[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, wherein said macro-initiator is prepared from n-butyllithium
- 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.

[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.

[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.

CLAIMS

1. 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, wherein said macro-initiator is prepared from n-butyllithium,
- 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.

2. The method as claimed in claim 1, characterized in that the constituent monomers of the copolymers are selected from styrene or (meth)acrylic or vinylpyridine monomers, and more particularly styrene and methyl methacrylate.

3. The method as claimed in claim 1, characterized in that the single polymerization solvent is toluene or ethylbenzene.

4. The method as claimed in claim 1, characterized in that the alkali metal alcoholate is lithium methoxyethanolate and in that the molar ratio of lithium methoxyethanolate / nonpolar macro-initiator is between 1 and 10, and preferably equal to 6.

5. The method as claimed in one of claims 1 to 4, characterized in that the concentration of nonpolar macro-initiator in the mixture from the micro-mixer is between 95 and 5, preferably between 95 and 50, and even more preferably between 85 and 50 and the concentration of polar monomer is between 5 and 95, preferably between 5 and 50 and even more preferably between 15 and 50.

6. The method as claimed in one of claims 1 to 5, characterized in that the block copolymer is a PS-*b*-PMMA copolymer, the first nonpolar block is in the form of a macro-initiator of PS-diphenylethyllithium (PS-DPEL) and in that more than one equivalent of diphenylethylene (DPE) is used to one equivalent of polystyryllithium, in the step of preparation of said macro-initiator of PS-DPEL.

7. The method as claimed in claim 6, characterized in that an additional step of purification of the PS-*b*-PMMA block copolymer obtained is carried out by dropwise precipitation of a solution of methanol containing said block copolymer obtained, into a solution containing an 80/20 mixture by volume of cyclohexane/heptane, then recovery of the purified block copolymer by removal of the supernatant and filtration.