

A method of hydrogenating aromatic polymers in the presence of branched hydrocarbons

The present invention relates to a method of hydrogenating aromatic polymers, which is characterised in that branched saturated hydrocarbons are used as solvents, which branched saturated hydrocarbons possess a maximum of one hydrogen atom at the branching point, a boiling temperature higher than 45°C and an ignition temperature (DIN 51794) higher than or equal to 280°C, or a mixture is used of solvents which contain these hydrocarbons with solvents which are customary for hydrogenation reactions. This invention also relates to the polymers produced in this manner.

The hydrogenation of aromatic polymers is already known. DE-AS 1 131 885 describes the hydrogenation of polystyrene in the presence of catalysts and solvents. Aliphatic and cycloaliphatic hydrocarbons, ethers, alcohols and aromatic hydrocarbons are mentioned in general as solvents. A mixture of cyclohexane and tetrahydrofuran is cited as being preferred.

WO 96/34 896 (= US-A-5 612 422) describes a method of hydrogenating aromatic polymers, for example, in which hydrogenation is effected in the presence of a metal on a silica support as a hydrogenation catalyst, wherein the silica has a defined pore size distribution. Aliphatic or cycloaliphatic hydrocarbons are mentioned as solvents, and isopentane (2-methylbutane) is cited as a branched saturated hydrocarbon. Diethylene glycol dimethyl ether and tetrahydrofuran are cited as ethers.

EP-A-322 731 describes the production of what are predominantly syndiotactic polymers based on vinylcyclohexane, wherein a styrene-based polymer is hydrogenated in the presence of hydrogenation catalysts and solvents. Cycloaliphatic and aromatic hydrocarbons are mentioned as solvents.

The specialised solvents of the present invention are not mentioned.

Apart from isopentane, the hydrocarbons described in the aforementioned documents possess ignition temperatures lower than or equal to 260°C and are solvents which are not easy to handle in an industrial process. Solvents for an industrial process
5 have to have sufficiently high ignition temperatures (DIN 51 794), since contact with hot metal surfaces, possibly in the presence of air, occurs during the work-up of polymers, and the processing temperatures employed for a polymer solution of hydrogenated polystyrene in the presence of solvent, for example, can reach or exceed 240°C. The possibility thus exists of ignition and explosion unless a
10 sufficient temperature difference is maintained between the processing temperature and the ignition temperature.

Replacing the solvent before the work-up step for the production of granules is associated with considerable costs and engineering expenditure.

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Measures which render the entire polymer work-up step inert, and which prevent the occurrence of solvent/air contact, are costly, and can scarcely be realised in practice for a large-scale industrial process, since the entire installation would have to be encapsulated under an inert gas, for example.

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Apart from isopentane, the solvents which are known from the aforementioned documents (WO96/34896; US 5 612 422) are capable of igniting without precautions of this type, or without other complex, expensive precautions, and constitute a considerable safety risk. However, isopentane is not a solvent for
25 polystyrene, for example, and this solvent is thus unsuitable for the hydrogenation of this polymer. Moreover, as a solvent isopentane has the disadvantage of boiling at 28°C, which firstly makes the handling of solutions difficult and secondly results in costly cooling and condensation installations as a consequence of the requisite cooling during the work-up step.

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The object of the present invention was that the solvent used should dissolve the polymer starting material, and should result in the practically complete

hydrogenation of aromatic units, with the reaction product being dissolved, to provide a system which can be fed directly to the work-up step, with a temperature difference (of at least 15 % with respect to the Celsius temperature scale) being maintained between the processing temperature and the ignition temperature of the solvent.

It has now been found that certain branched hydrocarbons possess the requisite properties, and a large-scale process for the hydrogenation of aromatic polymers and the polymer work-up step thereof are thereby considerably simplified. The present method is distinguished in that the hydrogenated polymer solution can be fed directly to the work-up step and no complex technical measures are necessary in order to exclude solvent/air contact at a surface at temperatures higher than or equal to the ignition temperature. Another advantage of using these specialised branched hydrocarbons is that the solvent can be separated from the polymer at higher temperatures, which results in lower residual contents of solvent and higher throughputs of polymer.

The present invention relates to a method of hydrogenating aromatic polymers, optionally in the presence of catalysts, wherein branched hydrocarbons are used as solvents, which branched hydrocarbons possess at most one hydrogen atom at the branching point, a boiling temperature higher than 45°C and an ignition temperature (DIN 51794) above 280°C, or a mixture is used of hydrocarbons such as these with solvents which are suitable for hydrogenation reactions.

The reaction is generally conducted at concentrations by volume of the branched saturated hydrocarbons of 0.1 % - 100 %, preferably 1 % - 80 %, most preferably 5 - 70 %, with respect to the total solvent.

In general, the method according to the invention results in the practically complete hydrogenation of aromatic units. As a rule, the degree of hydrogenation is ≥ 80 %, preferably ≥ 90 %, more preferably ≥ 99 %, most preferably 99.5 to 100 %. The

degree of hydrogenation can be determined by NMR or UV spectroscopy, for example.

5 The aromatic polymers which are used as starting materials are selected, for example, from polystyrene, which is optionally substituted within the phenyl ring and/or at the vinyl group, or from copolymers thereof with monomers selected from the group consisting of olefins, (meth)acrylates or mixtures thereof. Other suitable polymers include aromatic polyethers, particularly polyphenylene oxide, aromatic polycarbonates, aromatic polyesters, aromatic polyamides, polyphenylenes, 10 polyxylylenes, polyphenylene vinylenes, polyphenylene ethylenes, polyphenylene sulphides, polyaryl ether ketones, aromatic polysulphones, aromatic polyether sulphones and aromatic polyimides, as well as mixtures and copolymers thereof, optionally copolymers with aliphatic compounds.

15 Suitable substituents in the phenyl ring include C₁-C₄ alkyl groups, such as methyl and ethyl, C₁-C₄ alkoxy groups, such as methoxy or ethoxy, and aromatic compounds which are incorporated by condensation and which are bonded to the phenyl ring via a hydrocarbon atom or via two carbon atoms, comprising phenyl, biphenyl or naphthyl.

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Suitable substituents on the vinyl group include C₁-C₄ alkyl groups, such as methyl, ethyl and n- or iso-propyl, particularly methyl in the α -position.

25 Suitable olefinic comonomers include ethylene, propylene, isoprene, isobutylene, butadiene, cyclohexadiene, cyclohexene, cyclopentadiene, norbornene, which is optionally substituted, dicyclopentadiene, which is optionally substituted, tetracyclododecenes, which are optionally substituted, or dihydrocyclopentadienes, which are optionally substituted,

30 C₁-C₈, preferably C₁-C₄ alkyl esters of (meth)acrylic acid, particularly preferably the methyl or ethyl esters,

C₁-C₈, preferably C₁-C₄ alkyl ethers of vinyl alcohol, particularly preferably the methyl or ethyl ethers,

5 C₁-C₈, preferably C₁-C₄ alkyl esters of vinyl alcohol, particularly preferably esters of ethanoic acid,

derivatives of maleic acid, preferably maleic anhydride, and derivatives of acrylonitrile, preferably acrylonitrile and methacrylonitrile.

10 The aromatic polymers generally have molecular weights M_w of 1000 to 10,000,000, preferably 60,000 to 1,000,000, most preferably 70,000 to 600,000, as determined by light scattering.

15 The polymers may possess a linear chain structure, or may also comprise branching points due to co-units (e.g. graft copolymers). The branching centres may comprise star-shaped polymers, for example, or may comprise other geometric forms of the primary, secondary, tertiary or optionally quaternary polymer structure.

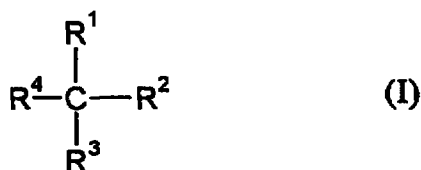
20 The copolymers may exist as random polymers, or alternatively they may exist as block copolymers.

Block copolymers comprise di-blocks, tri-blocks, multi-blocks and star-shaped block copolymers.

25 The polymer starting materials are generally known (e.g. WO 94/21 694).

The solvents which are preferably used are branched hydrocarbons of formula (I), which have boiling temperatures above 45°C and ignition temperatures (DIN 51 794) higher than or equal to 280°C.

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wherein

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the R^1 , R^2 , R^3 , and R^4 radicals represent straight chain or branched C_1 - C_{10} alkyl radicals and a maximum of one of the R^1 , R^2 , R^3 and R^4 radicals may also represent hydrogen,

10 The following are particularly preferred:

2,2,3-trimethylbutane; 2,2-dimethylbutane; 2,3-dimethylbutane; methylcyclopentane; 2-methylpentane; 3-methylpentane; 3,3-diethylpentane; 2,4-dimethylpentane; 2,2-dimethylpentane, 2,3-dimethylpentane; 2,4-dimethyl-3-ethylpentane; 2,2,3-trimethylpentane; 2,3,3-trimethylpentane; 2,2,4-trimethylpentane (isooctane); 2,2,3,3-tetramethylpentane; 2,2,3,4-tetramethylpentane; 2,3,3,4-tetramethylpentane; 2-methylhexane; 3-methylhexane; 2-methyl-4-ethylhexane; tert.-butylcyclohexane; 2-methylheptane; 2,5,5-trimethylheptane; 3,3-dimethylheptane; 2,2,5-trimethylheptane.

20 The solvent which is particularly preferred for the hydrogenation of polystyrene and derivatives thereof is methylcyclopentane, which is a good solvent by comparison with the hydrocarbons which are known for hydrogenation from the aforementioned documents, and which has a boiling temperature of 72°C and an ignition temperature of 315°C.

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The amount of catalyst used is described in WO 96/34896 for example.

The amount of catalyst used depends on the process which is carried out. This process may be effected continuously, semi-continuously or batch-wise.

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In a continuous system, the time of reaction is significantly shorter, and is influenced by the dimensions of the reaction vessel. In a continuous procedure, the

trickling system and the reactor bottom system, which both comprise fixed catalysts, are operated as far as possible as a system comprising suspended catalyst which is recycled, for example. The fixed catalysts may exist in the form of tablets or as extruded shapes.

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The polymer concentrations with respect to the total weight of solvent and polymer generally range from 80 to 1, preferably 50 to 10, particularly 40 to 15 % by weight.

- 10 Hydrogenation of the polymer starting material is generally conducted by methods which are generally known (e.g. WO 94/21 694, WO 96/34 895, EP-A-322 731). There is a multiplicity of known hydrogenation catalysts which can be used as catalysts. The preferred metal catalysts are cited, for example, in WO 94/21 694 or WO 96/34 896. Any catalyst which is known for hydrogenation reactions can be
- 15 used. Suitable catalysts comprise both those of large surface area (e.g. 100 - 600 m²/g) and small average pore sizes (e.g. 20 - 500 Å) and those which have a small surface area (e.g. ≥ 10 m²/g) and which have a large average pore size which is characterised in that 98 % of the pore volume is defined as being larger than 600 Å (e.g. about 1000 - 4000 Å) (see US-A 5,654,253, US-A 5,612,422, JP-A 03076706,
- 20 for example). Raney nickel, nickel on silica, alumina or silica/alumina, nickel on carbon as a support, and/or noble metal catalysts, e.g. Pt, Ru, Rh, Pd, are used in particular.

- The reaction is generally conducted at temperatures between 0 and 500°C,
- 25 preferably between 20 and 250°C, particularly preferably between 60 and 200°C.

The solvents which can customarily be used for hydrogenation reactions are described in DE-AS 1 131 885, for example (see above).

- 30 The reaction is generally conducted at pressures of 1 bar to 1000 bar, preferably 20 to 300 bar, particularly preferably 40 to 200 bar.

Examples:**Examples 1 and 2**

- 5 A 1 litre autoclave was flushed with inert gas. The polymer solution and the catalyst were added (Table). After closing the autoclave, it was repeatedly subjected to the action of protective gas and then hydrogen. After releasing the pressure, the respective hydrogen pressure was set and the batch was heated to the corresponding reaction temperature with stirring. After hydrogen absorption had set in, the
- 10 reaction pressure was held constant.

The time of reaction was the time from heating up the batch to the time of complete hydrogenation of the polystyrene, or for incomplete hydrogenation was the time until the hydrogen absorption approached its saturation value.

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After the reaction was terminated, the polymer solution was filtered. The product was precipitated in methanol and dried. The isolated product had the physical properties listed in the Table.

Table

Hydrogenation of polystyrene as a function of the solvent system

Example No.	Weight of polystyrene (g)	Solvent (ml)	Weight of catalyst (g)	Reaction temperature (°C)	H ₂ pressure (bar)	Time of reaction (min)	Degree of hydrogenation ¹⁾ (%)	Ignition temperature of the solvent (DIN51794) (°C)
1 Comparison (US-A-5 612 422)	200	2300 CYH	13.5 ⁴	150	875(psig)	110	98.4	260
2 According to the invention	100.2 ²⁾	200 MCP + 100 MTBE	12.5 ³	160	100	360	100	315 460

1) Determined by ¹H NMR spectroscopy

2) polystyrene Type 158 k, Mw = 280,000 g/mole, BASF AG, Ludwigshafen, Germany

3) Engelhard, Ni-5136 P, nickel on silica/alumina

4) US-A-5 612 422, 5 % platinum/silica

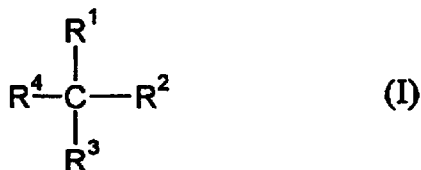
CYH = cyclohexane, MCP = methylcyclopentane, MTBE = methyl tert.-butyl ether

The platinum catalyst (Table) resulted in the hydrogenation of polystyrene in cyclohexane at 140°C (comparative example 1). Cyclohexane has an ignition temperature of 260°C and leads to problems when working up the product, since
5 solvent/air contact on hot metal surfaces at temperatures approaching the ignition temperature has to be avoided. The method according to the invention (example 2) resulted in complete hydrogenation compared with comparative example 1, but all the solvents used had ignition temperatures above 310°C.



Claims

1. A method of hydrogenating aromatic polymers, optionally in the presence of catalysts, wherein branched hydrocarbons are used as solvents, which branched hydrocarbons possess at most one hydrogen atom at the branching point, a boiling temperature higher than 45°C and an ignition temperature (DIN 51794) above 280°C, or a mixture is used of hydrocarbons such as these with solvents which are suitable for hydrogenation reactions.
2. A method according to claim 1, wherein branched hydrocarbons of formula (I) are used as solvents,



wherein

the R^1 , R^2 , R^3 , and R^4 radicals represent straight chain or branched C_1 - C_{10} alkyl radicals and a maximum of one of the R^1 , R^2 , R^3 and R^4 radicals may also represent hydrogen.

3. A method according to claims 1 and 2, wherein the solvent is selected from at least one of the following solvents:
 2,2,3-trimethylbutane; 2,2-dimethylbutane; 2,3-dimethylbutane; methylcyclopentane; 2-methylpentane; 3-methylpentane; 3,3-diethylpentane; 2,4-dimethylpentane; 2,2-dimethylpentane, 2,3-dimethylpentane; 2,4-dimethyl-3-ethylpentane; 2,2,3-trimethylpentane; 2,3,3-trimethylpentane; 2,2,4-trimethylpentane (iso-octane); 2,2,3,3-tetramethylpentane; 2,2,3,4-tetramethylpentane; 2,3,3,4-tetramethylpentane; 2-methylhexane; 3-methyl-



hexane; 2-methyl-4-ethylhexane; tert.-butylcyclohexane; 2-methylheptane; 2,5,5-trimethylheptane; 3,3-dimethylheptane; 2,2,5-trimethylheptane.

4. A method according to one or more of the preceding claims, wherein a
5 mixture of solvents is used which contains at least one branched, saturated hydrocarbon and at least one solvent which can be used for hydrogenation reactions.
5. A method according to one or more of the preceding claims, wherein the
10 concentration by volume of saturated, branched hydrocarbons in relation to the total solvent ranges from 0.1 to 100 %.
6. A method according to one or more of the preceding claims, wherein the
15 concentration by volume of saturated, branched hydrocarbons ranges from 1 to 80 %.
7. A method according to one or more of the preceding claims, wherein the
20 concentration by volume of saturated, branched hydrocarbons ranges from 5 to 70 %.
8. A method according to one or more of the preceding claims, wherein the
polymer concentration ranges from 80 to 1 % by weight with respect to the total weight of solvent and polymer.
- 25 9. A method according to one or more of the preceding claims, wherein the polymer concentration ranges from 50 to 10 % by weight with respect to the total weight of solvent and polymer.
10. A method according to one or more of the preceding claims, wherein the
30 polymer concentration ranges from 40 to 15 % by weight with respect to the total weight of solvent and polymer.



11. A method according to one or more of the preceding claims, wherein the aromatic polymers are selected from the group consisting of the following polymers:
- 5 polystyrene, which is optionally substituted within the phenyl ring and/or at the vinyl group, or copolymers thereof, aromatic polyethers, aromatic polyesters, aromatic polyamides, polyphenylenes, polyxylylenes, polyphenylene vinylenes, polyphenylene ethylenes, polyphenylene sulphides, polyaryl ether ketones, aromatic polysulphones, aromatic polyether sulphones and aromatic polyimides, as well as mixtures and copolymers thereof, optionally copolymers with aliphatic compounds.
- 10
12. A method according to claim 11, wherein the aromatic polymers are selected from the group consisting of the following polymers:
- 15 polystyrene, which is optionally substituted within the phenyl ring and/or at the vinyl group, or copolymers thereof with monomers selected from the group comprising olefins, (meth)acrylates or mixtures thereof.
13. A method according to claim 12, wherein the comonomers are selected from ethylene, propylene, isoprene, isobutylene, butadiene, cyclohexadiene, 20 cyclohexene, cyclopentadiene, norbornene, which is optionally substituted, dicyclopentadiene, which is optionally substituted, tetracyclododecenes, which are optionally substituted, or dihydrocyclopentadienes, which are optionally substituted,
- 25 C₁-C₈ alkyl esters of (meth)acrylic acid,
- C₁-C₈ alkyl ethers of vinyl alcohol,
- C₁-C₈ alkyl esters of vinyl alcohol,
- 30 derivatives of maleic acid; derivatives of acrylonitrile.

14. A method according to one or more of the preceding claims, wherein the aromatic polymers have (weight average) molecular weights of 1000 to 10,000,000.
- 5 15. A method according to one or more of the preceding claims, wherein the aromatic polymers have (weight average) molecular weights of 60,000 to 1,000,000.
- 10 16. Hydrogenated polymers obtainable by a method according to one or more of the preceding claims.

