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Preparation of poly(vinylaromatics) by dispersion polymerization with the addition of lubricants

- 5 The invention relates to a process for preparing polymers of vinylaromatic compounds in dispersion in the presence of a dispersing auxiliary and a catalyst, obtainable from A) a transition metal complex of subgroups II to VIII, B) a cation-forming agent and C), if desired, an aluminum compound.

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The polymers thereby obtainable can be used to produce fibers, films and moldings.

- 15 Polymerizing styrene in the presence of metallocene catalyst systems leads to polymers of high stereoregularity and is described at length, for example, in EP-A 0 210 615. Because of its high crystallinity, syndiotactic polystyrene has a very high melting point of about 270°C, high rigidity and tensile strength,
- 20 dimensional stability, a low dielectric constant and high chemical stability. The profile of mechanical properties is retained even above the glass transition temperature.

- 25 In the metallocene-catalyzed polymerization of styrene, there is frequently crystallization of the resulting syndiotactic polystyrene starting at a level of only about 10% conversion. This leads firstly to the formation of deposits on the walls and secondly to an extreme viscosity rise during the polymerization, which makes handling and dissipation of the heat of reaction more
- 30 difficult, especially on the industrial scale.

- To solve this problem a variety of techniques using special reactors or extruders have been tried out. EP-A-0 535 582
- 35 describes a process for preparing syndiotactic polystyrene in a stirred bed of solids, which is able to reduce the wall deposits but not prevent them. The reactor has to be equipped with a special stirrer in order to produce a homogeneous fluidized bed. Temperature control is by way of partial evaporation of styrene by reduced pressure, using a complex vacuum control system.
- 40

- EP-A 0 584 646 and EP-A 0 389 939 describe the preparation of syndiotactic polystyrene in self-cleaning twin-screw extruders or compounders with no dead spaces. In both processes, owing to the
- 45 sudden rise in frictional forces at higher levels of conversion, and to the motor output required for continued operation, polymerization is carried out not to complete conversion but only

to a level where the polymer powder, soaked with monomers, no longer agglomerates in the course of subsequent processing steps.

In the case of anionic initiation, the technique of dispersion polymerization is known. It is employed specifically to prepare small polystyrene particles, as described for example in Journal of Polymer Science, Part A, Polymer Chemistry, Vol. 34 (1996), pages 2633 - 2649. Of critical importance is the selection of the dispersing auxiliary for stabilizing the dispersion.

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DE-A 43 30 969 describes a process for preparing polystyrene mixtures by polymerizing styrene in an organic liquid in the presence of a styrene-butadiene block copolymer and of a metallocene catalyst system. For the preferred embodiment, however, pressures of from 5 to 20 bar are required; otherwise the resulting polymers have a very low molecular weight of around 30,000 g/mol.

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It is an object of the present invention to provide a process for preparing syndiotactic vinylaromatic polymers using metallocene catalysts, which does not have the above disadvantages, the reaction mixture being of low viscosity and increasing the productivity of the catalyst.

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We have found that this object is achieved by a process for preparing polymers of vinylaromatic compounds in dispersion in the presence of a dispersing auxiliary and a catalyst, obtainable from

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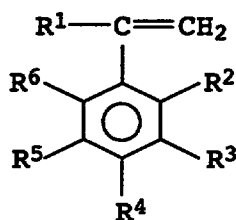
A) a transition metal complex of subgroups II to VIII,

B) a cation-forming agent and

C), if desired, an aluminum compound, wherein lubricants are added.

Particularly suitable vinylaromatic compounds are those of the formula I

40



(I),

45

where

R¹ is hydrogen or C₁-C₄-alkyl,

5 R² to R⁶ independently are hydrogen, C₁-C₁₂-alkyl, C₆-C₁₈-aryl or halogen, or two adjacent radicals together are cyclic groups having 4 to 15 carbons, for example C₄-C₈-cyclo-alkyl, or fused ring systems.

10 It is preferred to employ vinylaromatic compounds of the formula I in which

R¹ is hydrogen.

15

Particularly suitable substituents R² to R⁶ are hydrogen, C₁-C₄-alkyl, chlorine or phenyl, biphenyl, naphthalene or anthracene. Two adjacent radicals may also together be cyclic groups having 4 to 12 carbons, so that compounds of the formula I
20 may also, for example, be naphthalene derivatives or anthracene derivatives.

Examples of such preferred compounds are:

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styrene, p-methylstyrene, p-chlorostyrene, 2,4-dimethylstyrene, 4-vinylbiphenyl, 2-vinylnaphthalene or 9-vinylanthracene.

It is also possible to employ mixtures of different vinylaromatic
30 compounds, in which case one component may also carry further hydrocarbon radicals, such as vinyl, allyl, methallyl, butenyl or pentenyl groups, preferably vinyl groups, on the phenyl ring. It is preferred, however, to use only one vinylaromatic compound.

35 Particularly preferred vinylaromatic compounds are styrene and p-methylstyrene.

The preparation of vinylaromatic compounds of the formula I is
40 known per se and is described, for example, in Beilstein 5, 367, 474, 485.

Suitable dispersion auxiliaries are block copolymers having at least one diene block B and at least one block S comprising a
45 copolymer of a vinylaromatic monomer of the formula (I) and 1,1-diphenylethylene or its aromatic ring-substituted

derivatives, including those substituted with alkyl of up to 22 carbons, as are described, for example, in DE-A 44 20 917.

- Suitable examples are block copolymers with blocks S and B, of the general structures $(S-B)_n$, $S-B-S$, $B-S-B$, $X[(S-B)_n]_m$, $X[(B-S)_n]_m$, $X(S-B-S)_m$ and $X(B-S-B)_m$, where X is the radical of an m-functional coupling agent or of an m-functional initiator, n is an integer from 1 to 5 and m is an integer from 2 to 20.
- 10 All dienes are suitable in principle as the diene component for the block B, although preference is given to those having conjugated double bonds, such as butadiene, isoprene, dimethylbutadiene and phenylbutadiene. The diene block may be partially or completely hydrogenated or unhydrogenated. The
- 15 molecular weights M_w of the blocks B are generally from 10,000 to 500,000, preferably from 50,000 to 350,000 and, with particular preference, from 70,000 to 250,000, g/mol.
- 20 The blocks S consist of a copolymer of a vinylaromatic monomer of the formula (I) and 1,1-diphenylethylene or its ring-substituted derivatives, including those substituted with alkyl of up to 22 carbons, preferably of 1 to 4 carbons, such as methyl, ethyl, isopropyl, n-propyl and n-, iso- or tert-butyl. Particular
- 25 preference, however, is given to the use of unsubstituted 1,1-diphenylethylene itself. The proportion of diphenylethylene in the block S is from 15 to 65% by weight, preferably from 25 to 60% by weight. The molar ratio of the units derived from the vinylaromatic monomer to units derived from 1,1-diphenylethylene
- 30 is generally in the range from 1 : 1 to 1 : 25, preferably from 1 : 1.05 to 1 : 15 and, with particular preference, in the range from 1 : 1.1 to 1 : 10.
- The copolymer block S is preferably random in composition and has
- 35 a molecular weight M_w of in general from 20,000 to 500,000, preferably from 50,000 to 300,000. Particular preference is given to a copolymer block S of styrene and 1,1-diphenylethylene.
- The block ratio S to B is generally in the range from 90 : 10 to
- 40 20 : 80, particularly preferably from 90 : 15 to 65 : 35. The block transitions can be either clean-cut or tapered. A tapered transition is one where the adjacent blocks B and S may, in the transition region, also contain monomers of the other block.
- 45 The block copolymers can be prepared by customary methods of anionic polymerization, as described for example in M. Morton, Anionic Polymerisation, Principles and Practice, Academic Press,

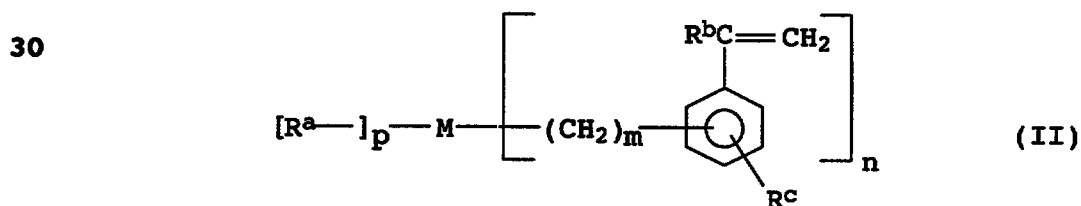
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New York 1983. The anionic polymerization is initiated by means of organometallic compounds. Preference is given to compounds of the alkali metals, especially of lithium. Examples of initiators are lithium alkyls such as methyllithium, ethyllithium, isopropyllithium, n-, sec- or tert-butyllithium. It is particularly preferred to employ n- or s-butyllithium. Suitable solvents are those which are inert toward the organometallic initiator. Aliphatic or aromatic hydrocarbons are judiciously used. Examples of suitable solvents are cyclohexane, methylcyclohexane, benzene, toluene, ethylbenzene and xylene.

To influence the polymerization parameters, small amounts of polar aprotic substances may be added to the solvent. Suitable examples are ethers, such as diethyl ether, diisopropyl ether, diethylene glycol dimethyl ether, diethylene glycol dibutyl ether or, in particular, tetrahydrofuran, and also tertiary amines, such as tetramethylethylenediamine or pyridine. The polar cosolvent is added to the apolar solvent in a small amount of from about 0.01 to 5% by volume. Particular preference is given to tetrahydrofuran in an amount of from about 0.1 to 0.3% by volume.

In a preferred embodiment of the novel process, at least one branching monomer can be employed.

As branching monomers it is possible to use compounds of the formula II



where

R^a is hydrogen, halogen or an inert organic radical of up to 20 carbons, where if $p \geq 2$ each R^a can be identical or different and two radicals R^a can form a 3- to 8-membered ring together with the metal atom attached to them, and R^a can also be a customary complex ligand if M is a transition metal,

R^b is hydrogen, C_1 - C_4 -alkyl or phenyl;

6

R^c is hydrogen, C_1 - C_4 -alkyl, phenyl, chlorine or an unsaturated hydrocarbon radical of 2 to 6 carbons;

M is C, Si, Ge, Sn, B, Al, Ga, N, P, Sb, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Zn or Cd,

n is 2-6;

m is 0-20;

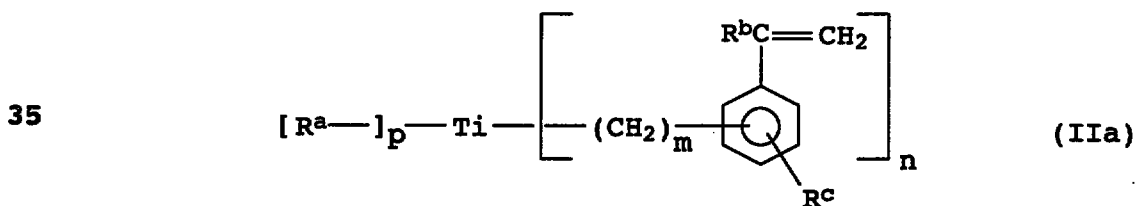
p is 0-4;

with the proviso that the sum of $n + p$ corresponds to the valency of M.

These monomers can be obtained, for example, by way of the Grignard compounds of the chloro(alkyl)styrenes with the corresponding carbon, metal or transition metal compounds, for example the halogen compounds. Where M is silicon, germanium or tin, for example, such reactions are described in K. Nakanishi, J. Chem. Soc. Perkin Trans I, 1990, page 3362.

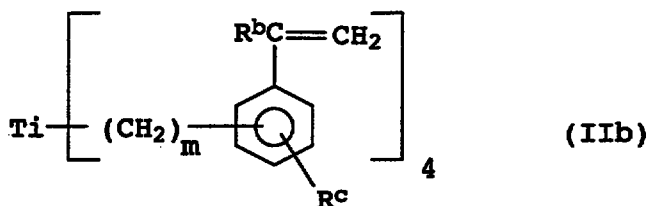
Particularly preferred branching monomer units are those of the formula II in which M is carbon, silicon, germanium, tin or titanium, because they are easy to obtain. The index m is preferably from 0 to 8, particularly preferably from 0 to 4.

For example, the titanium-containing monomers of the formula IIa



and the titanium compound IIb

7



where R^a , R^b , R^c , m , n and p are as defined above, can be employed as branching monomers.

The inert organic radical or radicals R^a are not of great importance to the process. Rather, they serve merely to satisfy the free valencies of M and can be selected for ease of availability. Examples of suitable radicals are aliphatic and cycloaliphatic radicals, aryls, hetaryls and aralkyls. Aliphatic radicals include alkyls, alkoxys, alkenyls or alkynyls having, for example, from 1 to 2 or 20 carbons. Cycloaliphatic radicals include cycloalkyls or cycloalkane radicals of 3 to 8 carbons. Instead of a methylene in the alkyl or cycloalkyl it is also possible for there to be an oxygen in ether function. Examples of aryls are phenyls or naphthyls, it also being possible for two phenyls to be connected by an oxygen. Examples of aralkyls are those of 7 to 20 carbons that result from combination of a phenyl with an alkyl. Examples of hetaryls are pyridyl, pyrimidyl and furyl. These radicals can also be substituted further, for example by alkyl, alkoxy, halogen, such as fluorine, chlorine or bromine, cyano, nitro, epoxy, carbonyl, ester groups, amides, and so on. Two of the radicals R^a can also form a 3- to 6-membered ring with the atom M , for example where two radicals R^a form an alkylene chain in which one or more CH_2 groups may also have been replaced by O in ether function.

If M is a transition metal, R^a can also be a customary σ - or π -bonded complex ligand, such as ethylene, allyl, butadiene or cyclopentadiene, mono- or polysubstituted cyclopentadienes, such as methylcyclopentadiene or pentamethylcyclopentadiene, benzene, cyclohexadiene, cycloheptatriene, cycloheptadiene, cyclooctatetraene, cyclooctatriene, cyclooctadiene, carbonyl, oxalato, cyano, isonitrile, fulminato-C, fulminato-O, cyanato, dinitrogen, ethylenediamine, diethylenetriamine, triethylenetetramine, ethylenediaminetetraacetate, nitrosyl, nitro, isocyano, pyridine, α, α -bipyridyl, trifluorophosphane, phosphane, diphosphane, arsane, acetylacetonato.

R^b is with particular preference hydrogen or methyl. R^c is hydrogen, C_1 - C_4 -alkyl such as methyl, ethyl, propyl, isopropyl, n-butyl and the isomeric butyls, phenyl, chlorine or an unsaturated hydrocarbon radical of 2 to 6 carbons such as vinyl, allyl, methallyl, butenyl or pentenyl.

The branching monomer unit is judiciously employed in a molar ratio of vinylaromatic monomer to branching unit of from 10,000,000 : 1 to 10 : 1.

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Transition metal complexes of subgroups II to VIII, preferably III to VIII, are used as catalyst component A). Very particular preference is given to complexes of the transition metals of subgroup IV, i.e. of titanium, zirconium or hafnium.

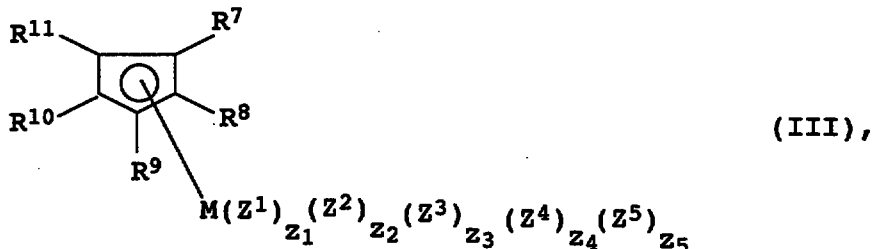
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If the branching monomer unit of the formula II already has a transition metal M, especially titanium, then depending on the concentration used it can also simultaneously be employed as catalyst component A in addition to its function as a branching unit.

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Particularly preferred catalyst components A) are metallocene complexes, especially those of the formula III

25



30

where

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R^7 to R^{11} are hydrogen, C_1 - C_{10} -alkyl, 5- to 7-membered cycloalkyl which in turn can carry C_1 - C_6 -alkyls as substituents, C_6 - C_{15} -aryl or arylalkyl, and where two adjacent radicals may if desired together be cyclic groups of 4 to 15 carbons, for example fused ring systems of 4 to 12 carbons, or are $Si(R^{12})_3$,

40

where R^{12} is C_1 - C_{10} -alkyl, C_6 - C_{15} -aryl or C_3 - C_{10} -cycloalkyl,

45

M is a metal from subgroups III to VI of the Periodic Table of the Elements or is a metal of the lanthanide series,

5 z^1 to z^5 are hydrogen, halogen, C_1 - C_{10} -alkyl, C_6 - C_{15} -aryl, C_1 - C_{10} -alkoxy or C_1 - C_{15} -aryloxy

and

10 z_1 to z_5 are 0, 1, 2, 3, 4 or 5, the sum $z_1+z_2+z_3+z_4+z_5$ corresponding to the valency of M minus 1.

Particularly preferred metallocene complexes of the formula III
15 are those in which

M is a metal from subgroup IV of the Periodic Table of the Elements, i.e. titanium, zirconium or hafnium, especially titanium,
20

and

z^1 to z^5 are C_1 - C_{10} -alkyl, C_1 - C_{10} -alkoxy or halogen.

25

Examples of such preferred metallocene complexes are:

pentamethylcyclopentadienyltitanium trichloride,
pentamethylcyclopentadienyltitanium trimethyl and
30 pentamethylcyclopentadienyltitanium trimethylate.

It is also possible to employ those metallocene complexes described in EP-A 584 646.

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Mixtures of different metallocene complexes can also be used.

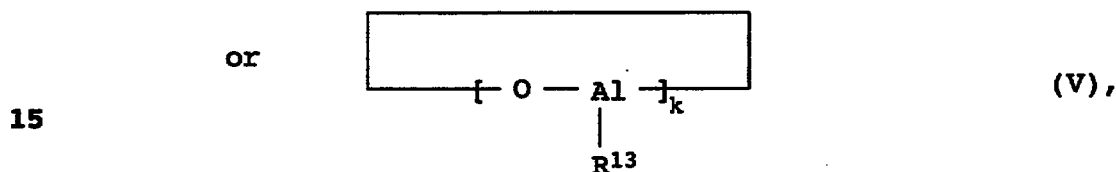
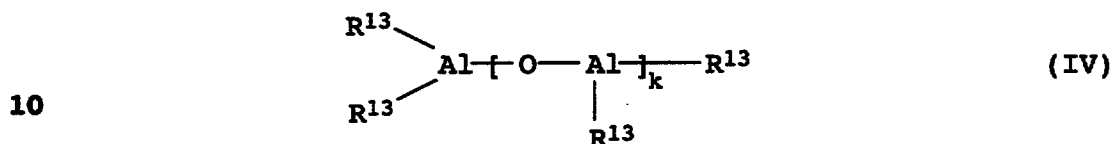
Complex compounds of this kind can be synthesized by methods known per se, preference being given to reacting the
40 correspondingly substituted, cyclic hydrogen anions with halides of titanium, zirconium, hafnium, vanadium, niobium or tantalum.

Examples of appropriate preparation techniques are described, inter alia, in Journal of Organometallic Chemistry, 369 (1989),
45 359-370.

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As compound B which forms cations, especially metallocenium ions, the catalyst systems can comprise open-chain or cyclic alumoxane compounds.

- 5 Suitable examples are open-chain or cyclic alumoxane compounds of the formula IV or V



where R¹³ is C₁-C₄-alkyl, preferably methyl or ethyl, and k is an integer from 5 to 30, preferably from 10 to 25.

20

The preparation of these oligomeric alumoxane compounds is usually carried out by reacting a solution of a trialkylaluminum with water and is described, inter alia, in EP-A 284 708 and US-A 4,794,096.

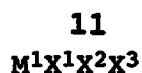
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In general, the oligomeric alumoxane compounds obtained are in the form of mixtures of both linear and cyclic chain molecules of different lengths, so that k is to be regarded as an average value. The alumoxanes may also be present in a mixture with other
30 metal alkyls, preferably with aluminum alkyls.

It has been found advantageous to use the metallocene complexes and the oligomeric alumoxane compound in amounts such that the
35 atomic ratio between aluminum from the oligomeric alumoxane and the transition metal from the metallocene complexes is in the range from 10:1 to 10⁶:1, in particular from 10:1 to 10⁴:1.

As compound B) forming metallocenium ions it is also possible to
40 employ coordination complex compounds selected from the group consisting of strong, neutral Lewis acids, ionic compounds having Lewis-acid cations and ionic compounds having Brönsted acids as cations.

45 Preferred strong neutral Lewis acids are compounds of the formula VI



(VI)

where

- 5 M^1 is an element from main group III of the Periodic Table, especially B, Al or Ga, preferably B,
- 10 X^1, X^2 and X^3 are hydrogen, C_1 - C_{10} -alkyl, C_6 - C_{15} -aryl, alkylaryl, arylalkyl, haloalkyl or haloaryl each of 1 to 10 carbons in the alkyl and 6 to 20 carbons in the aryl, or are fluorine, chlorine, bromine or iodine, especially haloaryls, preferably pentafluorophenyl.
- 15 Particular preference is given to compounds of the formula VI in which X^1, X^2 and X^3 are identical; preferably tris(pentafluorophenyl)borane. These compounds and processes for their preparation are known per se and are described, for example, in WO 93/3067.
- 20 Suitable ionic compounds having Lewis-acid cations are compounds of the formula VII
- $$25 \quad [(Y^{a+})Q_1Q_2 \dots Q_z]^{d+} \quad (VII)$$
- where
- 30 Y is an element from main groups I to VI or subgroups I to VIII of the Periodic Table,
- 35 Q_1 to Q_z are radicals with a single negative charge, such as C_1 - C_{28} -alkyl, C_6 - C_{15} -aryl, alkylaryl, arylalkyl, haloalkyl or haloaryl each having 6 to 20 carbons in the aryl and 1 to 28 carbons in the alkyl, C_1 - C_{10} -cycloalkyl, which can be unsubstituted or substituted by C_1 - C_{10} -alkyls, or are halogen, C_1 - C_{28} -alkoxy, C_6 - C_{15} -aryloxy, silyl or mercaptyl, such as trimethylsilyl,
- 40 a is an integer from 1 to 6,
- 45 z is an integer from 0 to 5, and

d corresponds to the difference $a - z$, but is greater than or equal to 1.

Particular suitability is possessed by carbonium cations, oxonium cations and sulfonium cations, and also cationic transition metal complexes. Particular mention may be made of the triphenylmethyl, silver and 1,1'-dimethylferrocenyl cations.

They preferably have noncoordinating counterions, especially boron compounds, as also mentioned in WO 91/09882, preferably tetrakis(pentafluorophenyl) borate.

Ionic compounds with Brönsted acids as cations and preferably also with likewise noncoordinated counterions are specified in WO 93/3067; a preferred cation is N,N-dimethylanilinium.

It has been found to be particularly appropriate if the molar ratio of boron from the compound that forms metallocenium ions to transition metal from the metal complex is in the range from 0.1:1 to 10:1, in particular from 1:1 to 5:1.

The catalyst system employed in the novel process may include as component C) an aluminum compound, for example of the formula VIII



where

R^{14} to R^{16} are hydrogen, fluorine, chlorine, bromine, iodine or C_1 - C_{12} -alkyl, preferably C_1 - C_8 -alkyl.

Preferably, R^{14} to R^{15} are identical and are C_1 - C_6 -alkyl, such as methyl, ethyl, isobutyl or n-hexyl, and R^{16} is hydrogen.

The content of component C) in the catalyst system is preferably from 1 : 2000 to 1 : 1, in particular from 1 : 800 to 1 : 10 (molar ratio of transition metal from III to Al from VIII).

As solvents for the metallocene complexes it is common to employ aromatic hydrocarbons, preferably those having 6 to 20 carbons, and especially xylenes, toluene and ethylbenzene and mixtures thereof.

The metallocene complexes can be employed with or without a support.

5 Examples of suitable support materials are silica gels,
preferably those of the formula $\text{SiO}_2 \cdot b\text{Al}_2\text{O}_3$, where b is a number
from 0 to 2, preferably from 0 to 0.5; i.e. essentially
alumosilicates or silicon dioxide. The supports preferably have a
particle diameter of from 1 to 200 μm , in particular from 30 to
80 μm . Such products are obtainable commercially, for example as
10 silica gel 332 from Grace.

Further supports include finely divided polyolefins, for example
finely divided polypropylene or polyethylene, and also
15 polyethylene glycol, polybutylene terephthalate, polyethylene
terephthalate, polyvinyl alcohol, polystyrene, syndiotactic
polystyrene, polybutadiene, polycarbonates and copolymers
thereof.

20 The molar ratio of transition metal catalyst A) to vinylaromatic
monomer is generally from 1 : 1000 to 1 : 10,000,000, but
preferably from 1 : 2000 to 1 : 1,000,000.

The process according to the invention is conducted as a
25 dispersion polymerization. The dispersing medium employed may
judiciously comprise aliphatic hydrocarbons, especially those of
4 to 10 carbon atoms, or hydrocarbon mixtures. Examples are
butane, pentane, hexane and heptane. The concentration of the
monomers that are to be polymerized in the dispersion medium is
30 in general from 5 to 65 percent by volume, preferably from 10 to
50 % by volume.

The dispersing auxiliary is preferably used in an amount of from
0.1 to 10% by weight, particularly preferably from 1 to 8% by
35 weight, based on the vinylaromatic compound employed. It is
judiciously dissolved in the vinylaromatic monomer that is to be
polymerized.

40 Suitable lubricants are organic and inorganic compounds. Examples
of organic lubricants are lubricating oils such as mineral oils,
i.e. liquid products obtained from petroleum, hard-coal tar or
lignite tar, such as benzines, white oils, petroleum or gas oils,
and also polyether oils, ester oils and silicone oils, or else
lubricant greases. Examples of inorganic lubricants are
45 molybdenum(IV) sulfide or titanium(IV) sulfide. Further suitable
lubricants are glyceryl esters or fatty acids. Preference is
given to hydrocarbons such as liquid paraffins, other paraffins,

- polar and nonpolar polyethylene waxes, alcohols such as cetyl alcohol or stearyl alcohol, carboxylic acids such as lauric acid, palmitic acid or stearic acid, metal salts of carboxylic acids, such as Ca stearate, Zn stearate, carboxamides and carboxylic
- 5 esters such as ethyl stearate, n-butyl stearate or distearyl phthalate. Further lubricants are described, for example, in the Taschenbuch der Kunststoff-Additive, edited by Gächter and Müller for the Carl Hanser Verlag, 2nd Edition, page 309 to 327.
- 10 Further lubricants which can be employed are polymers such as polystyrene, preferably low molecular mass polystyrene having molecular weights M_w of from 2000 to 40,000, polyethylene, polypropylene, or else copolymers of ethylene with other
- 15 1-alkenes.
- Particular preference is given to distearyl phthalate and mineral oil hydrocarbons such as white oils. Mixtures of different lubricants can also be employed.
- 20 The amount of lubricants can vary within wide ranges, with preference being given to from 0.01 to 50% by weight, in particular from 0.1 to 40% by weight and, with particular preference, from 0.2 to 10% by weight based on monomer employed.
- 25 The lubricants are preferably added, prior to the addition of the transition metal complex, to the vinylaromatic compound, the dispersant, the dispersing medium, the cation-forming agent and, if appropriate, the aluminum compound.
- 30 The polymerization conditions are not critical. Polymerization is preferably conducted at from 50 to 100°C under a pressure of from 0.05 to 30 bar, preferably from 0.1 to 20 bar. The polymerization is generally at an end after from 0.5 to 10 hours. It can be
- 35 terminated by adding protic compounds, for example methanol, and the dispersion medium can be removed by filtration or evaporation and recycled to the process.
- 40 The novel process is technically simple and permits the preparation of vinylaromatic polymers having a high syndiotactic content with low viscosities of less than 5 mPas with high catalyst productivity. Furthermore, the polymers are obtained in particulate form. The resultant polymers are suitable for
- 45 producing fibers, films and moldings.

Examples

Purifying 1,1-diphenylethylene (DPE)

- 5 Crude DPE (Aldrich or prepared by reacting phenylmagnesium
bromide with acetophenone, acetylating with acetic anhydride and
thermally eliminating the acetic acid) is distilled to 99.8%
purity on a column having at least 50 theoretical plates
10 (spinning band column; for larger quantities, a column with
Sulzer packing). The distillate, which is usually pale yellow, is
filtered through a 20 cm alox column (Woelm alumina for
chromatography, anhydrous), titrated with 1.5 N sec-butyllithium
until there is a strong red coloration, and distilled over under
15 reduced pressure (1 mbar). The resulting product is completely
colorless and can be employed directly in the anionic
polymerization.

Purifying the monomers and solvent

- 20 The cyclohexane (H) employed as solvent was dried over anhydrous
alumina and titrated with the adduct of sec-butyllithium and
1,1-diphenylethylene until a yellow coloration was obtained. The
butadiene (Bu) was distilled off from triisobutylaluminum, the
25 1,1-diphenylethylene (DPE) from sec-butyllithium (s-BuLi). A 0.5
molar solution of s-BuLi in cyclohexane was used as initiator.
Styrene (S) was dried over alumina directly before use.

- 30 All polymerizations were conducted under purified nitrogen with
rigorous exclusion of air and moisture. The reactors were
pretreated for a number of hours with a solution of
1,1-diphenylethylene and sec-butyllithium in cyclohexane under
reflux before being filled.

- 35 In the Examples below, Bu is 1,3-butadiene, S is styrene and DPE
is 1,1-diphenylethylene. Also, the proportions are by weight.

Preparing a Bu-S/DPE block copolymer

40

Dispersant D1

- 7.1 l of cyclohexane and a few drops (about 2 ml) of DPE were
charged to a 10 l stirred reactor and titrated with a 0.278 molar
45 sec-butyllithium solution until the mixture began to take on a
red coloration. Following the addition of 15.1 ml (4.2 mmol) of
the 0.278 molar sec-butyllithium solution, 1.6 l (19.4 mol) of

1,3-butadiene were added in portions (100 ml) over the course of one hour at 70°C and the mixture was polymerized at 70°C for a further hour. The molecular weights of the resulting polybutadiene block were determined on a sample by means of gel permeation chromatography (GPC) with polybutadiene calibration: $M_w = 248,000$ g/mol, $M_w/M_n = 1.28$, M (peak maximum) = 226,000 g/mol. To the resulting polybutadiene block there were added, in succession at an interval of 15 minutes, 98.3 ml (0.56 mol) of 1,1-diphenylethylene and 259 ml (2.25 mol) of styrene, and polymerization was continued at 70°C for 5 hours more. After the reaction had subsided, the reaction mixture was titrated with ethanol until it became colorless and was acidified with CO₂/water. The colorless solution was freed from solvent under reduced pressure in a devolatilizing extruder, and the product was granulated.

GPC (polybutadiene calibration): two peaks: 1st peak (20%) M (peak maximum) = 32,000 g/mol; 2nd peak (80%): peak maximum at 260,000 g/mol.

Examples 1 to 4

532 ml of pentane and a mixture of 2.61 g of dispersant D1 in 104.2 g (1 mol) of styrene were introduced with stirring into an autoclave which had been rendered inert [sic] with argon. 8.16 ml of a 1.53 molar solution of methylaluminoxane (MAO) in toluene (obtained from Witco) and 2.08 ml of a 1.0 molar solution of diisobutylaluminum hydride (DIBAH) in cyclohexane (obtained from Aldrich) were added. Prior to the addition of the transition metal complex, a defined amount of lubricant was then added to this mixture. Subsequently, 1.5 l of hydrogen were injected at room temperature and the reaction solution was heated to 80°C. Then 1.14 mg (0.05 mmol) of pentamethylcyclopentadienyltitanium trimethyl Cp*TiMe₃ were added, and an internal pressure of 7.5 bar developed. After 2 hours, the polymerization was terminated by adding 10 ml of methanol. After cooling to room temperature, a homogeneous, readily flowing suspension was obtained. The resultant polymer was washed with methanol and dried under reduced pressure at 50°C.

The molecular weights M_w and M_n were determined by means of high-temperature gel permeation [sic] chromatography GPC (135°C, 1,2,4-trichlorobenzene, polystyrene standard). The syndiotactic content was determined by means of ¹³C-NMR spectroscopy. The particle sizes lay within the range from 2 to 10 μm and were determined on a sample, slurried in immersion oil, between two

planar glass plates under the transition microscope (Axiophot from Carl Zeiss).

The conversion is based on the amount of styrene employed.

Comparative Experiment C1

Polymerization was carried out as in Examples 1 to 4 but without the addition of a lubricant.

Ex.	Lubricant	M _w [g/mol]	M _w /M _n	Vis- cosity [mPas]	Con- ver- sion [%]	Productivity [kg s-Ps/gTi)
1	0.5% by wt. Winog 60	422,800	1.9	2.99	67	69.2
2	5% by wt. Winog 60	278,500	2.0	4.81	73	82.1
3	1% by wt. distearyl phthalate	296,700	2.0	2.43	69	49.7
4	8% by wt. Winog 70	301,400	2.2	4.01	71	66.5
C1	-	321,500	2.1	2.35	34	15.4

The syndiotacticity of the polymers was $\geq 95\%$.

The percentages by weight for the lubricants are based on styrene monomer employed.

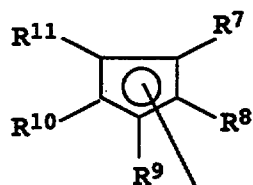
Winog®60 and Winog®70 are white oils (mineral oil hydrocarbons) to DAB [German Pharmacopeia] 9 from Wintershall Mineralöl GmbH. Winog 70 has a dynamic viscosity [to DIN 51562] of 136 mPas, a molecular weight in the range from 400 to 550, and a density of 0.865 g/cm³.

Winog 60 has a dynamic viscosity [to DIN 51562] of 180 mPas and a density of 0.863 g/cm³.



We claim:-

- 5 1. A process for preparing polymers of vinylaromatic compounds in dispersion in the presence of a dispersing auxiliary and a catalyst, obtainable from A) a transition metal complex of subgroups II to VIII, B) a cation-forming agent and C), if desired, an aluminum compound, which comprises adding
10 lubricants.
2. A process as claimed in claim 1, wherein the dispersing auxiliary used comprises block copolymers having at least one diene block B and at least one block S comprising a copolymer
15 of a vinylaromatic monomer and 1,1-diphenylethylene or its aromatic ring-substituted derivatives, including those substituted by alkyls of up to 22 carbons.
3. A process as claimed in claim 2, wherein the block copolymer
20 comprises polybutadiene or polyisoprene in copolymerized form and the diene block B is partially or completely hydrogenated or unhydrogenated.
4. A process as claimed in either of claims 2 and 3, wherein the
25 block S of the block copolymer consists of a copolymer of styrene and 1,1-diphenylethylene.
5. A process as claimed in any of claims 1 to 4, wherein the
30 lubricant is used in an amount of from 0.01 to 50% by weight, based on the monomer employed.
6. A process as claimed in any of claims 1 to 5, wherein a
35 branching monomer unit comprising at least two vinylaromatic radicals is used in a molar ratio of vinylaromatic monomers to branching units of from 10,000,000 : 1 to 10 : 1.
7. A process as claimed in any of claims 1 to 6, wherein the
40 catalyst component A) employed is a metallocene complex of the formula (III)



(III),

$$M(z^1)_{z_1} (z^2)_{z_2} (z^3)_{z_3} (z^4)_{z_4} (z^5)_{z_5}$$

where

R⁷ to R¹¹ are hydrogen, C₁-C₁₀-alkyl, 5- to 7-membered cycloalkyl which in turn can carry C₁-C₆-alkyls as substituents, C₆-C₁₅-aryl or arylalkyl, and where two adjacent radicals may if desired together be cyclic groups of 4 to 15 carbons, or are Si(R¹²)₃,

where R¹² is C₁-C₁₀-alkyl, C₆-C₁₅-aryl or C₃-C₁₀-cycloalkyl,

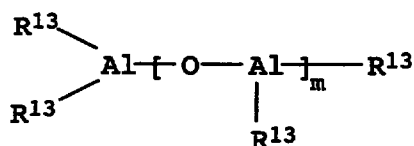
M is a metal from subgroups III to VI of the Periodic Table of the elements or is a metal of the lanthanide series.

Z¹ to Z⁵ are hydrogen, halogen, C₁-C₁₀-alkyl, C₆-C₁₅-aryl, C₁-C₁₀-alkoxy or C₁-C₁₅-aryloxy

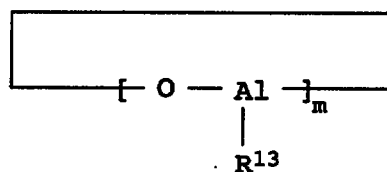
and

z_1 to z_5 are 0, 1, 2, 3, 4 or 5, the sum $z_1+z_2+z_3+z_4+z_5$ corresponding to the valency M minus 1.

8. A process as claimed in claims 1 to 7, wherein the cation-forming compound B) employed comprises open-chain or cyclic alumoxane compounds of the formula IV or V



IV



V

20

where R^{13} is C_1 - C_4 -alkyl and m is an integer from 5 to 30.

9. A process as claimed in any of claims 1 to 7, wherein the
cation-forming compound B) employed is a coordination complex
compound selected from the group consisting of strong,
neutral Lewis acids, ionic compounds having Lewis-acid
cations and ionic compounds having Brönsted acids as cations.

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Preparation of poly(vinylaromatics) by dispersion polymerization
with the addition of lubricants

5 Abstract

10 A description is given of a process for preparing polymers of
vinylaromatic compounds in dispersion, in the presence of a dis-
persing auxiliary and a catalyst, obtainable from A) a transition
metal complex of subgroups II to VIII, B) a cation-forming agent
and C), if desired, an aluminum compound, wherein additives are
added.

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We claim:-

1. A process for preparing polymers of vinylaromatic compounds
5 in dispersion in aliphatic C₄-C₁₀ hydrocarbons as dispersion
medium in the presence of a dispersing auxiliary and a
catalyst, obtainable from A) a transition metal complex of
subgroups II to VIII, B) a cation-forming agent and C), if
10 desired, an aluminum compound, which comprises adding
lubricants.
2. A process as claimed in claim 1, wherein the dispersing
auxiliary used comprises block copolymers having at least one
diene block B and at least one block S comprising a copolymer
15 of a vinylaromatic monomer and 1,1-diphenylethylene or its
aromatic ring-substituted derivatives, including those
substituted by alkyls of up to 22 carbons.
3. A process as claimed in claim 2, wherein the block copolymer
20 comprises polybutadiene or polyisoprene in copolymerized form
and the diene block B is partially or completely hydrogenated
or unhydrogenated.
4. A process as claimed in either of claims 2 and 3, wherein the
25 block S of the block copolymer consists of a copolymer of
styrene and 1,1-diphenylethylene.
5. A process as claimed in any of claims 1 to 4, wherein the
30 lubricant is used in an amount of from 0.01 to 50% by weight,
based on the monomer employed.
6. A process as claimed in any of claims 1 to 5, wherein a
branching monomer unit comprising at least two vinylaromatic
radicals is used in a molar ratio of vinylaromatic monomers
35 to branching units of from 10,000,000 : 1 to 10 : 1.

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* C L H S *

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REPLACEMENT SHEETS SG
☒ Description : paged ...1 to paged ...18
☒ Claim(s) : paged ...19 to paged ...21
☐ Drawing(s) : paged ... to paged ...
☒ Abstract : paged ...22 to paged ...23

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Preparation of poly(vinylaromatics) by dispersion polymerization with the addition of lubricants

5 Description

The invention relates to a process for preparing polymers of vinylaromatic compounds in dispersion in the presence of a dispersing auxiliary and a catalyst, obtainable from A) a transition metal complex of subgroups II to VIII, B) a cation-forming agent and C), if desired, an aluminum compound.

The polymers thereby obtainable can be used to produce fibers, films and moldings.

Polymerizing styrene in the presence of metallocene catalyst systems leads to polymers of high stereoregularity and is described at length, for example, in EP-A 0 210 615. Because of its high crystallinity, syndiotactic polystyrene has a very high melting point of about 270°C, high rigidity and tensile strength, dimensional stability, a low dielectric constant and high chemical stability. The profile of mechanical properties is retained even above the glass transition temperature.

In the metallocene-catalyzed polymerization of styrene, there is frequently crystallization of the resulting syndiotactic polystyrene starting at a level of only about 10% conversion. This leads firstly to the formation of deposits on the walls and secondly to an extreme viscosity rise during the polymerization, which makes handling and dissipation of the heat of reaction more difficult, especially on the industrial scale.

To solve this problem a variety of techniques using special reactors or extruders have been tried out. EP-A-0 535 582 describes a process for preparing syndiotactic polystyrene in a stirred bed of solids, which is able to reduce the wall deposits but not prevent them. The reactor has to be equipped with a special stirrer in order to produce a homogeneous fluidized bed. Temperature control is by way of partial evaporation of styrene by reduced pressure, using a complex vacuum control system.

EP-A 0 584 646 and EP-A 0 389 939 describe the preparation of syndiotactic polystyrene in self-cleaning twin-screw extruders or compounders with no dead spaces. In both processes, owing to the sudden rise in frictional forces at higher levels of conversion,

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and to the motor output required for continued operation, polymerization is carried out not to complete conversion but only to a level where the polymer powder, soaked with monomers, no longer agglomerates in the course of subsequent processing steps.

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In the case of anionic initiation, the technique of dispersion polymerization is known. It is employed specifically to prepare small polystyrene particles, as described for example in Journal of Polymer Science, Part A, Polymer Chemistry, Vol. 34 (1996),
10 pages 2633 - 2649. Of critical importance is the selection of the dispersing auxiliary for stabilizing the dispersion.

DE-A 43 30 969 describes a process for preparing polystyrene mixtures by polymerizing styrene in an organic liquid in the
15 presence of a styrene-butadiene block copolymer and of a metallocene catalyst system. For the preferred embodiment, however, pressures of from 5 to 20 bar are required; otherwise the resulting polymers have a very low molecular weight of around
20 30,000 g/mol.

DE-A 195 42 356 describes a process for the preparation of copolymers of vinylaromatic and olefinic polymers in the presence of metallocene catalysts in dispersion. As dispersing auxiliaries
25 two-block copolymers of styrene and dienes are used. However, process productivity still requires further improvements to be suited for technical processes.

It is an object of the present invention to provide a process for
30 preparing syndiotactic vinylaromatic polymers using metallocene catalysts, which does not have the above disadvantages, the reaction mixture being of low viscosity and increasing the productivity of the catalyst.

35 We have found that this object is achieved by a process for preparing polymers of vinylaromatic compounds in dispersion in the presence of a dispersing auxiliary and a catalyst, obtainable from

40 A) a transition metal complex of subgroups II to VIII,

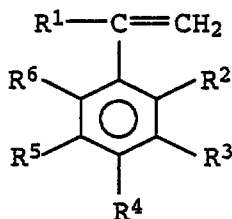
B) a cation-forming agent and,

45 C) if desired, an aluminum compound, wherein lubricants are added.

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Particularly suitable vinylaromatic compounds are those of the formula I

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(I),

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where

R^1 is hydrogen or C_1-C_4 -alkyl,

15

R^2 to R^6 independently are hydrogen, C_1-C_{12} -alkyl, C_6-C_{18} -aryl or halogen, or two adjacent radicals together are cyclic groups having 4 to 15 carbons, for example C_4-C_8 -cycloalkyl, or fused ring systems.

20

It is preferred to employ vinylaromatic compounds of the formula I in which

25 R^1 is hydrogen.

Particularly suitable substituents R^2 to R^6 are hydrogen, C_1-C_4 -alkyl, chlorine or phenyl, biphenyl, naphthalene or anthracene. Two adjacent radicals may also together be cyclic groups having 4 to 12 carbons, so that compounds of the formula I may also, for example, be naphthalene derivatives or anthracene derivatives.

30

Examples of such preferred compounds are:

35

styrene, p-methylstyrene, p-chlorostyrene, 2,4-dimethylstyrene, 4-vinylbiphenyl, 2-vinylnaphthalene or 9-vinylanthracene.

40

It is also possible to employ mixtures of different vinylaromatic compounds, in which case one component may also carry further hydrocarbon radicals, such as vinyl, allyl, methallyl, butenyl or pentenyl groups, preferably vinyl groups, on the phenyl ring. It is preferred, however, to use only one vinylaromatic compound.

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Particularly preferred vinylaromatic compounds are styrene and p-methylstyrene.

5 The preparation of vinylaromatic compounds of the formula I is known per se and is described, for example, in Beilstein 5, 367, 474, 485.

10 Suitable dispersion auxiliaries are block copolymers having at least one diene block B and at least one block S comprising a copolymer of a vinylaromatic monomer of the formula (I) and 1,1-diphenylethylene or its aromatic ring-substituted derivatives, including those substituted with alkyl of up to 22 carbons, as are described, for example, in DE-A 44 20 917.

15 Suitable examples are block copolymers with blocks S and B, of the general structures $(S-B)_n$, $S-B-S$, $B-S-B$, $X[(S-B)_n]_m$, $X[(B-S)_n]_m$, $X(S-B-S)_m$ and $X(B-S-B)_m$, where X is the radical of an m-functional coupling agent or of an m-functional initiator, n is
20 an integer from 1 to 5 and m is an integer from 2 to 20.

All dienes are suitable in principle as the diene component for the block B, although preference is given to those having conjugated double bonds, such as butadiene, isoprene,
25 dimethylbutadiene and phenylbutadiene. The diene block may be partially or completely hydrogenated or unhydrogenated. The molecular weights M_w of the blocks B are generally from 10,000 to 500,000, preferably from 50,000 to 350,000 and, with particular preference, from 70,000 to 250,000, g/mol.

30 The blocks S consist of a copolymer of a vinylaromatic monomer of the formula (I) and 1,1-diphenylethylene or its ring-substituted derivatives, including those substituted with alkyl of up to 22 carbons, preferably of 1 to 4 carbons, such as methyl, ethyl,
35 isopropyl, n-propyl and n-, iso- or tert-butyl. Particular preference, however, is given to the use of unsubstituted 1,1-diphenylethylene itself. The proportion of diphenylethylene in the block S is from 15 to 65% by weight, preferably from 25 to 60% by weight. The molar ratio of the units derived from the
40 vinylaromatic monomer to units derived from 1,1-diphenylethylene is generally in the range from 1 : 1 to 1 : 25, preferably from 1 : 1.05 to 1 : 15 and, with particular preference, in the range from 1 : 1.1 to 1 : 10.

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The copolymer block S is preferably random in composition and has a molecular weight Mw of in general from 20,000 to 500,000, preferably from 50,000 to 300,000. Particular preference is given to a copolymer block S of styrene and 1,1-diphenylethylene.

5

The block ratio S to B is generally in the range from 90 : 10 to 20 : 80, particularly preferably from 90 : 15 to 65 : 35. The block transitions can be either clean-cut or tapered. A tapered transition is one where the adjacent blocks B and S may, in the transition region, also contain monomers of the other block.

10

The block copolymers can be prepared by customary methods of anionic polymerization, as described for example in M. Morton, Anionic Polymerisation, Principles and Practice, Academic Press, New York 1983. The anionic polymerization is initiated by means of organometallic compounds. Preference is given to compounds of the alkali metals, especially of lithium. Examples of initiators are lithium alkyls such as methyllithium, ethyllithium, isopropyllithium, n-, sec- or tert-butyllithium. It is particularly preferred to employ n- or s-butyllithium. Suitable solvents are those which are inert toward the organometallic initiator. Aliphatic or aromatic hydrocarbons are judiciously used. Examples of suitable solvents are cyclohexane, methylcyclohexane, benzene, toluene, ethylbenzene and xylene.

15

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To influence the polymerization parameters, small amounts of polar aprotic substances may be added to the solvent. Suitable examples are ethers, such as diethyl ether, diisopropyl ether, diethylene glycol dimethyl ether, diethylene glycol dibutyl ether or, in particular, tetrahydrofuran, and also tertiary amines, such as tetramethylethylenediamine or pyridine. The polar cosolvent is added to the apolar solvent in a small amount of from about 0.01 to 5% by volume. Particular preference is given to tetrahydrofuran in an amount of from about 0.1 to 0.3% by volume.

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In a preferred embodiment of the novel process, at least one branching monomer can be employed.

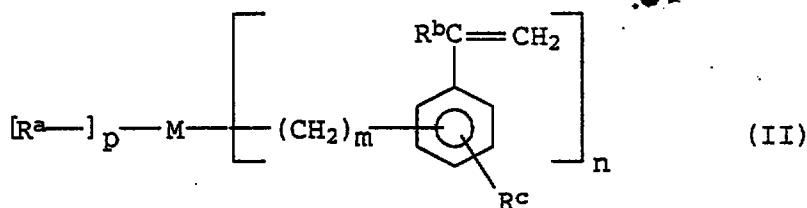
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As branching monomers it is possible to use compounds of the formula II

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where

R^a is hydrogen, halogen or an inert organic radical of up to 20 carbons, where if $p \geq 2$ each R^a can be identical or different and two radicals R^a can form a 3- to 8-membered ring together with the metal atom attached to them, and R^a can also be a customary complex ligand if M is a transition metal,

R^b is hydrogen, C_1 - C_4 -alkyl or phenyl;

R^c is hydrogen, C_1 - C_4 -alkyl, phenyl, chlorine or an unsaturated hydrocarbon radical of 2 to 6 carbons;

M is C, Si, Ge, Sn, B, Al, Ga, N, P, Sb, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Zn or Cd,

n is 2-6;

m is 0-20;

p is 0-4;

with the proviso that the sum of $n + p$ corresponds to the valency of M.

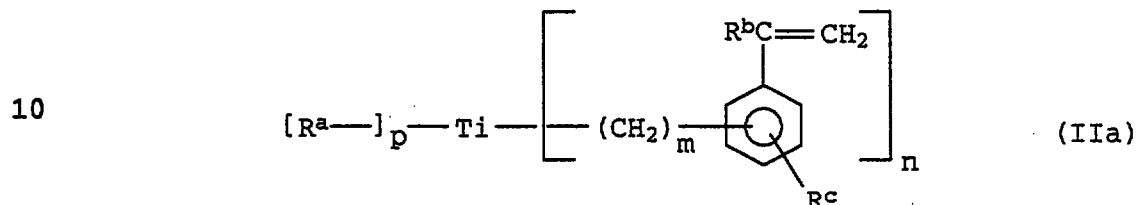
These monomers can be obtained, for example, by way of the Grignard compounds of the chloro(alkyl)styrenes with the corresponding carbon, metal or transition metal compounds, for example the halogen compounds. Where M is silicon, germanium or tin, for example, such reactions are described in K. Nakanishi, J. Chem. Soc. Perkin Trans I, 1990, page 3362.

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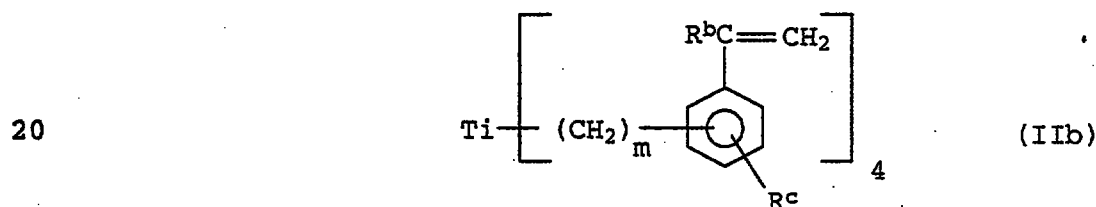
Particularly preferred branching monomer units are those of the formula II in which M is carbon, silicon, germanium, tin or titanium, because they are easy to obtain. The index m is preferably from 0 to 8, particularly preferably from 0 to 4.

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For example, the titanium-containing monomers of the formula IIa



15 and the titanium compound IIb



25 where R^a , R^b , R^c , m, n and p are as defined above, can be employed as branching monomers.

The inert organic radical or radicals R^a are not of great importance to the process. Rather, they serve merely to satisfy the free valencies of M and can be selected for ease of availability. Examples of suitable radicals are aliphatic and cycloaliphatic radicals, aryls, hetaryls and aralkyls. Aliphatic radicals include alkyls, alkoxys, alkenyls or alkynyls having, for example, from 1 to 2 or 20 carbons. Cycloaliphatic radicals include cycloalkyls or cycloalkane radicals of 3 to 8 carbons. Instead of a methylene in the alkyl or cycloalkyl it is also possible for there to be an oxygen in ether function. Examples of aryls are phenyls or naphthyls, it also being possible for two phenyls to be connected by an oxygen. Examples of aralkyls are those of 7 to 20 carbons that result from combination of a phenyl with an alkyl. Examples of hetaryls are pyridyl, pyrimidyl and furyl. These radicals can also be substituted further, for example by alkyl, alkoxy, halogen, such as fluorine, chlorine or bromine, cyano, nitro, epoxy, carbonyl, ester groups, amides, and so on. Two of the radicals R^a can also form a 3- to 6-membered ring with the atom M, for example where two radicals R^a form an

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alkylene chain in which one or more CH_2 groups may also have been replaced by O in ether function.

If M is a transition metal, R^a can also be a customary σ - or π -bonded complex ligand, such as ethylene, allyl, butadiene or cyclopentadiene, mono- or polysubstituted cyclopentadienes, such as methylcyclopentadiene or pentamethylcyclopentadiene, benzene, cyclohexadiene, cycloheptatriene, cycloheptadiene, cyclooctatetraene, cyclooctatriene, cyclooctadiene, carbonyl, oxalato, cyano, isonitrile, fulminato-C, fulminato-O, cyanato, dinitrogen, ethylenediamine, diethylenetriamine, triethylenetetramine, ethylenediaminetetraacetate, nitrosyl, nitro, isocyano, pyridine, α, α -bipyridyl, trifluorophosphane, phosphane, diphosphane, arsane, acetylacetonato.

15

R^b is with particular preference hydrogen or methyl. R^c is hydrogen, C_1 - C_4 -alkyl such as methyl, ethyl, propyl, isopropyl, n-butyl and the isomeric butyls, phenyl, chlorine or an unsaturated hydrocarbon radical of 2 to 6 carbons such as vinyl, allyl, methallyl, butenyl or pentenyl.

20

The branching monomer unit is judiciously employed in a molar ratio of vinylaromatic monomer to branching unit of from 10,000,000 : 1 to 10 : 1.

25

Transition metal complexes of subgroups II to VIII, preferably III to VIII, are used as catalyst component A). Very particular preference is given to complexes of the transition metals of subgroup IV, i.e. of titanium, zirconium or hafnium.

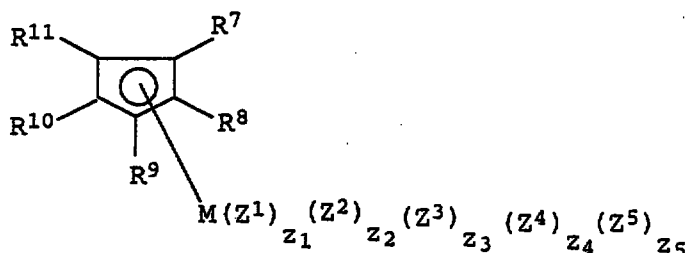
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If the branching monomer unit of the formula II already has a transition metal M, especially titanium, then depending on the concentration used it can also simultaneously be employed as catalyst component A in addition to its function as a branching unit.

35

Particularly preferred catalyst components A) are metallocene complexes, especially those of the formula III

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where

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10 R^7 to R^{11} are hydrogen, C_1 - C_{10} -alkyl, 5- to 7-membered cycloalkyl which in turn can carry C_1 - C_6 -alkyls as substituents, C_6 - C_{15} -aryl or arylalkyl, and where two adjacent radicals may if desired together be cyclic groups of 4 to 15 carbons, for example fused ring systems of 4 to 12 carbons, or are $Si(R^{12})_3$,

where R^{12} is C_1 - C_{10} -alkyl, C_6 - C_{15} -aryl or C_3 - C_{10} -cycloalkyl,

15

M is a metal from subgroups III to VI of the Periodic Table of the Elements or is a metal of the lanthanide series,

20 Z^1 to Z^5 are hydrogen, halogen, C_1 - C_{10} -alkyl, C_6 - C_{15} -aryl, C_1 - C_{10} -alkoxy or C_1 - C_{15} -aryloxy

and

25

z_1 to z_5 are 0, 1, 2, 3, 4 or 5, the sum $z_1+z_2+z_3+z_4+z_5$ corresponding to the valency of M minus 1.

Particularly preferred metallocene complexes of the formula III
30 are those in which

M is a metal from subgroup IV of the Periodic Table of the Elements, i.e. titanium, zirconium or hafnium, especially titanium,

35

and

Z^1 to Z^5 are C_1 - C_{10} -alkyl, C_1 - C_{10} -alkoxy or halogen.

40

Examples of such preferred metallocene complexes are:

pentamethylcyclopentadienyltitanium trichloride,
45 pentamethylcyclopentadienyltitanium trimethyl and
pentamethylcyclopentadienyltitanium trimethylate.

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complexes

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It has been found advantageous to use the metallocene complexes and the oligomeric alumoxane compound in amounts such that the atomic ratio between aluminum from the oligomeric alumoxane and the transition metal from the metallocene complexes is in the 5 range from 10:1 to 10⁶:1, in particular from 10:1 to 10⁴:1.

As compound B) forming metallocenium ions it is also possible to employ coordination complex compounds selected from the group consisting of strong, neutral Lewis acids, ionic compounds having 10 Lewis-acid cations and ionic compounds having Brönsted acids as cations.

Preferred strong neutral Lewis acids are compounds of the formula 15 VI



where

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M¹ is an element from main group III of the Periodic Table, especially B, Al or Ga, preferably B,

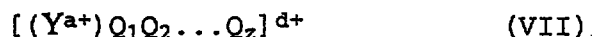
25 X¹, X² and X³ are hydrogen, C₁-C₁₀-alkyl, C₆-C₁₅-aryl, alkylaryl, arylalkyl, haloalkyl or haloaryl each of 1 to 10 carbons in the alkyl and 6 to 20 carbons in the aryl, or are fluorine, chlorine, bromine or iodine, especially haloaryls, preferably pentafluorophenyl.

30

Particular preference is given to compounds of the formula VI in which X¹, X² and X³ are identical; preferably tris(pentafluorophenyl)borane. These compounds and processes for their preparation are known per se and are described, for 35 example, in WO 93/3067.

Suitable ionic compounds having Lewis-acid cations are compounds of the formula VII

40



where

45 Y

is an element from main groups I to VI or subgroups I to VIII of the Periodic Table,

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- Q₁ to Q_z are radicals with a single negative charge, such as C₁-C₂₈-alkyl, C₆-C₁₅-aryl, alkylaryl, arylalkyl, haloalkyl or haloaryl each having 6 to 20 carbons in the aryl and 1 to 28 carbons in the alkyl,
- 5 C₁-C₁₀-cycloalkyl, which can be unsubstituted or substituted by C₁-C₁₀-alkyls, or are halogen, C₁-C₂₈-alkoxy, C₆-C₁₅-aryloxy, silyl or mercaptyl, such as trimethylsilyl,
- 10 a is an integer from 1 to 6,
- z is an integer from 0 to 5, and
- 15 d corresponds to the difference a - z, but is greater than or equal to 1.

Particular suitability is possessed by carbonium cations, oxonium cations and sulfonium cations, and also cationic transition metal

20 complexes. Particular mention may be made of the triphenylmethyl, silver and 1,1'-dimethylferrocenyl cations.

They preferably have noncoordinating counterions, especially boron compounds, as also mentioned in WO 91/09882, preferably

25 tetrakis(pentafluorophenyl) borate.

Ionic compounds with Brønsted acids as cations and preferably also with likewise noncoordinated counterions are specified in WO

30 93/3067; a preferred cation is N,N-dimethylanilinium.

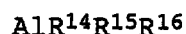
It has been found to be particularly appropriate if the molar ratio of boron from the compound that forms metallocenium ions to transition metal from the metal complex is in the range from

35 0.1:1 to 10:1, in particular from 1:1 to 5:1.

The catalyst system employed in the novel process may include as component C) an aluminum compound, for example of the formula

VIII

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(VIII),

where

45 R¹⁴ to R¹⁶ are hydrogen, fluorine, chlorine, bromine, iodine or C₁-C₁₂-alkyl, preferably C₁-C₈-alkyl.

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Preferably, R^{14} to R^{15} are identical and are C_1 - C_6 -alkyl, such as methyl, ethyl, isobutyl or n-hexyl, and R^{16} is hydrogen.

5 The content of component C) in the catalyst system is preferably from 1 : 2000 to 1 : 1, in particular from 1 : 800 to 1 : 10 (molar ratio of transition metal from III to Al from VIII).

10 As solvents for the metallocene complexes it is common to employ aromatic hydrocarbons, preferably those having 6 to 20 carbons, and especially xylenes, toluene and ethylbenzene and mixtures thereof.

15 The metallocene complexes can be employed with or without a support.

20 Examples of suitable support materials are silica gels, preferably those of the formula $SiO_2 \cdot bAl_2O_3$, where b is a number from 0 to 2, preferably from 0 to 0.5; i.e. essentially aluminosilicates or silicon dioxide. The supports preferably have a particle diameter of from 1 to 200 μm , in particular from 30 to 80 μm . Such products are obtainable commercially, for example as silica gel 332 from Grace.

25 Further supports include finely divided polyolefins, for example finely divided polypropylene or polyethylene, and also polyethylene glycol, polybutylene terephthalate, polyethylene terephthalate, polyvinyl alcohol, polystyrene, syndiotactic polystyrene, polybutadiene, polycarbonates and copolymers
30 thereof.

35 The molar ratio of transition metal catalyst A) to vinylaromatic monomer is generally from 1 : 1000 to 1 : 10,000,000, but preferably from 1 : 2000 to 1 : 1,000,000.

40 The process according to the invention is conducted as a dispersion polymerization. The dispersing medium employed may judiciously comprise aliphatic hydrocarbons, especially those of 4 to 10 carbon atoms, or hydrocarbon mixtures. Examples are butane, pentane, hexane and heptane. The concentration of the monomers that are to be polymerized in the dispersion medium is in general from 5 to 65 percent by volume, preferably from 10 to 50 % by volume.

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The dispersing auxiliary is preferably used in an amount of from 0.1 to 10% by weight, particularly preferably from 1 to 8% by weight, based on the vinylaromatic compound employed. It is judiciously dissolved in the vinylaromatic monomer that is to be
5 polymerized.

Suitable lubricants are organic and inorganic compounds. Examples of organic lubricants are lubricating oils such as mineral oils, i.e. liquid products obtained from petroleum, hard-coal tar or
10 lignite tar, such as benzines, white oils, petroleum or gas oils, and also polyether oils, ester oils and silicone oils, or else lubricant greases. Examples of inorganic lubricants are molybdenum(IV) sulfide or titanium(IV) sulfide. Further suitable lubricants are glyceryl esters or fatty acids. Preference is
15 given to hydrocarbons such as liquid paraffins, other paraffins, polar and nonpolar polyethylene waxes, alcohols such as cetyl alcohol or stearyl alcohol, carboxylic acids such as lauric acid, palmitic acid or stearic acid, metal salts of carboxylic acids, such as Ca stearate, Zn stearate, carboxamides and carboxylic
20 esters such as ethyl stearate, n-butyl stearate or distearyl phthalate. Further lubricants are described, for example, in the Taschenbuch der Kunststoff-Additive, edited by Gächter and Müller for the Carl Hanser Verlag, 2nd Edition, page 309 to 327.

25 Further lubricants which can be employed are polymers such as polystyrene, preferably low molecular mass polystyrene having molecular weights M_w of from 2000 to 40,000, polyethylene, polypropylene, or else copolymers of ethylene with other
30 1-alkenes.

Particular preference is given to distearyl phthalate and mineral oil hydrocarbons such as white oils. Mixtures of different lubricants can also be employed.

35 The amount of lubricants can vary within wide ranges, with preference being given to from 0.01 to 50% by weight, in particular from 0.1 to 40% by weight and, with particular preference, from 0.2 to 10% by weight based on monomer employed.

40 The lubricants are preferably added, prior to the addition of the transition metal complex, to the vinylaromatic compound, the dispersant, the dispersing medium, the cation-forming agent and, if appropriate, the aluminum compound.

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The polymerization conditions are not critical. Polymerization is preferably conducted at from 50 to 100°C under a pressure of from 0.05 to 30 bar, preferably from 0.1 to 20 bar. The polymerization is generally at an end after from 0.5 to 10 hours. It can be
5 terminated by adding protic compounds, for example methanol, and the dispersion medium can be removed by filtration or evaporation and recycled to the process.

10 The novel process is technically simple and permits the preparation of vinylaromatic polymers having a high syndiotactic content with low viscosities of less than 5 mPas with high catalyst productivity. Furthermore, the polymers are obtained in particulate form. The resultant polymers are suitable for
15 producing fibers, films and moldings.

Examples

Purifying 1,1-diphenylethylene (DPE)

20 Crude DPE (Aldrich or prepared by reacting phenylmagnesium bromide with acetophenone, acetylating with acetic anhydride and thermally eliminating the acetic acid) is distilled to 99.8% purity on a column having at least 50 theoretical plates
25 (spinning band column; for larger quantities, a column with Sulzer packing). The distillate, which is usually pale yellow, is filtered through a 20 cm alox column (Woelm alumina for chromatography, anhydrous), titrated with 1.5 N sec-butyllithium until there is a strong red coloration, and distilled over under
30 reduced pressure (1 mbar). The resulting product is completely colorless and can be employed directly in the anionic polymerization.

35 Purifying the monomers and solvent

The cyclohexane (H) employed as solvent was dried over anhydrous alumina and titrated with the adduct of sec-butyllithium and 1,1-diphenylethylene until a yellow coloration was obtained. The
40 butadiene (Bu) was distilled off from triisobutylaluminum, the 1,1-diphenylethylene (DPE) from sec-butyllithium (s-BuLi). A 0.5 molar solution of s-BuLi in cyclohexane was used as initiator. Styrene (S) was dried over alumina directly before use.

45 All polymerizations were conducted under purified nitrogen with rigorous exclusion of air and moisture. The reactors were pretreated for a number of hours with a solution of

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1,1-diphenylethylene and sec-butyllithium in cyclohexane under reflux before being filled.

In the Examples below, Bu is 1,3-butadiene, S is styrene and DPE is 1,1-diphenylethylene. Also, the proportions are by weight.

Preparing a Bu-S/DPE block copolymer

10 Dispersant D1

7.1 l of cyclohexane and a few drops (about 2 ml) of DPE were charged to a 10 l stirred reactor and titrated with a 0.278 molar sec-butyllithium solution until the mixture began to take on a red coloration. Following the addition of 15.1 ml (4.2 mmol) of the 0.278 molar sec-butyllithium solution, 1.6 l (19.4 mol) of 1,3-butadiene were added in portions (100 ml) over the course of one hour at 70°C and the mixture was polymerized at 70°C for a further hour. The molecular weights of the resulting polybutadiene block were determined on a sample by means of gel permeation chromatography (GPC) with polybutadiene calibration: $M_w = 248,000$ g/mol, $M_w/M_n = 1.28$, M (peak maximum) = 226,000 g/mol. To the resulting polybutadiene block there were added, in succession at an interval of 15 minutes, 98.3 ml (0.56 mol) of 1,1-diphenylethylene and 259 ml (2.25 mol) of styrene, and polymerization was continued at 70°C for 5 hours more. After the reaction had subsided, the reaction mixture was titrated with ethanol until it became colorless and was acidified with CO₂/water. The colorless solution was freed from solvent under reduced pressure in a devolatilizing extruder, and the product was granulated.

GPC (polybutadiene calibration): two peaks: 1st peak (20%) M (peak maximum) = 32,000 g/mol; 2nd peak (80%): peak maximum at 260,000 g/mol.

Examples 1 to 4

532 ml of pentane and a mixture of 2.61 g of dispersant D1 in 104.2 g (1 mol) of styrene were introduced with stirring into an autoclave which had been rendered inert [sic] with argon. 8.16 ml of a 1.53 molar solution of methylaluminumoxane (MAO) in toluene (obtained from Witco) and 2.08 ml of a 1.0 molar solution of diisobutylaluminum hydride (DIBAH) in cyclohexane (obtained from Aldrich) were added. Prior to the addition of the transition metal complex, a defined amount of lubricant was then added to this mixture. Subsequently, 1.5 l of hydrogen were injected at

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room temperature and the reaction solution was heated to 80°C. Then 1.14 mg (0.05 mmol) of pentamethylcyclopentadienyltitanium trimethyl Cp*TiMe₃ were added, and an internal pressure of 7.5 bar developed. After 2 hours, the polymerization was terminated by adding 10 ml of methanol. After cooling to room temperature, a homogeneous, readily flowing suspension was obtained. The resultant polymer was washed with methanol and dried under reduced pressure at 50°C.

The molecular weights Mw and Mn were determined by means of high-temperature gel permeation [sic] chromatography GPC (135°C, 1,2,4-trichlorobenzene, polystyrene standard). The syndiotactic content was determined by means of ¹³C-NMR spectroscopy. The particle sizes lay within the range from 2 to 10 µm and were determined on a sample, slurried in immersion oil, between two planar glass plates under the transmission microscope (Axiophot from Carl Zeiss).

The conversion is based on the amount of styrene employed.

Comparative Experiment C1

Polymerization was carried out as in Examples 1 to 4 but without the addition of a lubricant.

Ex.	Lubricant	M _w [g/mol]	M _w /M _n	Vis- cosity [mPas]	Con- ver- sion [%]	Productivity [kg s-Ps/gTi]
1	0.5% by wt. Winog 60	422,800	1.9	2.99	67	69.2
2	5% by wt. Winog 60	278,500	2.0	4.81	73	82.1
3	1% by wt. distearyl phthalate	296,700	2.0	2.43	69	49.7
4	8% by wt. Winog 70	301,400	2.2	4.01	71	66.5
C1	-	321,500	2.1	2.35	34	15.4

The syndiotacticity of the polymers was ≥ 95%.

The percentages by weight for the lubricants are based on styrene monomer employed.

Winog®60 and Winog®70 are white oils (mineral oil hydrocarbons)

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to DAB [German Pharmacopeia] 9 from Wintershall Mineralöl GmbH.
Winog 70 has a dynamic viscosity [to DIN 51562] of 136 mPas, a
molecular weight in the range from 400 to 550, and a density of
0.865 g/cm³.

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Winog 60 has a dynamic viscosity [to DIN 51562] of 180 mPas and a
density of 0.863 g/cm³.

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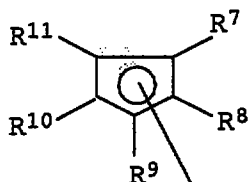
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We claim:

- 5 1. A process for preparing polymers of vinylaromatic compounds in dispersion in aliphatic hydrocarbons of 4 to 10 carbon atoms as the dispersing medium in the presence of a dispersing auxiliary and a catalyst, obtainable from A) a transition metal complex of subgroups II to VIII, B) a cation-forming agent and C), if desired, an aluminum
10 compound, which comprises adding lubricants.
2. A process as claimed in claim 1, wherein the dispersing auxiliary used comprises block copolymers having at least one
15 diene block B and at least one block S comprising a copolymer of a vinylaromatic monomer and 1,1-diphenylethylene or its aromatic ring-substituted derivatives, including those substituted by alkyls of up to 22 carbons.
- 20 3. A process as claimed in claim 2, wherein the block copolymer comprises polybutadiene or polyisoprene in copolymerized form and the diene block B is partially or completely hydrogenated or unhydrogenated.
- 25 4. A process as claimed in either of claims 1 and 3, wherein the block S of the block copolymer consists of a copolymer of styrene and 1,1-diphenylethylene.
- 30 5. A process as claimed in any of claims 1 to 4, wherein the lubricant is used in an amount of from 0.01 to 50% by weight, based on the monomer employed.
6. A process as claimed in any of claims 1 to 5, wherein a
35 branching monomer unit comprising at least two vinylaromatic radicals is used in a molar ratio of vinylaromatic monomers to branching units of from 10,000,000 : 1 to 10 : 1.
7. A process as claimed in any of claims 1 to 6, wherein the
40 catalyst component A) employed is a metallocene complex of the formula (III)



(III),

where

R^7 to R^{11} are hydrogen, C_1 - C_{10} -alkyl, 5- to 7-membered cycloalkyl which in turn can carry C_1 - C_6 -alkyls as substituents, C_6 - C_{15} -aryl or arylalkyl, and where two adjacent radicals may if desired together be cyclic groups of 4 to 15 carbons, or are $Si(R^{12})_3$,

where R^{12} is C_1 - C_{10} -alkyl, C_6 - C_{15} -aryl or C_3 - C_{10} -cycloalkyl,

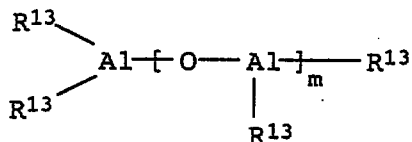
M is a metal from subgroups III to VI of the Periodic Table of the elements or is a metal of the lanthanide series,

Z^1 to Z^5 are hydrogen, halogen, C_1 - C_{10} -alkyl, C_6 - C_{15} -aryl, C_1 - C_{10} -alkoxy or C_1 - C_{15} -aryloxy

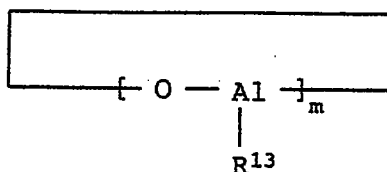
and

z_1 to z_5 are 0, 1, 2, 3, 4 or 5, the sum $z_1+z_2+z_3+z_4+z_5$ corresponding to the valency M minus 1.

8. A process as claimed in claims 1 to 7, wherein the cation-forming compound B) employed comprises open-chain or cyclic alumoxane compounds of the formula IV or V



IV



V



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where R¹³ is C₁-C₄-alkyl and m is an integer from 5 to 30.

9. A process as claimed in any of claims 1 to 7, wherein the cation-forming compound B) employed is a coordination complex compound selected from the group consisting of strong, neutral Lewis acids, ionic compounds having Lewis-acid cations and ionic compounds having Brønsted acids as cations.

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Preparation of poly(vinylaromatics) by dispersion polymerization with the addition of lubricants

5 Abstract

10 A description is given of a process for preparing polymers of vinylaromatic compounds in dispersion, in the presence of a dispersing auxiliary and a catalyst, obtainable from A) a transition metal complex of subgroups II to VIII, B) a cation-forming agent and C), if desired, an aluminum compound, wherein additives are added.

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