copolymers. These block copolymers are modified to reduce the value of the Flory–Huggins interaction parameter χ, so that the block copolymer is able to self–assemble into nano–domains of small size with faster kinetics. More particularly, these documents seek to reduce the Flory–Huggins parameter χ of a PS–*b*–PDMS block copolymer (polystyrene –*block*– poly(dimethylsiloxane)) having nano–domains oriented parallel to the surface in which they are deposited. The assembly kinetics of the block copolymers described in tense documents remain very slow however since they may last a few hours, typically up to 4 hours.

[0015] Document WO 2013/019679 describes the possibility of modifying at least one of the blocks of a basic block copolymer. The modification of at least one of the blocks of the block copolymer impacts the surface and interface energies of the nano–domains and involves modification of the morphology and orientation of the nano–domains in the block copolymer. This document remains silent on the organisation kinetics of the modified block copolymer and does not seek to modify the value of the interaction parameter χ to allow nano–structuring of a block copolymer non–structured at a given temperature.

[0016] Since PS–*b*–PMMA block copolymers already allow dimensions close to 10 nm to be obtained, the applicant has sought a solution to modify this type of block copolymer so that it self–nanostructures into nano–domains of smaller size whilst preserving its very fast organisation kinetics.

[0017] More particularly, the applicant has sought a solution to modify a said block copolymer non–structured at a given temperature via its χN value less than 10, so as to increase the Flory–Huggins parameter χ and gain access to structuring of the nano–domains without however penalising the organisation kinetics of the blocks of the copolymer which must be rapid i.e. in the order of a few minutes.

[Technical problem]

[0018] The objective of the ~~invention~~ embodiments disclosed herein is therefore to overcome at least one of the disadvantages of the prior art. In particular, the disclosure~~invention~~ sets out to propose a process for nano–structuring a block copolymer film into nano–domains of size smaller than 10 nm, starting from a basic block copolymer non–structured at a determined temperature and having at least one block comprising styrene and at least another block comprising methyl methacrylate. For this purpose, the block copolymer is modified so that the product χN is greater than or equal to 7, preferably greater

than or equal to 10 to allow good phase segregation between the nano–domains and the obtaining of resolution in the order of one nanometre. The nano–structuring process must also allow very rapid organisation of the block copolymer with organisation kinetics in the order of a few minutes. Preferably, to obtain organisation kinetics in the order of a few minutes, the product χN must be less than or equal to 500, and preferably less than or equal to 200. The ~~invention~~ disclosure also sets out to propose a block copolymer film nanostructured into nano–domains of size smaller than 10 nm at a determined temperature, obtained from a basic block copolymer non–structured at said determined temperature and having at least one block comprising styrene and at least one other block comprising methyl methacrylate, said copolymer being modified so that it self–nanostructures into nano–domaines with rapid organisation kinetics of the blocks.

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

[0019] It has surprisingly been discovered that a block copolymer film nano–structured into nano–domains at a determined temperature, obtained from a basic block copolymer non–structured at said determined temperature and having at least one block comprising styrene and at least one other block comprising methyl methacrylate, said block copolymer film being characterized in that it has the following modified chemical formula:

$$(A_{\alpha(i)}\text{–co–}C_{\gamma})_n\text{–}b\text{–}(B_{\beta(k)}\text{–co–}D_{\delta})_{n-1}\text{–}b\text{–}(A_{\alpha(i+1)}\text{–co–}E_{\varepsilon})_{n-2}\text{–}b\text{–}(B_{\beta(k+1)}\text{–co–}F_{\zeta})_{n-3}\text{–}b\text{–}\ldots\text{–}b\text{–}(B_{\beta(k+x)}\text{–co–}W_{\omega})_{n-p} \quad (I)$$

where:

"n" represents the number of blocks of the block copolymer;

"A" represents styrene and "B" represents methyl methacrylate, or conversely;

"C", "D", "E", "F", …, "W" respectively represent a co–monomer or mixture of co–monomers incorporated in each of the blocks of the block copolymer, the co–monomer or mixture of co–monomers incorporated in a styrene–based block differing from the co–monomer or mixture of co–monomers incorporated in a methyl methacrylate–based block;

the subscripts αi and βk represent the number of units of styrene or methyl methacrylate monomers contained in each block of the block copolymer, and are all independent of one another;

the subscripts γ, δ, ε, ζ ..., and ω represent the number of units of co–monomers in a given block, and are all independent of one another;

the subscripts αi, βk, γ, δ, ε, ζ ..., and ω all greater than or equal to 1,

allows a value χN to be obtained within the desired range and allows the obtaining of small–sized nano–domains, typically smaller than 10 nm, whilst preserving organisation and defect reduction kinetics which are suitable and of the same order of magnitude as the organisation kinetics of a basic PS–*b*–PMMA, block copolymer i.e. non–modified, typically in the order of a few minutes to a few tens of minutes.

[0019a] In a first aspect, there is provided a block copolymer film nano–structured into nano–domains at a determined temperature, obtained from a basic block copolymer non–structured at said determined temperature and having at least one block comprising styrene and at least one other block comprising methyl methacrylate, said block copolymer film being characterized in that it has the following modified chemical formula:

$$(A_{\alpha(i)}\text{-co-}C_{\gamma})_n\text{-}b\text{-}(B_{\beta(k)}\text{-co-}D_{\delta})_{n-1}\text{-}b\text{-}(A_{\alpha(i+1)}\text{-co-}E_{\varepsilon})_{n-2}\text{-}b\text{-}(B_{\beta(k+1)}\text{-co-}F_{\zeta})_{n-3}\text{-}b\text{-}\ldots\text{-}b\text{-}(B_{\beta(k+x)}\text{-co-}W_{\omega})_{n-p} \quad (I)$$

where:

"n" represents the number of blocks of the block copolymer;

"A" represents styrene and "B" represents methyl methacrylate, or conversely;

"C", "D", "E", "F", ..., "W" respectively represent a co–monomer or mixture of co–monomers incorporated in each of the blocks of the block copolymer, the co–monomer or mixture of co–monomers incorporated in a styrene block differing from the co–monomer or mixture of co–monomers incorporated in a methyl methacrylate block;

the subscripts αi and βk represent the number of units of styrene or methyl methacrylate monomers contained in each block of the block copolymer, and are all independent of one another;

the subscripts γ, δ, ε, ζ ..., and ω represent the number of co–monomer units in a given block, and are all independent of one another;

the subscripts αi, βk, γ, δ, ε, ζ ..., and ω all greater than or equal to 1.

[0020] ~~The invention further relates to~~In another aspect, there is provided a process for the nanostructuring into nano–domains of a block copolymer film starting from a basic block copolymer non–structured at a determined temperature and having at least one block comprising styrene and at least one other block comprising methyl methacrylate, said process being characterized in that it comprises the following steps:

- synthesis of said block copolymer by incorporating at least one co–monomer in each of the blocks of said basic block copolymer, said block copolymer then meeting following modified formula (I):

$$(A_{\alpha(i)}\text{-co-}C_{\gamma})_n\text{-}b\text{-}(B_{\beta(k)}\text{-co-}D_{\delta})_{n-1}\text{-}b\text{-}(A_{\alpha(i+1)}\text{-co-}E_{\varepsilon})_{n-2}\text{-}b\text{-}(B_{\beta(k+1)}\text{-co-}F_{\zeta})_{n-3}\text{-}b\text{-}\ldots\text{-}b\text{-}(B_{\beta(k+x)}\text{-co-}W_{\omega})_{n-p} \quad (I)$$

where:

"n" represents the number of blocks of the block copolymer;

"A" represents styrene and "B" represents methyl methacrylate, or conversely;

"C", "D", "E", "F", ..., "W" respectively represent co–monomers or mixtures of co–monomers incorporated in each of the blocks of the block copolymer, the co–monomer or mixture of co–monomers incorporated in a styrene–based block differing from the co–monomer or mixture of co–monomers incorporated in the methyl methacrylate–based block;

the subscripts αi and βk represent the number of units of styrene or methyl methacrylate monomers contained in each block of the block copolymer, and are all independent of one another;

the subscripts γ, δ, ε, ζ ..., and ω represent the number of co–monomer units in a given block and are all independent of one another;

the subscripts αi, βk, γ, δ, ε, ζ ..., and ω all greater than or equal to 1;

- application of a solution of said block copolymer in film form onto a surface;

- evaporation of the solvent of the solution and annealing at said determined temperature.

[0021] ~~Finally, the invention relates to~~In another aspect, there is provided a nano–lithography mask obtained from a film of said block copolymer described above, deposited on a surface to be etched following the above–described process, said copolymer film comprising nano–domains oriented perpendicular to the surface to be etched.

[0022] Other particular aspects and advantages of the invention will become apparent on reading the description given as an illustrative, non–limiting example with reference to the appended Figures which illustrate:

- Figure 1, a schematic of an example of polymerisation installation able to be used;
- Figure 2, a photo taken under scanning electron microscope of a sample of a film of PS–*b*–PMMA block copolymer modified and nano–structured according to the invention.

[Detailed description of the invention]

[0023] The term "monomer" such as used relates to a molecule which can undergo polymerisation.

[0024] The term "polymerisation" such as used relates to the process to convert a monomer or mixture of monomers to a polymer.

[0025] By "copolymer block" or "block" is meant a copolymer grouping together several monomer units of several types.

[0026] By "block copolymer" is meant a polymer comprising at least two copolymer blocks such as defined above, the two copolymer blocks differing from one another and having a phase segregation parameter such that they are not miscible and separate into nano–domains.

[0027] The term "miscibility" used above means the capability of two compounds to mix together in full to form a homogeneous phase.

[0028] The principle of the invention is to modify the chemical backbone of a basic PS–*b*–PMMA block copolymer, whilst preserving styrene and methyl methacrylate repeat units in each block, by incorporating co–monomers at the time of the polymerisation reaction of each block. This incorporation of co–monomers in each of the blocks allows gradual modulating of the Flory–Huggins interaction parameter χ of a PS– and PMMA–based block copolymer, as a function of the magnitude of