[Brief description]

[020] Surprisingly, it was discovered that a method for controlling the synthesis of a block copolymer containing at least two blocks, with at least one nonpolar block and at least one polar block, said method making it possible in particular to control the ratio between the blocks and the molecular weight of each of the blocks, said copolymer being a block copolymer intended to be used as a mask in a method of nanolithography by direct self-assembly (DSA), said control being achieved by semicontinuous anionic polymerization in an aprotic nonpolar medium and comprising the following steps:

- synthesizing a first nonpolar block in the form of a macro-initiator,
- preparing a solution of said macro-initiator previously synthesized by mixing it with an alkali metal alcoholate in an aprotic nonpolar solvent,
- preparing a solution of a polar monomer in an aprotic nonpolar solvent,
- injecting the two solutions previously prepared of macro-initiator and of polar monomer into a micro-mixer, connected to a polymerization reactor, at a constant flow ratio,
- recovering the copolymer obtained,

makes it possible to obtain, with increased reproducibility, nonpolar-b-polar block copolymers of the PS-*b*-PMMA type whose nanodomains have controlled properties, notably in terms of shapes, sizes and periods, and meet precise specifications, so that the block copolymers can be used industrially as masks in methods of nanolithography by direct self-assembly (DSA).

[020a] In an aspect, there is provided a method for controlling the synthesis of a block copolymer containing at least two blocks, with at least one nonpolar block and at least one polar block, said method making it possible in particular to control the ratio between the blocks and the molecular weight of each of the blocks, said copolymer being a block copolymer intended to be used as a mask in a method of nanolithography by direct self-assembly (DSA), said control being achieved by semicontinuous anionic polymerization in an aprotic nonpolar medium and comprising the following steps:

- synthesizing a first nonpolar block in the form of a macro-initiator,
- preparing a solution of said macro-initiator previously synthesized by mixing it with an alkali metal alcoholate in an aprotic nonpolar solvent,

- preparing a solution of a polar monomer in an aprotic nonpolar solvent,
- injecting the two solutions previously prepared of macro-initiator and of polar monomer into a micro-mixer, connected to a polymerization reactor, at a constant flow ratio,
- recovering the copolymer obtained.

[021] The disclosure further relates to a block copolymer containing at least two blocks, with at least one nonpolar block and at least one polar block, intended to be used as a mask in a method of nanolithography by direct self-assembly (DSA), said block copolymer being synthesized in a controlled manner according to the method of control described above, and having nanodomains in the form of lamellae when the nonpolar block / polar block weight ratio is between 35/65 and 60/40 and in the form of cylinders when the nonpolar block / polar block weight ratio is between 64/36 and 75/25 or between 25/75 and 36/64.

[021a] In another aspect, there is provided a block copolymer containing at least two blocks, with at least one nonpolar block and at least one polar block, intended to be used as a mask in a method of nanolithography by direct self-assembly (DSA), said block copolymer being a PS-*b*-PMMA block copolymer synthesized in a controlled manner according to the method of control as defined above, and having nanodomains in the form of lamellae when the PS/PMMA weight ratio is between 35/65 and 60/40 and in the form of cylinders when the PS/PMMA weight ratio is between 64/36 and 75/25.

[022] The disclosure finally relates to the use of a film of the block copolymer containing at least two blocks, with at least one nonpolar block and at least one polar

block, as a mask in a method of nanolithography by direct self-assembly (DSA), said film of the block copolymer being synthesized in a controlled manner according to the method of control described above.

[022a] In an aspect, there is also provided the use of a film of block copolymer containing at least two blocks, with at least one nonpolar block and at least one polar block, as a mask in a method of nanolithography by direct self-assembly (DSA), said film of block copolymer being synthesized in a controlled manner according to the method of control as defined above.

[023] Other particular features and advantages of the disclosure will become clear on reading the description given as an illustrative, nonlimiting example, referring to the appended figures, which show:

- Fig. 1, a flow sheet of an example of polymerization installation that can be used,
- Figs. 2A and 2B, curves showing the molecular weight of the PS block in several PS-*b*-PMMA block copolymers that were synthesized according to a conventional method, or in a controlled manner according to the disclosure.

[Detailed description of the invention]

[024] The term "monomer" as used here relates to a molecule that can undergo polymerization.

[025] The term "polymerization" as used here relates to the method of transforming a monomer or a mixture of monomers into a polymer.

[026] "Copolymer block" or "block" means a polymer combining several monomer units of several types, or of one and the same type.

[027] "Block copolymer" means a polymer comprising at least two blocks as defined above, the two blocks being different from one another and having a phase segregation parameter such that they are not miscible and separate into nanodomains for a given temperature and a given chain length.

[028] The term "miscibility" used above is to be understood as the ability of two compounds to mix completely to form a homogeneous phase.

[029] Period, designated Lo, means the minimum distance separating two neighbouring domains of the same chemical composition, separated by a domain with a different chemical composition.

[030] In the description, when talking of the molecular weight of a block, it is the peak molecular weight Mp, measured by size exclusion chromatography (SEC).

[031] "Polar" solvent or monomer or block means a solvent or monomer or block selected from solvents, monomers or blocks or mixtures, having Hansen solubility parameters, calculated at 25°C, such that $\delta_{tot} = \delta_D + \delta_P + \delta_H < 22.0$ MPa.