to 2,400 ppm, but the most favorable effect is obtained in the molecular weight range where the Mg content is not greater than 100 ppm.

"Mg" and " M^1 " which may be left in the styrene
15 polymers of the present invention mean the Mg and M^1 compounds which are produced after deactivation of the compounds used as polymerization initiator. The Mg to M^1 molar ratio ($[Mg]/[M^1]$) is preferably 4-10, more preferably 5-90, even more preferably 6-80.

20 Further research by the present inventor has led to the discovery of a styrene resin composition having excellent heat decomposability, moldability and, in particular, foaming characteristics. This styrene resin composition can be obtained from anionic polymerization
25 and its molecular weight distribution M_w/M_n is from 2.0 to 10.0 and the content of the styrene-derived trimer is not greater than 250 ppm.

A method for inhibiting formation of styrene

from polystyrene by thermal load in a mold or extruder is disclosed in JP-A-7-292188. This method, however, is still unsatisfactory in its effect of inhibiting formation of styrene by thermal load since polystyrene obtained from radical polymerization is used as polymer. Use of polystyrene obtained by anionic polymerization can afford a certain improvement of the styrene formation inhibitory effect, but this patent document sheds no light on the amount of trimer present in the produced polymer and the effect of the foaming characteristics.

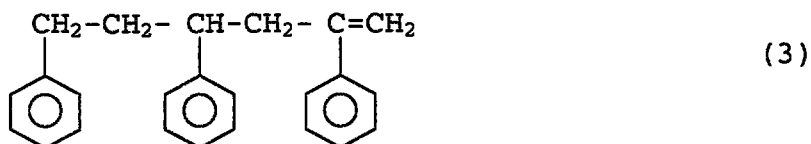
The present inventor discovered a styrene resin composition whose foaming characteristics are improved in a specific region of molecular weight distribution and which is very stable thermally and minimized in formation of monomers by decomposition, and this discovery is embodied in the present invention.

The term "styrene resin" used in the present invention refers to styrene polymers that can be obtained by anionic polymerization and whose molecular weight distribution M_w/M_n (weight-average molecular weight/number-average molecular weight) is from 2.0 to 10.0, preferably from 2.1 to 9.5, more preferably from 2.2 to 9.0. When M_w/M_n is less than 2.0, the foaming characteristics are deteriorated while when it exceeds 10.0, the low-molecular weight component increases, resulting in increased formation of styrene monomers by decomposition of the polymer in the course of secondary working such as injection foam molding or extrusion

foaming.

The term "trimer" used in the present invention refers to trimers having the molecular structure represented by the following formula (3):

5



The amount of trimer existing in the styrene polymers is not greater than 250 ppm, preferably not greater than 230 ppm, more preferably not greater than 200 ppm. When the trimer content exceeds 250 ppm, the amount of the styrene monomers formed under heat retention increases, which may cause problems with the migration of such monomers to the packed fat-containing foods when the molded product of the styrene polymer is used as a food packaging material.

The styrene resin composition of the present invention is minimized in formation of styrene monomers by heat decomposition and has excellent foaming characteristics, so that it is very suitable for use as an injection or extrusion molding material.

The styrene resin composition of the present invention may contain additives such as lubricants, releasing agents, plasticizers, colorants, flame retardants, foaming agents, etc., within the limits of the conception of the present invention.

The present invention will be further illustrated by the following Examples and Comparative

Examples, but it should not be construed to be restricted by these examples.

The monomers and solvents used in the present invention were purified in the following way before use.

5 The organic metal compounds, alcohols, secondary amines and other reagents used in the Examples and Comparative Examples are explained below.

(1) Styrene (SM)

A commercial product manufactured by Asahi
10 Chemical Industry Co., Ltd. It was distilled under reduced pressure once under CaH_2 , subjected to a deaeration treatment and then sealed under a dry nitrogen atmosphere.

(2) Ethylbenzene (EB) and cyclohexane

Commercial products manufactured by Wako Pure
15 Chemical Industries Co., Ltd. The special grade products were distilled under reduced pressure once under CaH_2 , subjected to a deaeration treatment, mixed with molecular sieves and then sealed under dry nitrogen.

(3) n-Butyl lithium (nBuLi)

20 Product manufactured by Kanto Chemical Co., Ltd. Used as a 1.6 M n-hexane solution.

(4) sec-Butyl lithium (sBuLi)

Product manufactured by Kanto Chemical Co., Ltd. Used as a 1.0 M cyclohexane solution.

25 (5) tert-Butyl lithium (tBuLi)

Product manufactured by Kanto Chemical Co., Ltd. Used as a 1.6 M n-heptane solution.

(6) Dibutyl magnesium (Bu_2Mg)

Product manufactured by Aldrich Inc. A 1.0M heptane solution of 1:1 mixture of n-dibutyl magnesium and sec-dibutyl magnesium.

- (7) n-Butyl alcohol (nBuOH), sec-butyl alcohol (sBuOH),
5 tert-butyl alcohol (tBuOH) and di-n-butylamine (Bu₂NH)

Special grade products manufactured by Kanto Chemical Co., Ltd. Distilled under CaH₂, subjected to deaeration treatment, mixed with molecular sieves and
10 sealed under dry nitrogen.

- (8) tert-Butoxysodium (tBuONa) and tert-butoxypotassium (tBuOK)

Products manufactured by Aldrich Inc.

- (9) Polymerization terminator

- 15 A 90/10 (by volume) mixture of tetrahydrofuran (THF) and methanol (MeOH) was used.

The polymerization rate, molecular weight and molecular weight distribution of the obtained polymers were determined in the following ways.

- 20 (10) Polymerization rate

Unreacted SM was measured by gas chromatography (GC) under the conditions 1, and the polymerization rate (conversion) was determined from the following equation:

- 25
$$\text{Polymerization rate (\%)} = \frac{([\text{supplied SM concentration}] - [\text{unreacted SM concentration}])}{[\text{supplied SM concentration}]} \times 100$$

(11) Number-average molecular weight (M_n), weight-average molecular weight (M_w) and M_w/M_n

Determined by gel permeation chromatography (GPC).

5 (12) Measurement of trimer

Conducted under the conditions 2.

[GC determination conditions]

Conditions 1

Measuring device: GC 14B mfd. by Shimadzu Corp.

10 Column: PEG 20M (ϕ 3 mm x 3 m)

Carrier gas: nitrogen, flow rate = 50 ml/min

Detector: FID

Column temp.: Maintained at 125°C for 10 minutes and
then further heated at a rate of 35°C/min
15 until reaching 230°C. Injection and
detector temp. = 230°C.

Internal standard reagent: EB

Conditions 2

Measuring device: GC 14B mfd. by Shimadzu Corp.

20 Column: TC-1 (inner diameter: 0.25 mm; thickness:
0.25 μ m;

length: 30 m; mfd. by GL Science Inc.)

Carrier gas: nitrogen, flow rate = 50 ml/min

Detector: FID

25 Column temp.: Maintained at 50°C for 5 minutes and then
further heated at a rate of 20°C/min
until reaching 320°C.

Injection temp.: 260°C

Detector temp.: 330°C

Internal standard reagent: anthracene

[GPC measuring conditions]

Measuring device: TOSO HLC-8020 (with built-in
5 differential refractive index
detector)

Column: TOSO TSKgel-GMH_{XL} x 2

Temperature: 38°C

Solvent: tetrahydrofuran (THF)

10 Sample concentration: 0.1 wt/v%

Sampling pitch: once per 0.4 second

Determination of molecular weight:

Calibration curves were drawn by plotting the
relation between the molecular weight of TOSO
15 TSK standard polystyrenes and elution time as
third-order repression curve, and the molecular
weight was determined from the curve.

In the following Examples and Comparative
Examples, all the polymerization operations were carried
20 out according to the following procedure unless otherwise
noted.

[Polymerization operation]

A glass container and a syringe, which had been
heated to 140°C and dried, a monomer, a solvent and a
25 reagent were placed in a nitrogen globe (Model VDB-SA-Q
mfd. by Eiko Shokai KK). The inside atmosphere of the
nitrogen globe has been well substituted with nitrogen
which had been dehydrated and dried with molecular sieves.



Prescribed amounts of the monomer and solvent were put into a 50 ml pressure glass bottle, followed by further addition of a prescribed amount of a polymerization initiator. In case the concentration of the polymerization initiator was high, it was diluted with ethylbenzene and then added to the monomer solution. The polymerization solution was 10 ml in all cases. After feeding has been completed, the pressure bottle was stoppered with nitrile rubber, then taken out from the nitrogen globe and capped with a metal crown. The pressure bottle was put into an oil bath of a prescribed temperature. The time when the bottle was put into the oil bath was indicated as time 0. The pressure bottle was shaken properly to stir the reaction solution. On passage of a prescribed period of time, the pressure bottle was taken out from the oil bath and immediately put into water for cooling to room temperature. After cooling, 5 ml of the terminator was supplied into the pressure bottle so as to prevent entrance of air. Also, the pressure bottle was shaken quickly to effect uniform dispersion of the terminator. The resulting polymerization solution was diluted with THF and this diluted solution was used for GC and GPC analyses.

Examples 1-3

25 In the nitrogen globe, 9 ml of EB and 1 ml of Bu_2Mg were put into a 30 ml beaker to dilute Bu_2Mg . A mixed solution of SM and EB was supplied into the pressure bottle to a concentration shown in Table 1, then the

diluted initiator solution was added thereto to a prescribed concentration, and the resulting polymerization solution was mixed well by shaking. Three bottles of completely the same polymerization solution were prepared. On reaching the prescribed polymerization time shown in Table 1, the terminator was added to the solution to stop polymerization. The analytical results of the obtained polymers are shown in Table 1.

Generally, in the living polymerization systems, the molecular weight M_n of the polymer increases linearly in proportion to the conversion. A graph showing the relation between conversion and M_n in Examples 1-3 embodying the polymerization system of the present invention is shown in FIG. 1. In the polymerization solutions shown in these Examples, M_n increased linearly in proportion to conversion, indicating that these polymerization solutions are those of living polymerization. Also, in Examples 1-3, polymerization proceeded at a moderate rate without causing a runaway reaction as shown in Table 2.

Comparative Example 1

The procedure of Example 1 was followed except that an $n\text{BuLi}$ solution was used in place of Bu_2Mg to a concentration of 2.56 mM, and that the pressure bottle containing the polymerization initiator was placed in liquid nitrogen so as to prevent polymerization from starting. After being taken out of the nitrogen globe, it

was put into an oil bath of 120°C. In a few minutes, the polymerization solution was bumped to conclude polymerization (runaway reaction occurred).

5 Comparative Example 2

The procedure of Example 1 was followed except that polymerization was carried out at the concentration shown in Table 2. Polymerization proceeded without causing a runaway reaction, but as seen from FIG. 1, Mn increased
10 deviating from linearity with conversion and the living polymerization activity was decreased with increase of conversion.

Comparative Example 3

15 The procedure of Example 1 was followed except that polymerization was carried out at 150°C without adding the Bu₂Mg initiator solution.

As seen from plotting of Mn and conversion in FIG. 1, this polymerization solution (conventional heat
20 radical polymerization solution) was constant in molecular weight regardless of the progress of polymerization. Also, the polymers obtained only had a wide molecular weight distribution ($M_w/M_n = 2.2$).

The polymerization conditions of Examples 1-3
25 are 120-150°C and 6 hours, which are the conditions normally supposed to cause heat radical polymerization. However, no peak of the molecular weight such as shown in Comparative Example 3 was observed in GPC analysis. This



indicates that no heat radical polymerization but only anionic polymerization occurred in Examples 1-3.

Examples 4-8

5 In the nitrogen globe, dilute solutions of Bu_2Mg and nBuLi were each prepared in advance at the mixing ratios shown in Table 3. A dilute initiator solution was added to a mixed solution of SM and EB to the concentrations shown in Table 3 and mixed well. The
10 resulting solution was dispensed into pressure bottles in an amount of 10 ml per bottle and polymerized at the temperatures and for the times shown in Table 3.

 As seen from FIG. 3, polymerization proceeded without a runaway reaction despite the high-temperature
15 and high-monomer-concentration conditions.

 From FIG. 4 showing the relation between Mn and conversion, it is seen that the molecular weight increased with progress of polymerization, and that living polymerization proceeded. It is noted that the molecular
20 weight distribution was widened with increase of conversion. It is considered that this is not due to a decrease of living characteristics of the polymerization solution but is attributable to such factors as rise of viscosity of the polymerization solution and increase of
25 the ratio of propagation rate to exchange reaction rate between the polymerization active point (Mg) and polymerization activator (Li). The molecular weight distribution patterns of Examples 8-1 and 8-2 are shown in FIG. 5, from

which it is seen that the molecular weight distribution is generally shifted with progress of polymerization, and there exists no deactivated polymer.

5 Comparative Example 4

Polymerization was carried out in a region with a low concentration of SM relative to EB at $\text{Bu}_2\text{Mg}/\text{nBuLi} = 4$. Although polymerization proceeded without causing a runaway reaction, the molecular weight distribution
10 widened with progress of polymerization. GPC analysis showed pronounced tailing of the molecular weight distribution toward the low molecular weight side with the progress of polymerization, indicating that the active points were gradually deactivated in the course of
15 polymerization (decrease of living polymerization activity).

Comparative Example 5

Polymerization was carried out under the
20 conditions shown in Table 7. Progress of polymerization was very slow.

Examples 9-12

Polymerization was carried out under the
25 conditions shown in Table 4 using cyclohexane as solvent and Bu_2Mg and nBuLi as initiators. Polymerization was conducted at 80°C for 4 hours in the conversion range of 70% or less, then the temperature was raised to 120°C and

30 minutes after polymerization was stopped.

Polymerization had already been completed. In Example 12, however, polymerization had been completed in a polymerization time of 4 hours. The relation between Mn of the
5 obtained polymer and $[SM]/[Mg]$ ratio is shown in FIG. 6.

Comparative Examples 6-8

Polymerization was carried out under the conditions shown in Table 7 using cyclohexane as solvent
10 and Bu_2Mg and $nBuLi$ as initiators. Polymerization was performed at $50^\circ C$ in the conversion range of 70% or less, and then the temperature was raised to $80^\circ C$ to conclude polymerization. In Comparative Example 8, the internal temperature became slightly higher than the oil bath
15 temperature in the early phase of polymerization. The relation between Mn of the obtained polymer and $[SM]/[Mg]$ ratio is shown in FIG. 6.

From the results of FIG. 6, it is apparent that Mn of the polymer is decided by the $[SM]/[Mg]$ ratio in the
20 region of $[Mg] \geq [Li]$.

The relation between Mn and $[Mg]/[Li]$ ratio is shown in FIG. 7. In the region of $[Mg] \geq [Li]$, the value of Mn of the polymer is constant regardless of the $[Mg]/[Li]$ ratio, but in the region of $[Mg] < [Li]$ the molecular weight
25 is lowered.

H^1 and C^{13} NMR analyses of the polymer obtained in the region of $[Mg] \geq [Li]$ confirmed that the butyl groups attached to the end of the molecular chain of the polymer

were sec-butyl groups, that the number thereof was equal to the number of the benzyl protons at the polymerization termination ends, and that the value of Mn calculated from the number of sec-butyl groups substantially agreed with the value of Mn determined by GPC. From these facts, it was confirmed that the metal cation forming a counterpart to the carbonic anion at the polymerization active point was Mg.

10 Examples 13-14 and Comparative Examples 9-10

Polymerization was carried out under the conditions shown in Tables 4 and 7 using EB as polymerization solvent and Bu_2Mg and nBuLi as initiators. In each case, polymerization was conducted under a condition designed to complete the polymerization in 240 minutes.

The relation between the molecular weight distribution of the polymer obtained from the polymerization of 240 minutes (a polymer having a conversion of 95% or more) and the $[\text{Mg}]/[\text{Li}]$ ratio is shown in FIG. 8. The molecular weight distribution was narrow at $[\text{Mg}]/[\text{Li}] \leq 2$ but widened when the $[\text{Mg}]/[\text{Li}]$ ratio was made equal to or greater than 4.

25 Examples 15 and 17

Bu_2Mg and nBuOH or sBuOH were mixed at a molar ratio of 1 : 1 in EB, and nBuLi was added to the resulting solution at a $[\text{Mg}]/[\text{Li}]$ ratio shown in Table 5.

Polymerization was carried out by using this preparation as polymerization initiator. EB was used as polymerization solvent.

5 Examples 16, 18 and 19

 nBuLi and nBuOH or sBuOH or tBuOH were mixed in a molar ratio of 1 : 1 in EB, and nBuLi was added to the resulting solution at a [Mg]/[Li] ratio shown in Table 5. Polymerization was carried out using this preparation as
10 polymerization initiator and EB as solvent.

 Example 20

 nBuLi and nBuOH were mixed at a molar ratio of 1 : 1 in EB. In a separate container, Bu₂Mg and nBuOH were
15 mixed at a molar ratio of 1 : 1 in EB. Two solutions were mixed at a [Mg]/[Li] ratio shown in Table 6, and polymerization was carried out using the mixed solution as polymerization initiator and EB as solvent.

20 Example 21

 Bu₂Mg and Bu₂NH were mixed in a molar ratio of 1 : 1 in EB, and then nBuLi was added thereto at a [Mg]/[Li] ratio shown in Table 6. Polymerization was carried out using this preparation as polymerization
25 initiator and EB as solvent.

 Examples 22 and 23

 tBuONa or tBuOK powder was added to EB, and then

Bu₂Mg was mixed therewith at a [Mg]/[M¹] ratio shown in Table 6. Polymerization was carried out using this preparation as polymerization initiator and EB as solvent.

The polymerization results of Examples 15-23 are shown in Table 6. In each case, living polymerization proceeded without causing a runaway reaction as in the case of the Bu₂Mg/BuLi initiator.

R³OH and (R³)₂NH were mixed in each initiator so that the $\{[R^3OH] + [(R^3)_2NH]\} / \{2 \times [Mg] + [M^1]\}$ ratio would be quintuplicated, and each mixture was used as initiator, but polymerization was not initiated with any of these initiators.

Examples 24 and 25

Dilute solutions of Bu₂Mg and sBuLi or tBuLi were prepared at the mixing ratios shown in Table 8 in a nitrogen globe. EB was used as polymerization solvent. Polymerization was carried out under the condition shown in Table 8.

Polymerization was conducted under the same conditions as in Example 4, but the polymerization rate was lower and the molecular weight of the obtained polymer was also somewhat smaller. sBuLi and tBuLi showed completely the same polymerization behavior. The results of polymerization are shown in FIGS. 9 and 10.

Example 26

nBuLi was added to EB, followed by further

addition of SM at $[SM]/[Li]$ of 2. The solution changed in color after a while. Then Bu_2Mg was added at $[Mg]/[Li]$ of 4 to prepare an initiator solution. Polymerization was carried out under the conditions shown in Table 8. The result was completely the same as when the process was initiated with $Bu_2Mg/nBuLi$.

Example 27

Bu_2Mg and $sBuOH$ were mixed at a molar ratio of 1 : 1 in EB. Using this preparation as initiator, polymerization was carried out under the conditions shown in Table 8. Living polymerization proceeded without causing a runaway reaction.

Example 28

Bu_2Mg and $(Bu)_2NH$ were mixed at a molar ratio of 1 : 1 in EB, and using this preparation as initiator, polymerization was carried out under the conditions shown in Table 8. Living polymerization proceeded without causing a runaway reaction.

In the initiator solutions of Examples 27 and 28, $sBuOH$ and Bu_2Mg , and Bu_2NH and Bu_2Mg , were mixed so as to satisfy $[sBuOH]/[Bu_2Mg] = 10$ and $[Bu_2NH]/[Bu_2Mg] = 10$. Polymerization was attempted by using these mixed initiators, but polymerization could not be initiated in each case.

Although the polymerization reaction was conducted at a high temperature in Examples 1-28, there

was observed no peak of molecular weight attributable to radical polymerization.

Example 29

5 High-temperature bulk polymerization of SM was carried out using a polymerization initiator $\text{Bu}_2\text{Mg}/\text{nBuLi}$ (10/1) of the present invention in an extruder (ZSK-25 (L/D = 47) mfd. by Werner Corp.).

The 11 blocks of the extruder were set at the following temperatures: block 1 : room temperature; block 2 : 120°C; blocks 3 and 4 : 140°C; blocks 5 and 6 : 160°C; blocks 7 and 8 : 200°C; blocks 9-11 : 220°C. A liquid-adding device was provided between the blocks 8 and 9, from which the polymerization terminator (a mixed solution of BuOH and EB) was supplied under pressure. The purified and dehydrated SM, EB and EB-diluted $\text{Bu}_2\text{Mg}/\text{nBuLi}$ (10/1) initiators were stored in the respective containers under a closed nitrogen atmosphere. The materials in the respective containers can be fed into a tank provided with a 3-liter agitating element by a gear pump, and therefrom into the zone 1 of the extruder by another gear pump. The interior atmosphere of the extruder was well substituted with dry nitrogen and a mixed solution of EB and initiator was fed into the extruder to clean its interior. Then the concentration of SM was gradually raised to finally reach 100. The SM feed rate was set at 100 ml/min. The initiator was supplied in such an amount that $[\text{SM}]/[\text{Mg}]$ would become 1,000. The polymer extruded from the die was



immediately cooled in water and pelletized. The molecular weight of the produced polymer and its molecular weight distribution were as follows: $M_n = 91,000$; $M_w/M_n = 3.5$.

5 Example 30 and Comparative Examples 11 and 12

Polymers were produced under the conditions shown in Table 9. Each polymer was dissolved in EB to a concentration of about 20% and part of the metal residues was extracted with distilled water. The metal contents of
10 the polymers are shown in Table 9. Methanol was added to each polymer solution after washing to precipitate the polymer, and then the solution was dried in vacuo at 80°C. 0.2 g of each of the obtained polymers was put into a glass tube. The glass tubes were sealed in vacuo. The
15 glass tubes were placed in a 280°C oil bath for 10 minutes, 20 minutes and 40 minutes and then taken out. The taken-out glass tubes were put into water for cooling. The glass tubes were crushed and the contents were put into and dissolved in THF. The monomer formation rate was
20 determined by gas chromatography using anthracene as an internal standard.

The results are shown in Table 10.

Example 31

25 The polymer obtained in Example 29 was subjected to an extrusion foaming test using Freon 12. The rate of the open cells in the obtained foam was determined according to ASTM-2856. The monomers contained in the

obtained foam were also determined. The results are shown in Tables 11 and 12.

Comparative Example 13

5 Using uBuLi as initiator and EB as solvent, polymerization was carried out at an SM concentration of 50 vol% in a 100-liter autoclave. The polymerization temperature rose to 145°C. The solvent was removed from the obtained polymer solution by a drum dryer. The polymer
10 was then put into an extruder having a cylinder temperature of 220°C and the residual EB was vented away. The polymer was recovered as pellets. The results are shown in Tables 11 and 12.

15 Comparative Example 14

A polymer obtained from radical polymerization was extrusion foamed in the same way as in Example 31, and the open cell rate and monomer content of the obtained foam were examined. The results are shown in Tables 11 and
20 12.

This application is based on Japanese Patent Application No. 8-084474 filed in Japan on March 14, 1996, Japanese Patent Application No. 8-303483 filed in Japan on October 30, 1996, and Japanese Patent Applica-tion No. 8-
25 303484 filed in Japan on October 30, 1996, the contents of which are incorporated hereinto in its entirety by reference.

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Table 1

	[SM] (vol%)	[Bu ₂ Mg] (mM)	Polymerization temperature* (°C)	Polymeriza- tion time (min)	Conv. (%)	Mn (x10 ⁻³)	Mw (x10 ⁻³)	Mw/Mn
Example 1-1	50	5.16	150	60	19	12	19	1.62
Example 1-2	50	5.16	150	120	27	18	30	1.65
Example 1-3	50	5.16	150	240	42	25	42	1.68
Example 2-1	80	2.58	150	60	22	42	63	1.51
Example 2-2	80	2.58	150	120	36	83	134	1.62
Example 2-3	80	2.58	150	240	58	125	210	1.68
Example 3-1	80	2.58	120	120	10	20	27	1.40
Example 3-2	80	2.58	120	240	20	38	56	1.48
Example 3-3	80	2.58	120	480	33	61	92	1.50

* EB was used as solvent.

Table 2

	[SM] (vol%)	[Bu ₂ Mg] (mM)	Polymerization temperature* (°C)	Polymeriza- tion time (min)	Conv. (%)	Mn (x10 ⁻³)	Mw (x10 ⁻³)	Mw/Mn
Comp. Example 1	50	*1	120	*2	100	183	198	1.08
Comp. Example 2-1	20	2.06	150	60	15	10	17	1.71
Comp. Example 2-2	20	2.06	150	120	23	14	25	1.82
Comp. Example 2-3	20	2.06	150	240	38	18	38	2.10
Comp. Example 3-1	50	0	150	120	29	92	212	2.30
Comp. Example 3-2	50	0	150	240	43	92	207	2.25

* : EB was used as solvent.

*1: 2.56 mM of BuLi was added in place of Bu₂Mg.

*2: Runaway reaction occurred in the polymerization solution, and polymerization was concluded within one minute.

Table 3

	[SM] (vol%)	[Bu ₂ Mg] (mM)	$\frac{[\text{Bu}_2\text{Mg}]}{[\text{BuLi}]}$	Polymeriza- tion tem- perature (°C)	Polymeriza- tion time (min)	Conv. (%)	Mn ($\times 10^{-3}$)	Mw ($\times 10^{-3}$)	Mw/Mn
Example 4-1	80	6.9	4	80	60	60	70	82	1.17
Example 4-2	80	6.9	4	80	120	82	82	101	1.23
Example 4-3	80	6.9	4	80	240	96	91	114	1.25
Example 5-1	90	7.8	6	90	60	59	62	73	1.18
Example 5-2	90	7.8	6	90	120	80	77	95	1.24
Example 5-3	90	7.8	6	90	240	95	90	126	1.40
Example 6-1	90	7.8	10	100	60	38	35	43	1.23
Example 6-2	90	7.8	10	100	120	60	55	74	1.35
Example 6-3	90	7.8	10	100	240	85	79	130	1.65

- Cont'd -

Table 3 (Cont'd)

Example 7-1	100	8.6	20	110	60	36	31	43	1.40
Example 7-2	100	8.6	20	110	120	60	51	77	1.51
Example 7-3	100	8.6	20	110	240	83	57	98	1.72
Example 8-1	100	8.6	30	120	60	33	25	44	1.76
Example 8-2	100	8.6	30	120	120	61	48	85	1.78
Example 8-3	100	8.6	30	120	240	80	55	104	1.90

Table 4

	[SM] (vol%)	[Bu ₂ Mg] (mM)	$\frac{[\text{Bu}_2\text{Mg}]}{[\text{BuLi}]}$	Polymeriza- tion temperature* (°C)	Polymeriza- tion time (min)	Conv. (%)	Mn ($\times 10^{-3}$)	Mw ($\times 10^{-3}$)	Mw/Mn
Example 9-1	80	69	6	80	240	72	7.5	8.8	1.18
Example 9-2	80	69	6	80→120	240+30	100	11	13	1.17
Example 10-1	80	35	6	80	240	65	14	16	1.17
Example 10-2	80	35	6	80→120	240+30	100	21	24	1.17
Example 11-1	80	23	6	80	240	60	17	20	1.17
Example 11-2	80	23	6	80→120	240+30	100	29	34	1.16
Example 12	80	35	4	80	240	100	20	23	1.17
Example 13	100	6.9	10	100	240	100	88	150	1.70
Example 14	100	6.9	20	120	240	100	70	127	1.81

* Cyclohexane was used as solvent.

Table 5

	Initiator	Component ratio	[SM] (vol%)	[Mg] (mM)	[Mg] [Li]		Polymerization temperature (°C)
Example 15-1	nBuLi/Bu ₂ Mg/nBuOH	1/6/6	90	7.8	6		90
Example 15-2	nBuLi/Bu ₂ Mg/nBuOH	1/6/6	90	7.8	6		90
Example 15-3	nBuLi/Bu ₂ Mg/nBuOH	1/6/6	90	7.8	6		90
Example 16-1	nBuLi/Bu ₂ Mg/nBuOH	1/6/1	90	7.8	6		90
Example 16-2	nBuLi/Bu ₂ Mg/nBuOH	1/6/1	90	7.8	6		90
Example 16-3	nBuLi/Bu ₂ Mg/nBuOH	1/6/1	90	7.8	6		90
Example 17-1	nBuLi/Bu ₂ Mg/sBuOH	1/10/10	90	7.8	10		100
Example 17-2	nBuLi/Bu ₂ Mg/sBuOH	1/10/10	90	7.8	10		100
Example 17-3	nBuLi/Bu ₂ Mg/sBuOH	1/10/10	90	7.8	10		100
Example 18-1	nBuLi/Bu ₂ Mg/sBuOH	1/6/1	90	7.8	6		100
Example 18-2	nBuLi/Bu ₂ Mg/sBuOH	1/6/1	90	7.8	6		100
Example 18-3	nBuLi/Bu ₂ Mg/sBuOH	1/6/1	90	7.8	6		100
Example 19-1	nBuLi/Bu ₂ Mg/tBuOH	1/6/1	90	7.8	6		100
Example 19-2	nBuLi/Bu ₂ Mg/tBuOH	1/6/1	90	7.8	6		100

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Table 5 (Cont'd)

Polymerization time (min)	Conv. (%)	Mn ($\times 10^{-3}$)	Mw ($\times 10^{-3}$)	Mw/Mn
60	53	49	58	1.19
120	78	74	90	1.22
240	93	89	117	1.32
60	44	42	48	1.15
120	71	68	82	1.20
240	90	85	107	1.26
60	68	63	88	1.40
120	90	80	131	1.64
240	10	90	154	1.71
60	63	56	76	1.36
120	85	79	130	1.64
240	99	90	153	1.70
60	90	81	133	1.64
120	10	90	153	1.70

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Table 6

	Initiator	Component ratio	[SM] (vol%)	[Mg] (mM)	[Mg]		Polymerization temperature (°C)
					[Li]	[Mg]	
Example 20-1	nBuLi/Bu ₂ Mg/nBuOH	1/10/11	90	7.8	10		100
Example 20-2	nBuLi/Bu ₂ Mg/nBuOH	1/10/11	90	7.8	10		100
Example 20-3	nBuLi/Bu ₂ Mg/nBuOH	1/10/11	90	7.8	10		100
Example 21-1	nBuLi/Bu ₂ Mg/Bu ₂ NH	1/10/10	90	7.8	10		100
Example 21-2	nBuLi/Bu ₂ Mg/Bu ₂ NH	1/10/10	90	7.8	10		100
Example 21-3	nBuLi/Bu ₂ Mg/Bu ₂ NH	1/10/10	90	7.8	10		100
Example 22-1	tBuONa/Bu ₂ Mg	1/6	90	7.8	6		80
Example 22-2	tBuONa/Bu ₂ Mg	1/6	90	7.8	6		80
Example 22-3	tBuONa/Bu ₂ Mg	1/6	90	7.8	6		80
Example 23-1	tBuOK/Bu ₂ Mg	1/10	90	7.8	10		80
Example 23-2	tBuOK/Bu ₂ Mg	1/10	90	7.8	10		80
Example 23-3	tBuOK/Bu ₂ Mg	1/10	90	7.8	10		80

- Cont'd -

Table 6 (Cont'd)

Polymerization time (min)	Conv. (%)	Mn ($\times 10^{-3}$)	Mw ($\times 10^{-3}$)	Mw/Mn
60	37	34	42	1.23
120	59	54	73	1.36
240	84	79	131	1.66
60	70	65	92	1.42
120	91	81	134	1.66
240	100	90	156	1.73
60	60	59	67	1.14
120	82	79	95	1.20
240	98	95	121	1.27
60	62	60	82	1.36
120	83	80	132	1.65
240	99	91	156	1.71

Table 7

	[SM] (vol%)	[Bu ₂ Mg] (mM)	$\frac{[\text{Bu}_2\text{Mg}]}{[\text{BuLi}]}$	Polymeriza- tion temperature (C)	Polymeriza- tion time (min)	Conv. (%)	Mn (x10 ⁻³)	Mw (x10 ⁻³)	Mw/Mn
Comp. Example 4-1	10	0.9	4	80	60	19	18	22	1.21
Comp. Example 4-2	10	0.9	4	80	120	38	33	43	1.30
Comp. Example 4-3	10	0.9	4	80	240	62	45	70	1.55
Comp. Example 5-1	50	4.3	6	25	120	1	ND	ND	ND
Comp. Example 5-2	50	4.3	6	25	240	3	ND	ND	ND
Comp. Example 5-3	50	4.3	6	25	480	6	0.7	0.8	1.17
Comp. Example 6-1	50	22	2	50	240	71	16	17	1.09
Comp. Example 6-2	50	22	2	50→80	240→60	100	20	22	1.10

- Cont'd -

Table 7 (Cont'd)

Comp. Example 7-1	50	22	1	50	240	62	13	14	1.07
Comp. Example 7-2	50	22	1	50→80	240→60	100	20	22	1.08
Comp. Example 8	30	13	0.5	30	60	100	14	16	1.14
Comp. Example 9	80	6.9	2	80	240	95	105	114	1.09
Comp. Example 10	80	6.9	1	25	240	100	110	118	1.07

Table 8

	Initiator	[SM] (vol%)	[Mg] (mM)	[Mg] [Li]		Polymerization temperature (°C)
Example 24-1	Bu ₂ Mg/sBuLi	80	6.9	4		80
Example 24-2	Bu ₂ Mg/sBuLi	80	6.9	4		80
Example 24-3	Bu ₂ Mg/sBuLi	80	6.9	4		80
Example 25-1	Bu ₂ Mg/tBuLi	80	6.9	4		80
Example 25-2	Bu ₂ Mg/tBuLi	80	6.9	4		80
Example 25-3	Bu ₂ Mg/tBuLi	80	6.9	4		80
Example 26-1	Bu ₂ Mg/StLi	80	6.9	4		80
Example 26-2	Bu ₂ Mg/StLi	80	6.9	4		80
Example 26-3	Bu ₂ Mg/StLi	80	6.9	4		80
Example 27-1	Bu ₂ Mg/sBuOH (1/1)	100	8.6	--		150
Example 27-2	Bu ₂ Mg/sBuOH (1/1)	100	8.6	--		150
Example 27-3	Bu ₂ Mg/sBuOH (1/1)	100	8.6	--		150
Example 28-1	Bu ₂ Mg/Bu ₂ NH (1/1)	100	8.6	--		150
Example 28-2	Bu ₂ Mg/Bu ₂ NH (1/1)	100	8.6	--		150
Example 28-3	Bu ₂ Mg/Bu ₂ NH (1/1)	100	8.6	--		150

- Cont'd -

Table 8 (Cont'd)

Polymerization time (min)	Conv. (%)	Mn ($\times 10^{-3}$)	Mw ($\times 10^{-3}$)	Mw/Mn
60	40	32	36	1.13
120	63	47	55	1.16
240	89	68	84	1.24
60	40	32	36	1.13
120	63	47	55	1.16
240	89	68	84	1.24
60	60	70	82	1.17
120	82	82	101	1.23
240	96	91	114	1.25
60	50	47	66	1.40
120	76	74	104	1.41
240	90	85	120	1.41
60	40	37	55	1.50
120	58	55	82	1.50
240	83	39	59	1.51

Table 9

	Initiator	[SM] (vol%)	[Mg] (mM)	$\frac{[\text{Mg}]}{[\text{Li}]}$	Polymer- ization temperature (°C)	Polymeriza- tion time (min)	Conv. (%)	Mn ($\times 10^{-3}$)	Mw ($\times 10^{-3}$)	Mw/Mn
Example 30	Bu ₂ Mg/nBuLi (6/1)	100	8.6	6	80→120	120→30	100	95	103	1.09
Comp. Example 11	nBuLi	50	4.3	0	80	~1	100	94	127	1.35
Comp. Example 12	None	100	---	---	120	240	21	250	437	1.75

Notes: In Example 30, polymerization was first carried out at 80°C for 120 minutes and then further conducted at 120°C for 30 minutes. EB was used as polymerization solvent in Example 30 and Comparative Example 11.

In Comparative Example 11, runaway reaction took place and the internal temperature ultimately rose to 150-160°C.

In Comparative Example 12, radical polymerization was carried out. Unreacted monomer was removed by reprecipitating the polymer in methanol.

	Amount of metals after washing of polymer		
	Mg	Li	Mg/Li
Example 30	25	4	6.3
Comp. Example 11	---	30	---

Table 10

	SM concentration in polymer after heat retention test*		
	Retention time		
	10	20	40
Example 30	38	95	200
Comp. Example 11	90	190	410
Comp. Example 12	140	265	530

* Unit: ppm

Table 11

	Polymer characteristics			Content in polymer (ppm)	
	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n	SM	Trimer
Example 31	91	319	3.5	10	52
Comp. Example 13	254	305	1.2	16	75
Comp. Example 14	96	328	3.4	450	1810

Table 12

	Amount of SM existing in foam	Foam characteristics		
		Foaming rate	Form diameter (mm)	Ratio of open cells
Example 31	21	16	22	94
Comp. Example 13	28	12	21	38
Comp. Example 14	558	15	22	93



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1. A process for producing a vinyl polymer which comprises carrying out anionic polymerization under the conditions that the polymerization temperature is not
5 lower than 45°C and not higher than 250°C, and that the concentration of the vinyl monomer based on the polymerization solvent is 45-100% by weight, in which anionic polymerization the metal of the cation forming a counterpart to the carbonic anion at the polymerization
10 propagating species consists essentially of Mg, or Mg and M^1 wherein M^1 is at least one alkali metal selected from the group consisting of Li, Na and K, and the molar concentrations of Mg and M^1 satisfy the relation of $[Mg]/[M^1] \geq 4$.
- 15 2. The process according to Claim 1 wherein $(R^2)_2Mg$ wherein R^2 is a hydrocarbon group is used singly as polymerization initiator.
3. The process according to Claim 1 wherein organic compounds represented by $(R^2)_2Mg$ and R^1M^1 and/or R^1OM^1
20 wherein R^1 and R^2 are each a hydrocarbon group, O is an oxygen atom and M^1 is at least one alkali metal selected from the group consisting of Li, Na and K are used as polymerization initiator, and the molar concentrations of Mg and M^1 satisfy the relation of $[Mg]/[M^1] \geq 4$.
- 25 4. The process according to Claim 1 or 3 wherein said molar concentrations satisfy the relation of $[Mg]/[M^1] = 10-100$.
5. The process according to Claim 1 wherein

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- compounds represented by $(R^2)_2Mg$ and R^1M^1 and R^3OH and/or $(R^3)_2NH$ wherein R^1 , R^2 and R^3 are each a hydrocarbon group, O is an oxygen atom, N is a nitrogen atom and M^1 is at least one alkali metal selected from the group consisting of Li, Na and K are used as polymerization initiator by mixing them so as to satisfy the relations of $[Mg] > [M^1]$ and $2 \times [Mg] + [M^1] > [R^3OH] + [(R^3)_2NH]$.
6. The process according to Claim 1 wherein the polymerization temperature in the region of conversion of the vinyl monomer of 0-70% is not lower than 45°C and not higher than 200°C.
7. The process according to any one of Claims 3-5 wherein in the organic compounds represented by $(R^2)_2Mg$ and R^1M^1 , at least one of the carbons attached to the metals of the hydrocarbon groups R^1 and R^2 is a secondary carbon and/or tertiary carbon, and the total amount $[R^{1,2}]$ of R^1 and R^2 of the secondary carbon and/or tertiary carbon satisfies the relation of $[R^{1,2}] \geq [Mg]$.
8. The process according to Claim 7 wherein in the organic compounds represented by $(R^2)_2Mg$ and R^1M^1 , at least one of the hydrocarbon groups R^1 and R^2 is a polymer carbonic anion.
9. The process according to Claim 1 wherein the compounds represented by $(R^2)_2Mg$ and R^3OH and/or $(R^3)_2NH$ wherein R^2 and R^3 are each a hydrocarbon group, O is an oxygen atom and N is a nitrogen atom are used as polymerization initiator by mixing them so as to satisfy the relation of $2 \times [Mg] > [R^3OH] + [(R^3)_2NH]$.



10. The process according to Claim 1 wherein the polymerization solvent is a hydrocarbon compound.
11. The process according to Claim 1 wherein the concentration of the vinyl monomer based on the
5 polymerization solvent is substantially 100% by weight.
12. The process according to Claim 1 wherein the polymerization reaction is conducted in an extruder.
13. An initiator for polymerization of vinyl monomers, which comprises $(R^2)_2Mg$ wherein R^2 is a
10 hydrocarbon group.
14. A vinyl monomer polymerization initiator which comprises organic metal compounds represented by $(R^2)_2Mg$ and R^1M^1 and/or R^1OM^1 wherein R^1 and R^2 are each a hydrocarbon group, O is an oxygen atom and M^1 is at least
15 one alkali metal selected from the group consisting of Li, Na and K, and the molar concentrations of the metals satisfy the relation of $[Mg]/[M^1] \geq 4$.
15. A vinyl monomer polymerization initiator which comprises organic metal compounds represented by $(R^2)_2Mg$
20 and R^1M^1 and/or R^1OM^1 wherein R^1 and R^2 are each a hydrocarbon group, O is an oxygen atom and M^1 is at least one alkali metal selected from the group consisting of Li, Na and K, and the molar concentrations of the metals satisfy the relation of $[Mg]/[M^1] = 10-100$.
- 25 16. A vinyl monomer polymerization initiator comprising compounds represented by $(R^2)_2Mg$ and R^1M^1 and R^3OH and/or $(R^3)_2NH$ wherein R^1 , R^2 and R^3 are each a hydrocarbon group, O is an oxygen atom and N is a nitrogen



atom and M^1 is at least one alkali metal selected from the group consisting of Li, Na and K, and satisfying the relations of $[Mg] > [M^1]$ and $2 \times [Mg] + [M^1] > [R^3OH] + [(R^3)_2NH]$.

- 5 17. A vinyl monomer polymerization initiator comprising compounds represented by $(R^2)_2Mg$ and R^3OH and/or $(R^3)_2NH$ wherein R^2 and R^3 are each a hydrocarbon group, O is an oxygen atom and N is a nitrogen atom, and satisfying the relation of $2 \times [Mg] > [R^3OH] + [(R^3)_2NH]$.
- 10 18. A vinyl polymer obtainable from the process set forth in any one of Claims 1-12.
19. A styrene resin composition which is a styrene polymer obtained by anionic polymerization, wherein its molecular weight distribution Mw/Mn is 2.0-10.0 and
- 15 wherein the content of the trimer originating in the styrene monomer is 250 ppm or less.
20. A molded article obtained by injection molding or extrusion molding the styrene resin composition set forth in Claim 18 or 19.

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ABSTRACT

A process for producing a vinyl polymer which comprises carrying out anionic polymerization under the condition that the polymerization temperature is not lower than 45°C and not higher than 250°C and the concentration of the vinyl monomer based on the polymerization solvent is 45-100% by weight, wherein the metal of the cation forming a counterpart to the carbonic anion at the polymerization propagating species consists essentially of Mg, or Mg and M^1 wherein M^1 is at least one alkali metal selected from the group consisting of Li, Na and K, and the molar concentrations of the metals of Mg and M^1 satisfy the relation of $[Mg]/[M^1] \geq 4$, the invention also relates to a vinyl monomer polymerization initiator comprising $(R^2)_2Mg$ wherein R^2 is a hydrocarbon group.

FIG. 1

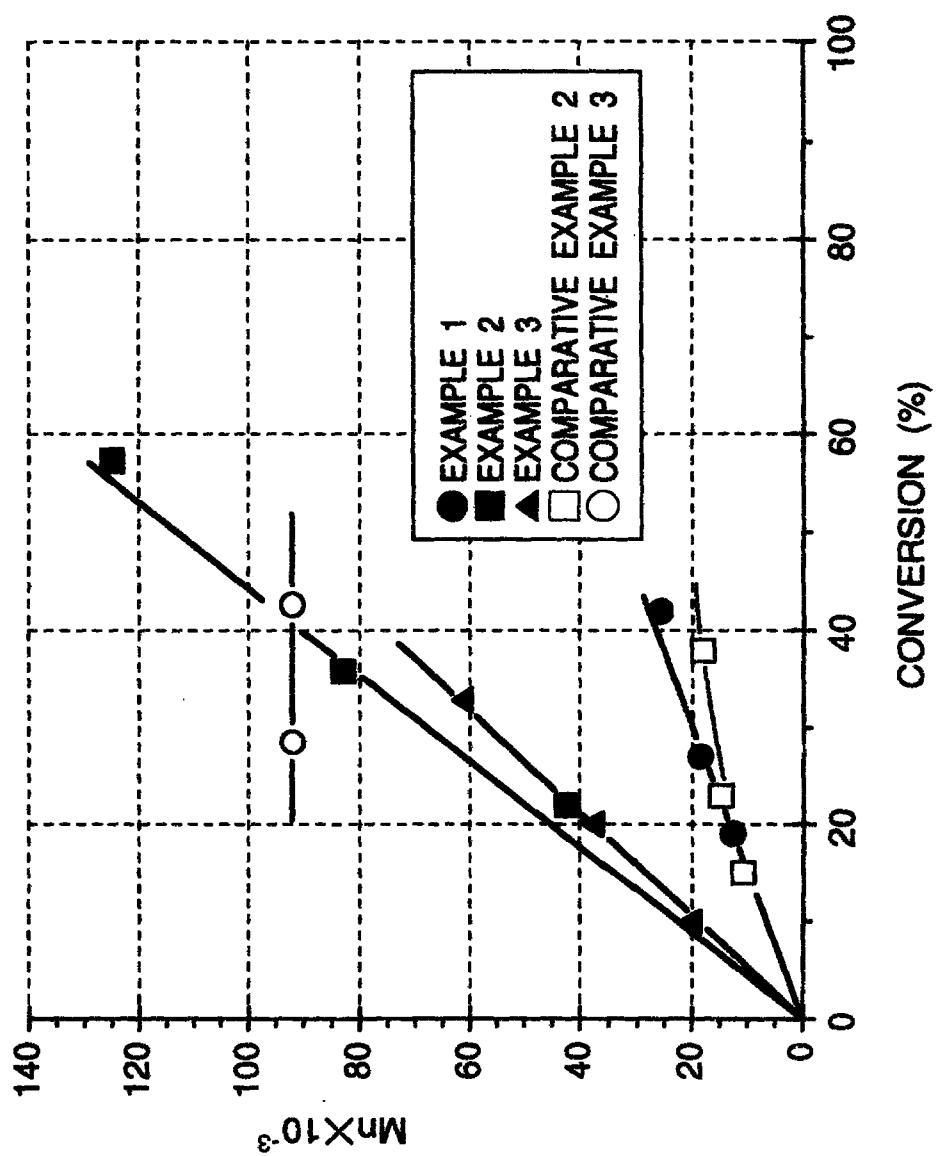


FIG. 2

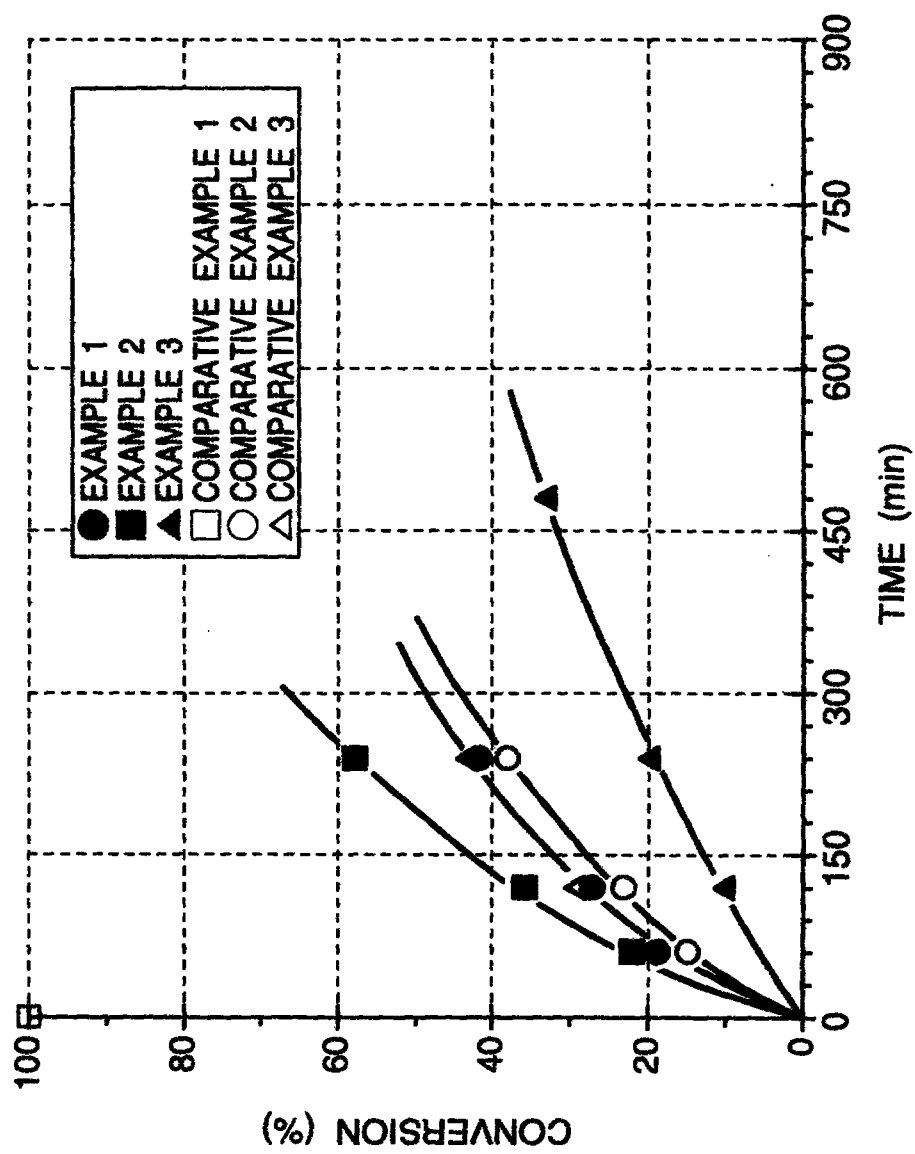


FIG. 3

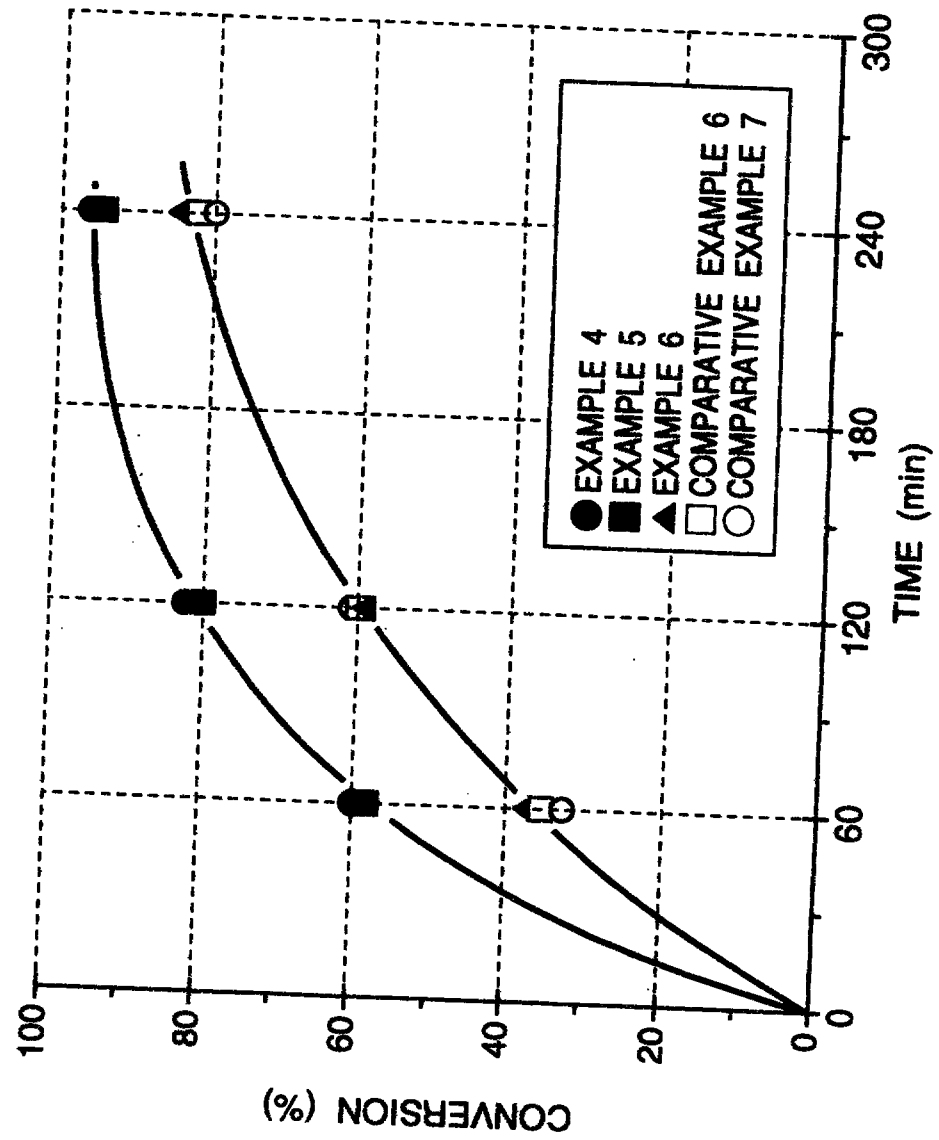


FIG. 4

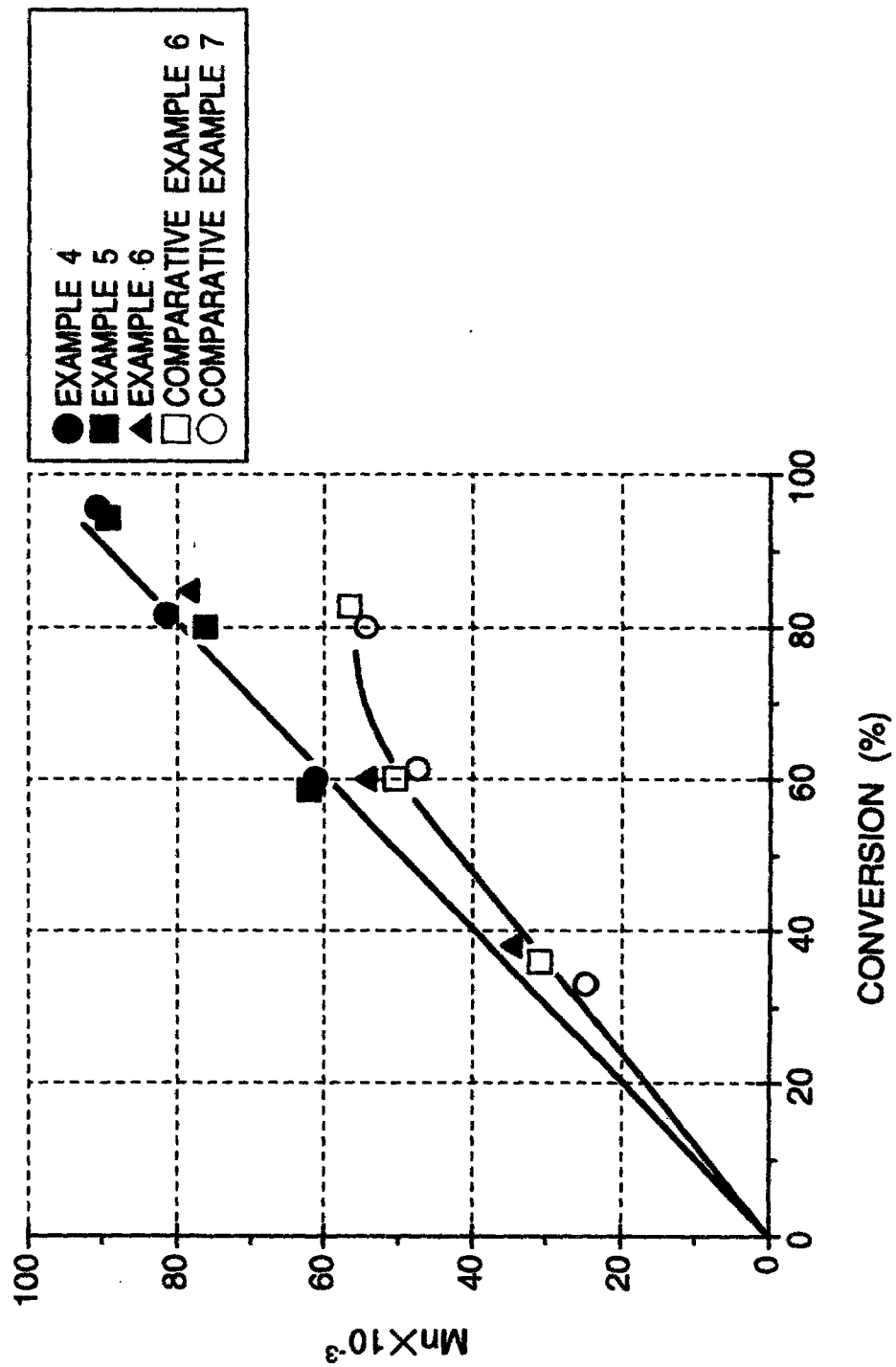


FIG. 5

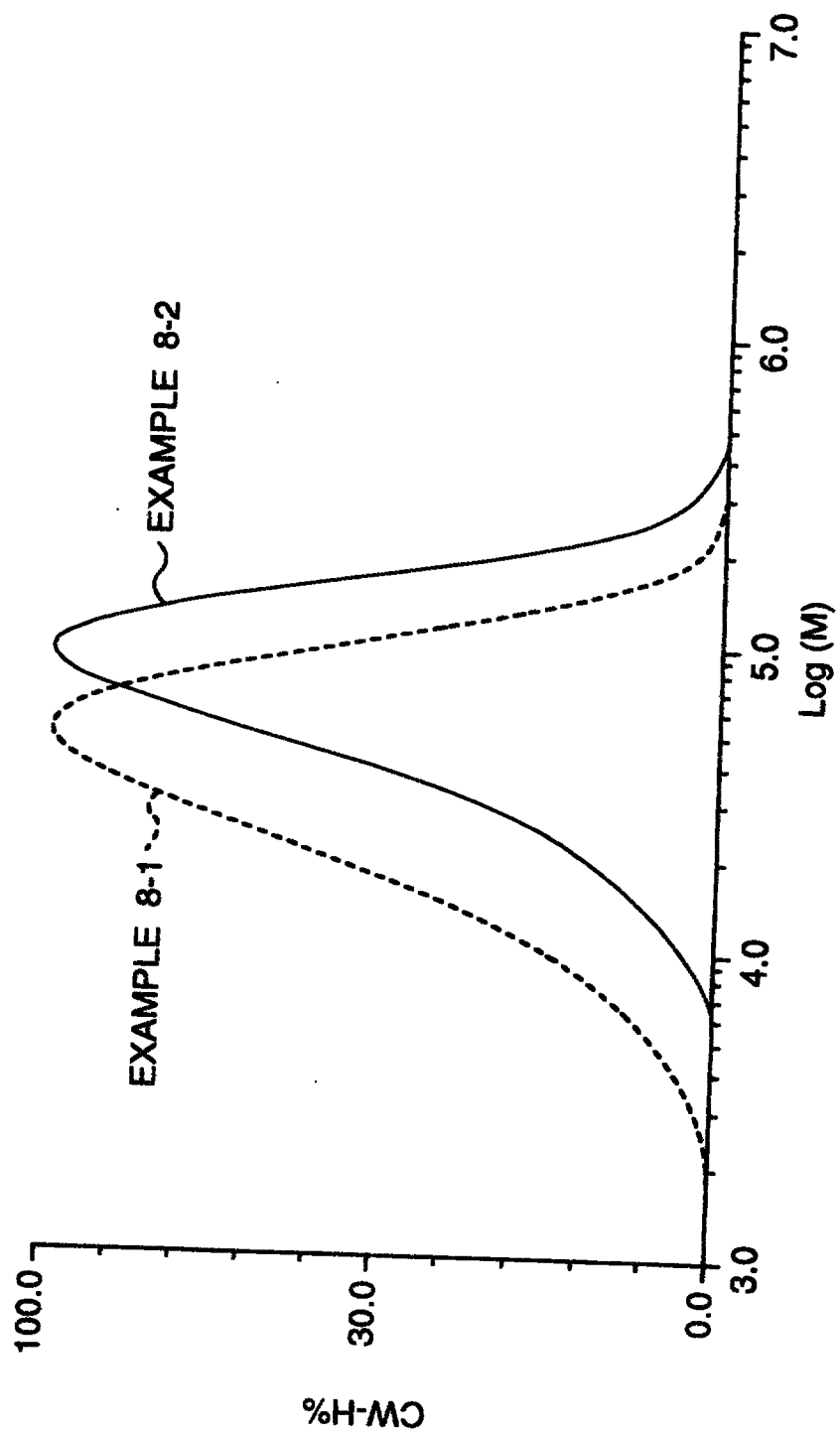


FIG. 6

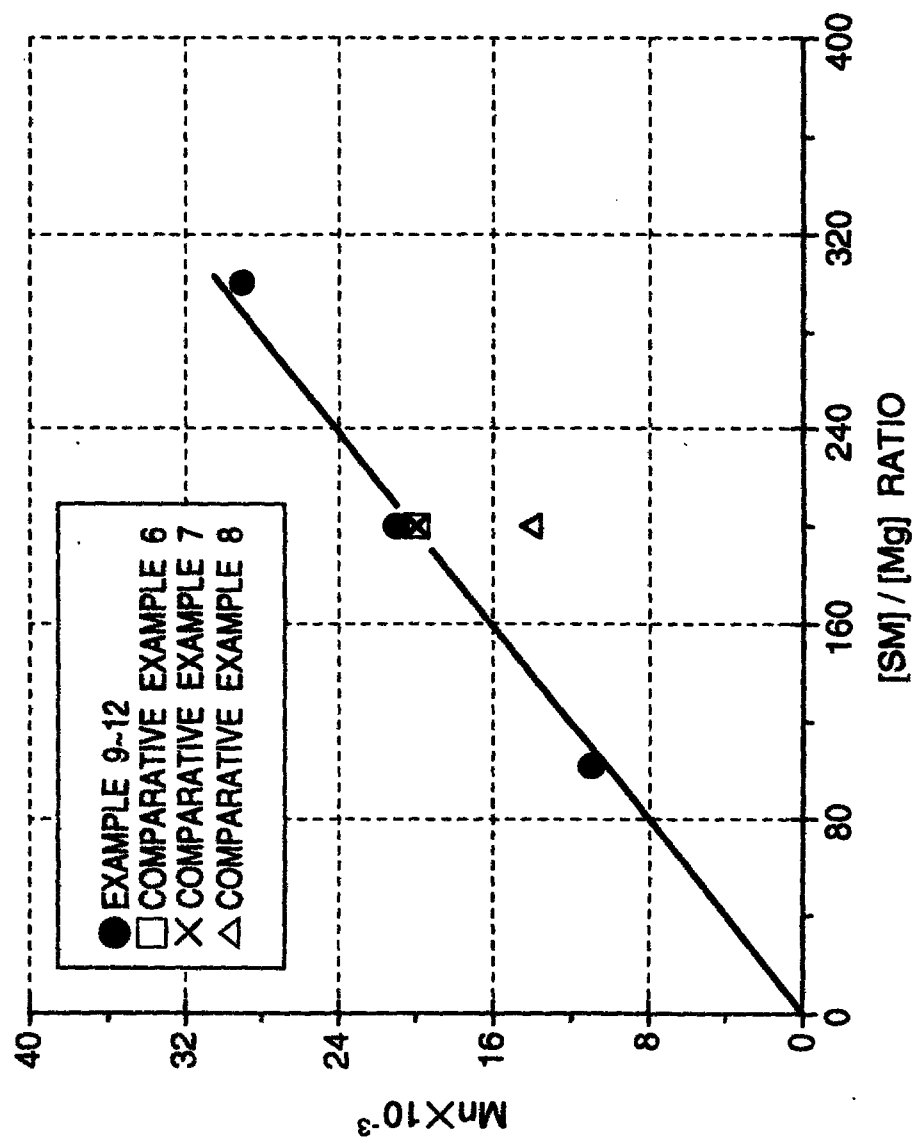


FIG. 7

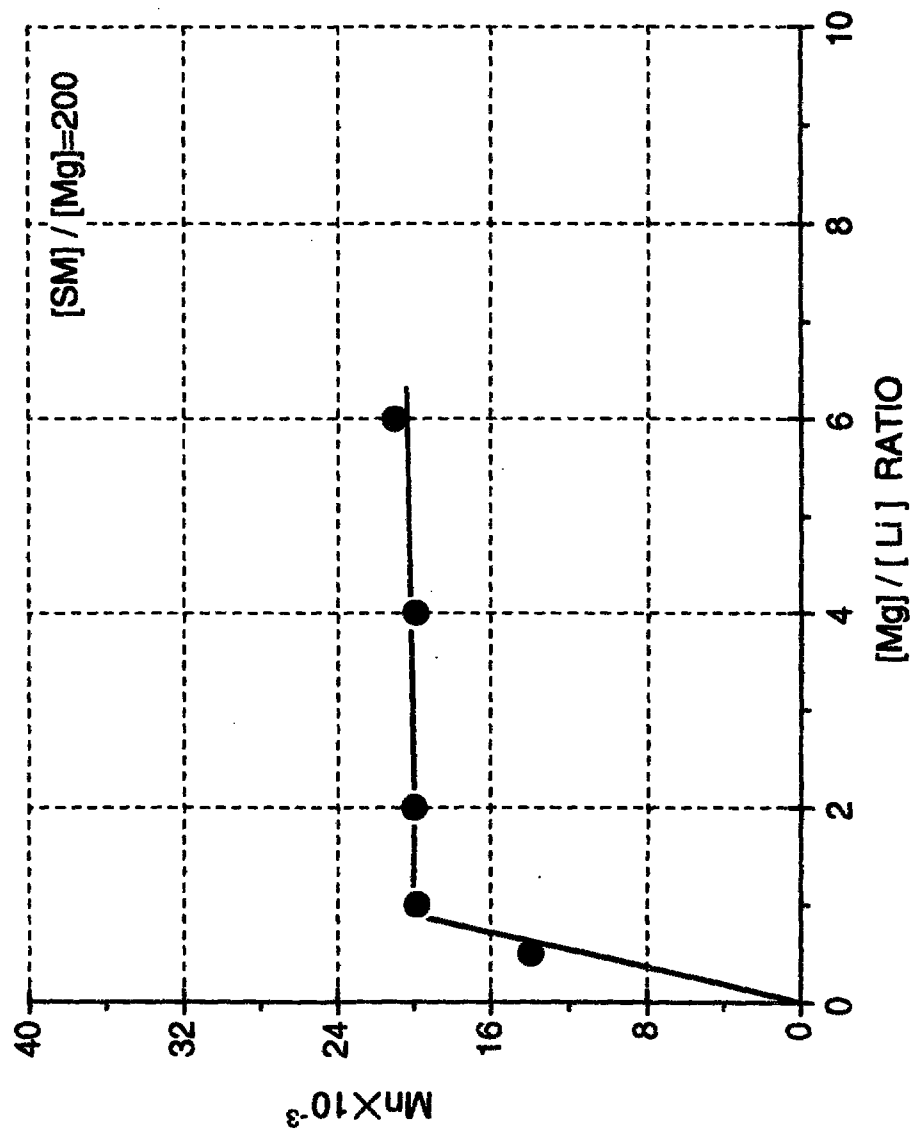


FIG. 8

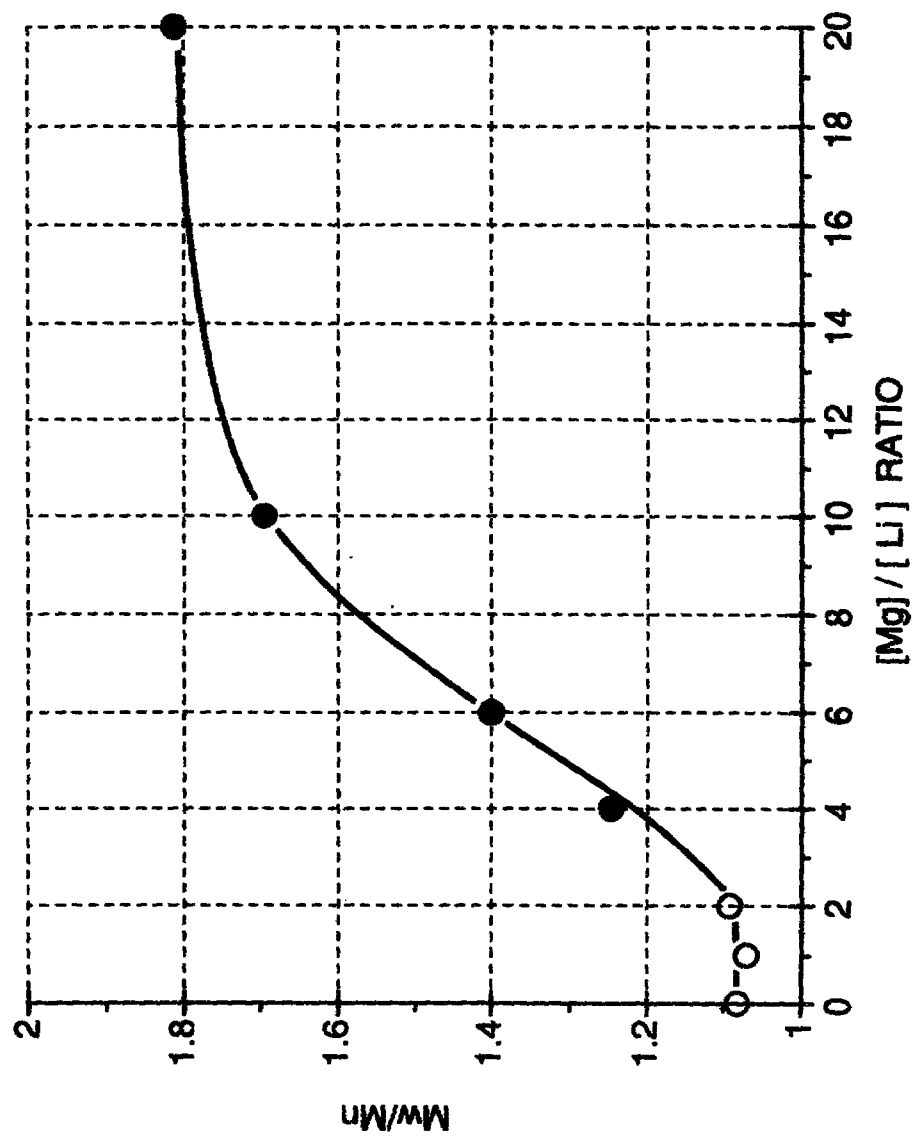


FIG. 9

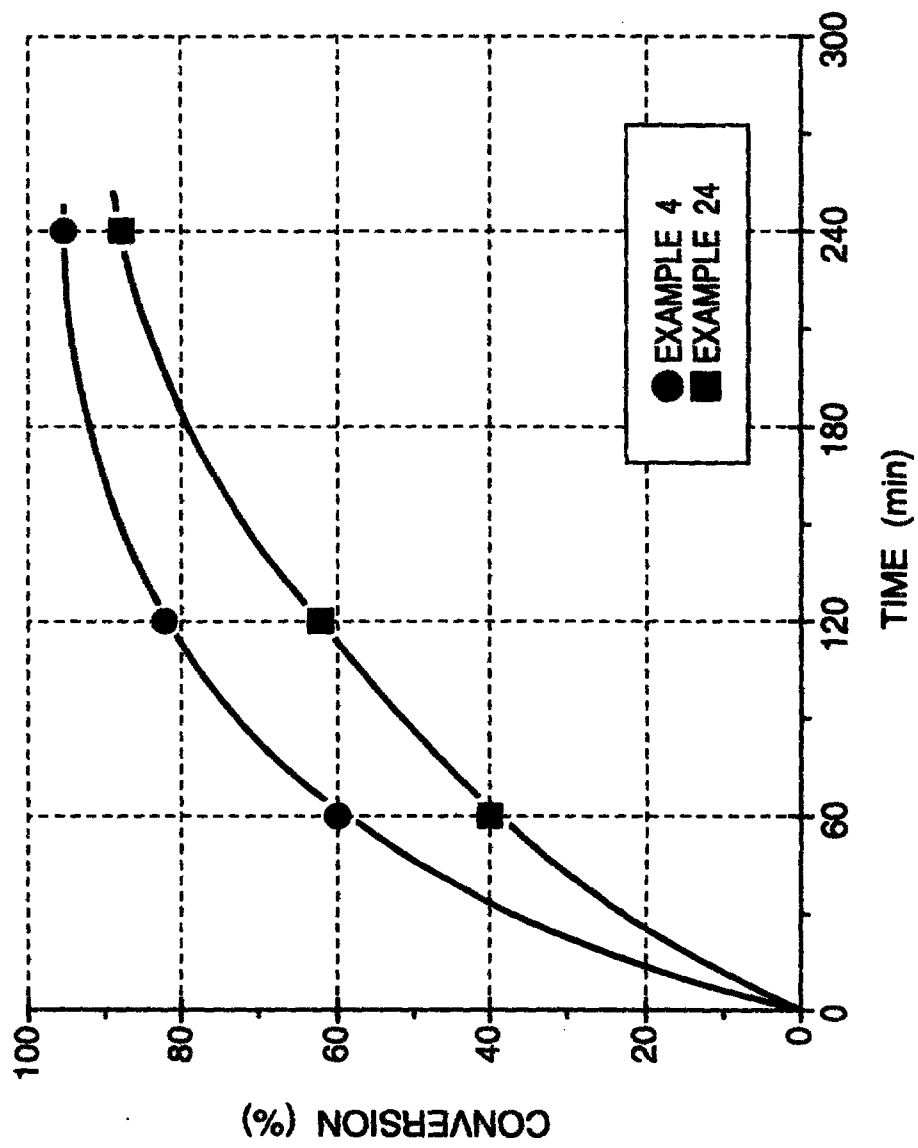
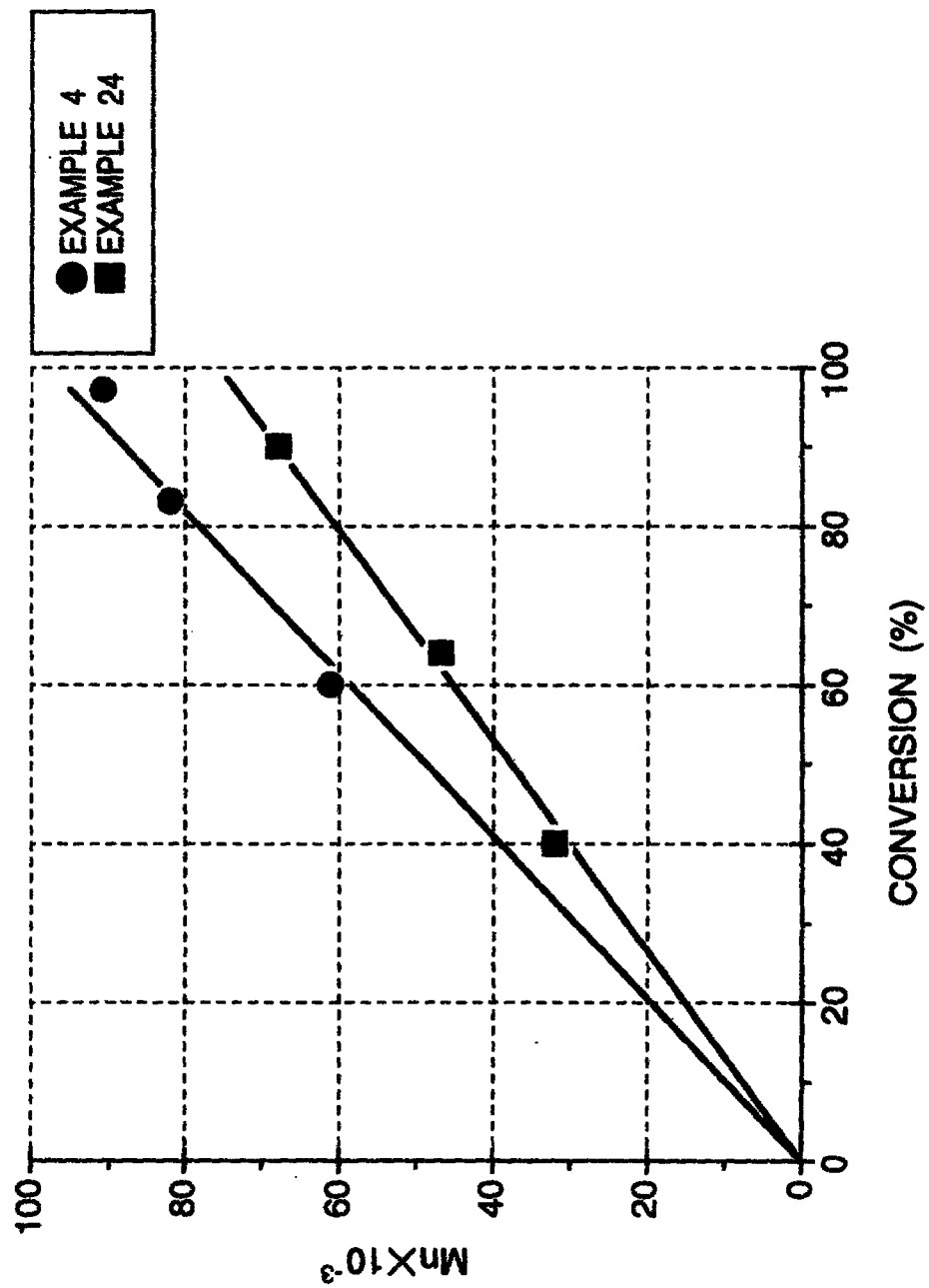


FIG. 10



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reaction. In view of the fact that the reaction rate is high and the volume of heat generated is large in the initial stage of the polymerization reaction when the monomer concentration is high, it is recommended to

5 initiate the polymer-ization reaction at a low temperature and gradually raise the temperature as the monomer concentration lowers with the progress of the reaction. Polymerization is preferably carried out in the temperature range of 45-200°C when the conversion of the

10 vinyl monomer is in the range of 0-70%, and a polymerization temperature in the range of not lower than 200°C and not higher than 250°C is preferred when the conversion is in the range of 70% or higher. In case the viscosity of the polymerization reaction solution is low

15 and there is no need of raising the polymerization temperature more than necessary, polymerization may be conducted at a temperature of 200°C or lower in the 70-100% conversion region.

The concentration of the vinyl monomer based on

20 the polymerization ^{solution}~~solvent~~ is not lower than 45% by weight and not higher than 100% by weight, preferably not lower than 50% by weight and not higher than 100% by weight. The higher the monomer concentration, the more desirable for the recovery of solvent, but there are the cases,

25 depending on the type of the polymer produced, where a solvent is required to some extent from the relation between temperature and viscosity of the polymerization solution. However, since an extremely low monomer

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for example, an ether compound such as tetrahydrofuran, dioxane, trioxane, etc., a tertiary amine such as tetramethylethylenediamine, a nitrogen compound such as pyridine, an aliphatic saturated hydrocarbon compound such as pentane, n-hexane, heptane, octane, nonane, decane, etc., and a weak Lewis acid such as triethylaluminum, diethyl zinc, etc., may be contained in the solvent within limits which do not jeopardize the effect of the present invention.

10 The "organic magnesium compounds represented by $(R^2)_2Mg$ " used in the present invention are the compounds in which a hydrocarbon group is attached to Mg. The hydrocarbon group is preferably a (linear or branched) alkyl group represented by $CH_3(CH_2)_n$ - such as methyl, ethyl, propyl, isopropyl, n-butyl, t-butyl, sec-butyl, amyl and hexyl. Preferred examples of the magnesium compounds include di-n-butylmagnesium, di-t-butylmagnesium, di-sec-butylmagnesium, n-butyl-sec-butylmagnesium, n-butylethylmagnesium and n-amylmagnesium. These compounds may be used either singly or in combination.

It has been known that no polymerization of a vinyl monomer is initiated when R^2Mg (R: alkyl) is used singly, and that no polymerization is initiated unless a polar compound such as hexamethylphosphoramide (~~hexamethylformamide~~) (HMPA) is added.

25 The present inventor found, however, that even if an R^2Mg compound is used singly, with no polar compound added, and even in a non-polar hydrocarbon solvent, the polymerization of a vinyl monomer is initiated under a specific

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using a polymerization initiator composed of dibutyl magnesium and butyl lithium at a concentration ratio ($[Mg]/[Li]$) of 2.5, and then polybutadiene ~~butadiene~~ is blocked with polystyrene to form a block copolymer, ~~styrene~~. In this case, however, the monomer concentration
5 based on the polymerization solvent (cyclohexane) is as low as 20%, and although no runaway reaction occurs, the activity of the living polymer lowers, so that unreacted polystyrene remains in the ensuing step of block
polymerization of butadiene. In addition, the molecular
10 weight M_n of the obtained copolymer is as low as 8,900.

The present inventor found that if the polymerization initiator composed of R^2Mg and R^1M^1 and/or R^1OM^1 satisfies the particular relation of $[Mg]/[M^1] \geq 4$ ($[]$: molar concentration) for the molar concentration ratio of
15 metals, living polymerization proceeds without causing a runaway reaction even under the high temperature and high monomer concentration conditions. Thus, it is possible to the control molecular weight, polymerization rate and molecular weight distribution independently of each other.

20 It has never been possible with the conventional anionic polymerization techniques to control molecular weight, polymerization rate and molecular weight distribution independently of each other in one pot of polymerization, so that this finding is quite surprising
25 and the present invention could have never been predicted from the prior art.

Such effect of the present invention is speculated to be attributable to the following mechanism.

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of Mg since Mg always exists at the propagating species of polymerization, the polymerization rate is governed by the $[Mg]/[M^1]$ ratio since M^1 is activated to permit the polymerization to advance, and the molecular weight distribution is also governed by the $[Mg]/[M^1]$ ratio because of the bias of equilibrium and exchange rate to the other dormant terminals of RM^1 .

As the activator of the polymerization initiator in the present invention (when the term "polymerization initiator" is used in this specification, it may include its activator), the organic metal compounds represented by R^1M^1 and/or R^1OM^1 (R^1 and R^2 : a hydrocarbon group; O: an oxygen atom; M^1 is at least one alkali metal selected from the group consisting of Li, Na and K) are preferably used. Specifically, R^1 in the formula R^1M^1 represents a hydrocarbon group, preferably a linear or branched alkyl group represented by $CH_3(CH_2)_n$ - such as methyl, ethyl, propyl, isopropyl, n-butyl, t-butyl, sec-butyl, amyl or hexyl. Typical examples of R^1M^1 include methyl lithium, n-butyl lithium, sec-butyl lithium, t-butyl lithium, isopropyl lithium, n-propyl lithium, iso-propyl lithium, benzyl lithium, phenyl lithium, hexyl lithium, butyl sodium, butyl ^{potassium}calcium, and cumyl potassium. These compounds may be used either singly or in combination.

R^1 in the formula R^1OM^1 represents a hydrocarbon group, preferably a linear or branched alkyl group represented by $CH_3(CH_2)_n$ - such as methyl, ethyl, propyl, isopropyl, n-butyl, t-butyl, sec-butyl, amyl or hexyl, a

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The present inventor found that when a vinyl monomer is polymerized by varying the $[Mg]/[M^1]$ ratio under conditions for completing polymerization in a certain prescribed period of time, quite surprisingly the

5 molecular weight distribution widens sharply in the region of $[Mg]/[M^1] \geq 4$. This is probably because the viscosity of the reaction system rises up with progress of polymerization in the high monomer concentration range, causing an apparent drop of exchange reaction rate of the

10 activator for the polymerization initiator.

For reducing the viscosity of the high concentration solution in the reaction system, it is recommended to carry out polymerization at a high temperature of 100 C or more, and to set the Mg and M^1

15 molar concentration ~~rate~~ ^{ratio} at $[Mg]/[M^1] \geq 10$ for allowing progress of living polymerization without causing a runaway reaction in such a situation. The present inventor also found that the molecular weight distribution widens consistently as the $[Mg]/[M^1]$ ratio increases. However,

20 excessive increase of the $[Mg]/[M^1]$ ratio is undesirable as it causes too much widening of the molecular weight distribution and also increases the amount of the low molecular weight components, for example, oligomer moieties including dimers and trimers. The most preferred

25 range of molar concentration ratio is $10 \leq [Mg]/[M^1] \leq 100$.

The present inventor further found that when a compound or compounds represented by R^3OH and/or $(R^3)_2NH$ (R^3 : a hydrocarbon group; O: an oxygen atom; N: a nitrogen

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atom), which normally can serve as an anionic

polymerization terminator, is added to an initiator consisting of $(R^2)_2Mg$ and R^1M^1 ($[Mg] > [M^1]$) at a specific ratio, quite surprisingly polymerization of vinyl monomers is initiated and further living polymerization proceeds under the high-temperature and high-concentration conditions.

In R^3OH and $(R^3)_2NH$ used in the present invention, R^3 's are the hydrocarbon groups, which are preferably linear or branched alkyl groups represented by $CH_3(CH_2)_n-$, such as methyl, ethyl, propyl, isopropyl, n-butyl, t-butyl, sec-butyl, amyl and hexyl, phenyl groups, alkyl-substituted phenyl groups, hydrocarbon-based ether compound groups represented by $CH_3(OCH_2CH_2)_n-$, and the groups represented by $(CH_3)_2N(CH_2CH_2)_n-$. Typical examples of R^3OH are methanol, ethanol, propanol, isopropanol, n-butyl alcohol, sec-butyl alcohol, tert-butyl alcohol, amyl alcohol, hexyl alcohol, phenol, 2,4-di-tert-butylphenol, 2,6-di-tert-butylphenol, 3,5-di-tert-butylphenol, 2,6-di-tert-butyl-4-methylphenol, 2-methoxyethanol, and 2-(2-di-tert-methoxyethoxy)ethanol. Examples of $(R^3)_2NH$ are N,N-dimethylethanolamine, dimethylamine, N-ethylmethylaniline, diethylamine, dipropylamine, dibutylamine, dihexylamine, dioctylamine, didecylamine, N,N,N'-trimethylethylenediamine, N,N,N',N'-tetramethyldiethylenetriamine and the like. These compounds may be used either singly or in combinations of two or more.

R^3OH and $(R^3)_2NH$ added must be in an amount that

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Detector temp.: 330°C

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Internal standard reagent: anthracene

[GPC measuring conditions]

5 Measuring device: TOSO HLC-8020 (with built-in
differential refractive index
detector)

Column: TOSO TSKgel-GMH_{XL} x 2

Temperature: 38°C

Solvent: tetrahydrofuran (THF)

10 Sample concentration: 0.1 wt/v%

Sampling pitch: once per 0.4 second

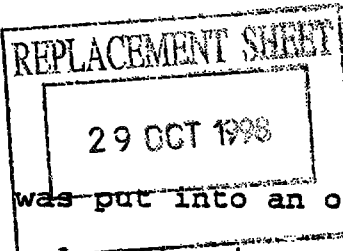
Determination of molecular weight:

15 Calibration curves were drawn by plotting the
relation between the molecular weight of TOSO
TSK standard polystyrenes and elution time as
third-order regression ~~repression~~ curve, and the molecular
weight was determined from the curve.

In the following Examples and Comparative
Examples, all the polymerization operations were carried
20 out according to the following procedure unless otherwise
noted.

[Polymerization operation]

25 A glass container and a syringe, which had been
heated to 140°C and dried, a monomer, a solvent and a
reagent were placed in a nitrogen globe (Model VDB-SA-Q
mfd. by Eiko Shokai KK). The inside atmosphere of the
nitrogen globe has been well substituted with nitrogen
which had been dehydrated and dried with molecular sieves.



was put into an oil bath of 120°C. In a few minutes, the suddenly boiled up polymerization solution was ~~/bumped~~ to conclude polymerization (runaway reaction occurred).

5 Comparative Example 2

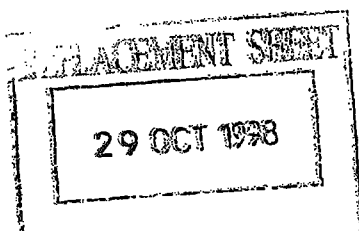
The procedure of Example 1 was followed except that polymerization was carried out at the concentration shown in Table 2. Polymerization proceeded without causing a runaway reaction, but as seen from FIG. 1, Mn increased
10 deviating from linearity with conversion and the living polymerization activity was decreased with increase of conversion.

Comparative Example 3

15 The procedure of Example 1 was followed except that polymerization was carried out at 150°C without adding the Bu₂Mg initiator solution.

As seen from plotting of Mn and conversion in FIG. 1, this polymerization solution (conventional heat
20 radical polymerization solution) was constant in molecular weight regardless of the progress of polymerization. Also, the polymers obtained only had a wide molecular weight distribution ($M_w/M_n = 2.2$).

The polymerization conditions of Examples 1-3
25 are 120-150°C and 6 hours, which are the conditions normally supposed to cause heat radical polymerization. However, no peak of the molecular weight such as shown in Comparative Example 3 was observed in GPC analysis. This



was observed no peak of molecular weight attributable to radical polymerization.

Example 29

5 High-temperature bulk polymerization of SM was carried out using a polymerization initiator $\text{Bu}_2\text{Mg}/\text{nBuLi}$ (10/1) of the present invention in an extruder (ZSK-25 (L/D = 47) mfd. by Werner Corp.).

The 11 blocks of the extruder were set at the following temperatures: block 1 : room temperature; block 10 2 : 120°C; blocks 3 and 4 : 140°C; blocks 5 and 6 : 160°C; blocks 7 and 8 : 200°C; blocks 9-11 : 220°C. A liquid-adding device was provided between the blocks 8 and 9, from which the polymerization terminator (a mixed solution 15 of BuOH and EB) was supplied under pressure. The purified and dehydrated SM, EB and EB-diluted $\text{Bu}_2\text{Mg}/\text{nBuLi}$ (10/1) initiators were stored in the respective containers under a closed nitrogen atmosphere. The materials in the respective containers can be fed into ~~a tank provided with~~ 20 a 3-liter tank provided with an agitating element by a gear pump, and therefrom into the zone 1 of the extruder by another gear pump. The interior atmosphere of the extruder was well substituted with dry nitrogen and a mixed solution of EB and initiator was fed into the extruder to clean its interior. Then the 25 concentration of SM was gradually raised to finally reach $\frac{100\%}{100}$. The SM feed rate was set at 100 ml/min. The initiator was supplied in such an amount that $[\text{SM}]/[\text{Mg}]$ would become 1,000. The polymer extruded from the die was

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obtained foam were also determined. The results are shown in Tables 11 and 12.

Comparative Example 13

5 Using nBuLi as initiator and EB as solvent, polymerization was carried out at an SM concentration of 50 vol% in a 100-liter autoclave. The polymerization temperature rose to 145°C. The solvent was removed from the obtained polymer solution by a drum dryer. The polymer
10 was then put into an extruder having a cylinder temperature of 220°C and the residual EB was vented away. The polymer was recovered as pellets. The results are shown in Tables 11 and 12.

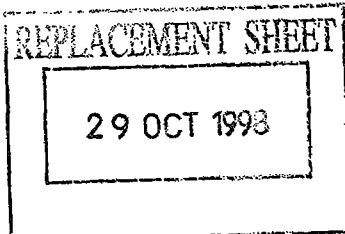
15 Comparative Example 14

A polymer obtained from radical polymerization was extrusion foamed in the same way as in Example 31, and the open cell rate and monomer content of the obtained foam were examined. The results are shown in Tables 11 and
20 12.

This application is based on Japanese Patent Application No. 8-084474 filed in Japan on March 14, 1996, Japanese Patent Application No. 8-303483 filed in Japan on October 30, 1996, and Japanese Patent Applica-tion No. 8-
25 303484 filed in Japan on October 30, 1996, the contents of which are incorporated hereinto in its entirety by reference.

Table 5 (Cont'd)

Polymerization time (min)	Conv. (%)	Mn ($\times 10^{-3}$)	Mw ($\times 10^{-3}$)	Mw/Mn
60	53	49	58	1.19
120	78	74	90	1.22
240	93	89	117	1.32
60	44	42	48	1.15
120	71	68	82	1.20
240	90	85	107	1.26
60	68	63	88	1.40
120	90	80	131	1.64
240	100 100	90	154	1.71
60	63	56	76	1.36
120	85	79	130	1.64
240	99	90	153	1.70
60	90	81	133	1.64
120	100 100	90	153	1.70



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CLAIMS

1. A process for producing a vinyl polymer which comprises carrying out anionic polymerization under the conditions that the polymerization temperature is not
5 lower than 45°C and not higher than 250°C, and that the concentration of the vinyl monomer based on the solution polymerization ~~solvent~~ is 45-100% by weight, in which anionic polymerization the metal of the cation forming a counterpart to the carbonic anion at the polymerization
10 propagating species consists essentially of Mg, or Mg and M¹ wherein M¹ is at least one alkali metal selected from the group consisting of Li, Na and K, and the molar concentrations of Mg and M¹ satisfy the relation of $[Mg]/[M^1] \geq 4$.
- 15 2. The process according to Claim 1 wherein (R²)₂Mg wherein R² is a hydrocarbon group is used singly as polymerization initiator.
3. The process according to Claim 1 wherein organic compounds represented by (R²)₂Mg and R¹M¹ and/or R¹OM¹
20 wherein R¹ and R² are each a hydrocarbon group, O is an oxygen atom and M¹ is at least one alkali metal selected from the group consisting of Li, Na and K are used as polymerization initiator, and the molar concentrations of Mg and M¹ satisfy the relation of $[Mg]/[M^1] \geq 4$.
- 25 4. The process according to Claim 1 or 3 wherein said molar concentrations satisfy the relation of $[Mg]/[M^1] = 10-100$.
5. The process according to Claim 1 wherein

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atom and M^1 is at least one alkali metal selected from the group consisting of Li, Na and K, and satisfying the relations of $[Mg] > [M^1]$ and $2 \times [Mg] + [M^1] > [R^3OH] + [(R^3)_2NH]$.

- 5 17. A vinyl monomer polymerization initiator comprising compounds represented by $(R^2)_2Mg$ and R^3OH and/or $(R^3)_2NH$ wherein R^2 and R^3 are each a hydrocarbon group, O is an oxygen atom and N is a nitrogen atom, and satisfying the relation of $2 \times [Mg] > [R^3OH] + [(R^3)_2NH]$.
- 10 18. A vinyl polymer obtainable from the process set forth in any one of Claims 1-12.
19. A styrene resin composition which is a styrene polymer obtained by anionic polymerization, wherein its molecular weight distribution Mw/Mn is 2.0-10.0 and
- 15 wherein the content of the trimer originating in the styrene monomer is 250 ppm or less.
20. A molded article obtained by injection molding vinyl polymer or extrusion molding the vinyl polymer ~~/styrene resin composition~~ set forth in Claim 18 ~~or 19~~.
21. A molded article obtained by injection molding or extrusion molding the styrene resin composition set forth in claim 19.



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(51) 国際特許分類6 C08F 4/50, 12/08	A1	(11) 国際公開番号 WO97/33923 (43) 国際公開日 1997年9月18日(18.09.97)
(21) 国際出願番号 PCT/JP97/00796 (22) 国際出願日 1997年3月13日(13.03.97) (30) 優先権データ 特願平8/84474 1996年3月14日(14.03.96) JP 特願平8/303483 1996年10月30日(30.10.96) JP 特願平8/303484 1996年10月30日(30.10.96) JP (71) 出願人 (米国を除くすべての指定国について) 旭化成工業株式会社 (ASAHI KASEI KOGYO KABUSHIKI KAISHA)[JP/JP] 〒530 大阪府大阪市北区堂島浜一丁目2番6号 Osaka, (JP) (72) 発明者; および (75) 発明者/出願人 (米国についてのみ) 江原賢司(EBARA, Kenji)[JP/JP] 〒233 神奈川県横浜市港南区大久保3丁目36番5号 Kanagawa, (JP) (74) 代理人 弁理士 浅村 皓, 外(ASAMURA, Kiyoshi et al.) 〒100 東京都千代田区大手町2丁目2番1号 新大手町ビル331 Tokyo, (JP)	(81) 指定国 CN, DE, JP, KR, SG, US. 添付公開書類 国際調査報告書	
(54)Title: PROCESS FOR THE PREPARATION OF VINYLIC POLYMERS, POLYMERIZATION INITIATOR FOR VINYLIC MONOMERS, AND STYRENE RESIN COMPOSITION (54)発明の名称 ビニル系重合体の製造方法、ビニル系単量体重合用開始剤及びスチレン系樹脂組成物 (57) Abstract A process for the preparation of vinylic polymers, which comprises conducting an anionic polymerization wherein the metal of the cation counter to the carb-anion of the propagation terminal is Mg or Mg/M¹ (wherein M¹ is at least one alkali metal selected from the group consisting of Li, Na and K and the molar concentrations of Mg and M¹ satisfy the relationship: [Mg]/[M¹] ≥ 4) under the conditions of polymerization temperature of 45 to 250 °C and concentration of vinylic monomers of 45 to 100 wt.% based on the solvent used in the polymerization; and a polymerization initiator for vinylic monomers containing (R²)₂Mg (wherein R² is hydrocarbyl).		

(57) 要約

重合成長末端の炭素アニオンと対になっているカチオンの金属がMgであるか、又はMg及びM' (M' は、Li, Na及びKからなる群から選ばれる少なくとも1種類のアルカリ金属であり、MgとM' の金属モル濃度が $[Mg] / [M'] \geq 4$ なる関係を満たす) であるアニオン重合を、重合温度45℃以上250℃以下、ビニル系単量体の重合溶媒に対する濃度が45wt%~100wt%の条件下で行うことからなるビニル系重合体の製造方法。(R²) : Mg (R² は炭化水素基) を含むビニル系単量体重合用開始剤。

情報としての用途のみ

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