[019] Consequently, in order to control the period Lo of a nanostructured block copolymer so that it is large, typically greater than 30 nm and more preferably still greater than 50 nm and less than 100 nm, it is necessary to control the adjustment of the product χN. Indeed, it is necessary that the Flory-Huggins parameter χ be sufficient to enable an optimal phase segregation between the blocks while having a high degree of polymerization N in order to enable a large period, preferably of greater than 30 nm, to be obtained.

[020] Document WO 2013/019679 describes the possibility of modifying at least one of the blocks of a base block copolymer. The modification of at least one of the blocks of the block copolymer has an influence on the surface and interfacial energies of the nanodomains and entails a modification of the morphology and of the orientation of the nanodomains in the block copolymer. This document remains silent regarding the kinetics of organization of the modified block copolymer and does not seek to increase the period of the nanostructured block copolymer.

[021] Due to the fact that PS-*b*-PMMA block copolymers make it possible to produce nanolithography masks that offer a good resolution, the applicant has sought a solution for modifying this type of block copolymer in order to be able to control the period thereof, and in particular to obtain a period which is greater than a threshold value of 30 nm and more preferably still greater than 50 nm and less than 100 nm, with rapid nanostructuring kinetics and a significantly reduced defectivity.

[022] More particularly, the applicant has sought a solution for modifying such a block copolymer of PS-*b*-PMMA type, so as to be able to increase its period Lo, without the appearance of defects due to an excessively high nanostructuring temperature and/or to excessively slow nanostructuring kinetics.

[Technical problem]

[023] The objective of the ~~invention~~ present disclosure is therefore to overcome at least one of the drawbacks of the prior art. The ~~invention~~ disclosure aims in particular to provide a process for controlling the period of nanostructuring, into nanodomains, of a block copolymer film using a base block copolymer having a molecular weight of greater than 50 kg/mol, and preferably greater than 100 kg/mol and less than 250 kg/mol, and at least one block of which contains polystyrene, and at least one block of which contains methyl methacrylate.

[024] For this, the block copolymer is modified so that the product χN is greater than or equal to 7 and preferably greater than or equal to 10 in order to allow good phase segregation between the nanodomains and a large period Lo, preferably of greater than 30 nm and more preferably still greater than 50 nm and less than 100 nm, to be obtained. The nanostructuring process must also allow a very rapid organization of the block copolymer with organization kinetics of the order of 1 to a few minutes, this being at a temperature, referred to as annealing temperature, below the degradation temperature of the polymer.

[025] The ~~invention~~ present disclosure also aims to provide a block copolymer film nanostructured into nanodomains, obtained from a base block copolymer, having a molecular weight of greater than 50 kg/mol, and preferably greater than 100 kg/mol and less than 250 kg/mol, and at least one block of which comprises styrene, and at least one block of which comprises methyl methacrylate, said copolymer being modified in order to be nanostructured with a large period, with fast organization kinetics of the blocks and/or at a temperature below the degradation temperature of the copolymer.

[Summary~~Brief description of the invention~~]

[026] Surprisingly, it has been discovered that a block copolymer film nanostructured into nanodomains, obtained from a base block copolymer having a molecular weight of greater than 50 kg/mol, and preferably greater than 100 kg/mol and less than 250 kg/mol, and at least one block of which comprises styrene, and at least one other block of which comprises methyl methacrylate, said block copolymer film being characterized in that the styrene-based block is formed by a copolymer of styrene and diphenylethylene (DPE),

makes it possible to obtain a value χN in the desired range and makes it possible to obtain nanodomains with a large period Lo, typically of greater than 30 nm, while enabling organization at a temperature below that required for organizing the blocks of the base, i.e. unmodified, PS-*b*-PMMA block copolymer and while retaining fast organization kinetics with a reduced defectivity with respect to that obtained with said base PS-b-PMMA block copolymer.

[0026a] In an aspect, there is provided a block copolymer film nanostructured into nanodomains, obtained from a base block copolymer having a molecular weight Mp of greater than 50 kg/mol, and preferably greater than 100 kg/mol and less than 250 kg/mol, and at least one block of which comprises styrene, and at least one other block of which comprises methyl methacrylate, said block copolymer film being characterized in that the styrene-based block is formed by a P(S-co-DPE) copolymer of styrene and diphenylethylene (DPE).

[027] ~~The invention also relates to~~In another aspect, there is provided a process for controlling the period of nanostructuring, into nanodomains, of a block copolymer film using a base block

copolymer having a molecular weight of greater than 50 kg/mol, and preferably greater than 100 kg/mol and less than 250 kg/mol, and at least one block of which comprises styrene, and at least one other block of which comprises methyl methacrylate, said process being characterized in that it comprises the following steps:

- synthesis of said block copolymer by incorporating, into the block of said base block copolymer containing styrene, one or more diphenylethylene (DPE) comonomers,
- application of a solution of said block copolymer in the form of a film to a surface,
- evaporation of the solvent of the solution and annealing at said predetermined temperature.

[028] ~~The invention finally relates to~~In another aspect, there is provided a nanolithography mask obtained from a film of said block copolymer described above, deposited on a surface to be etched in accordance with the above process, said copolymer film comprising nanodomains oriented perpendicular to the surface to be etched and having a period Lo of greater than 30 nm and more preferably still greater than 50 nm and less than 100 nm.

[029] Other features and advantages of the ~~invention~~ disclosure will appear on reading the description given by way of illustrative and nonlimiting example, with reference to the appended figures, which represent:

- Figure 1, a diagram of an example of polymerization equipment that can be used,
- Figure 2, photos, taken with a scanning electron microscope, of various samples of nanostructured block copolymer, of different and modified or unmodified composition,
- Figure 3, photos, taken with a scanning electron microscope, of several samples of a same modified block copolymer having 2 different thicknesses and having undergone 2 different heat treatments,
- Figure 4, photos, taken with a scanning electron microscope, of two samples of a same modified block copolymer having undergone a heat treatment for 2 different durations.

[Detailed description of the invention]