[021] The most widespread and what appears to be the least complex solution, which consists in grafting a statistical copolymer of specific composition to the surface of the substrate, makes it possible to effectively control the surface energy of the substrate. However, the difficulties of reproducibility of synthesis of a statistical or gradient copolymer with a restrictive composition in terms of ratios of comonomers and a well defined weight limit the advantage of the use of such a copolymer to easily and rapidly neutralize the surface of a substrate.

[022] The Applicant Company has thus taken an interest in this problem and has looked for a solution in order to overcome the experimental error and the deviations with regard to the composition and the weight of the statistical copolymer, while limiting the number of syntheses necessary which increase the cost, in order to produce a specific composition which makes it possible to effectively control the surface energy of the substrate on which the composition is deposited.

[Technical problem]

[023] The objective of the embodiments disclosed herein is thus to overcome at least one of the disadvantages of the prior art. The disclosure is targeted in particular at providing a simple, inexpensive and industrially realisable alternative solution in order to be able to exert fine control over the surface energy of a given substrate by the grafting and/or the crosslinking of a composition, while minimising as much as possible the number of syntheses of this composition.

[Brief description]

[024] To this end, there is provided a process for controlling the surface energy of a substrate in order to make it possible to obtain a specific orientation of the nanodomains of a film of block copolymer subsequently deposited on the said surface, the said process being characterized in that it comprises the following stages:

- preparing a blend of copolymers, each copolymer comprising at least one functional group which allows it to be grafted to or crosslinked on the surface of the substrate,
- depositing the said blend thus prepared on the surface of the said substrate,
- carrying out a treatment which results in the grafting to the said surface or the

- crosslinking on the said surface of each of the copolymers of the blend.

[024a] In an aspect, there is provided a process for controlling the surface energy of a substrate in order to make it possible to obtain a specific orientation of the nanodomains of a film of block copolymer subsequently deposited on the said surface, the said process being characterized in that it comprises the following stages:

- preparing a homogeneous blend of copolymers, each copolymer comprising at least one functional group which allows it to be grafted to or crosslinked on the surface of the substrate,
- depositing the said homogeneous blend thus prepared on the surface of the said substrate,

carrying out a treatment which results in the grafting to the said surface or the

[025] Thus, the process as defined above makes it possible to precisely and easily control the ratios of comonomers of the blend by blending, in chosen proportions, polymers of known compositions. The contents of comonomers are thus simply controlled and any experimental error is avoided. Furthermore, this process also makes it possible to blend polymers each comprising comonomers which are not directly polymerizable with one another and thus to be freed from the chemical nature of the comonomers.

[026] The constituent comonomers of each of the polymers of the blend can be at least in part different from those respectively present in each of the blocks of the block copolymer subsequently deposited on the surface in order to be nanostructured.

[027] There is provided a composition intended to be used for the implementation of the process for controlling the surface energy described above, characterized in that it comprises a blend of copolymers, each copolymer comprising at least one functional group which allows it to be grafted to or crosslinked on the surface of a substrate, so that, once grafted to or crosslinked on the surface of the said substrate, the said composition neutralizes the surface energy of the said substrate and makes possible a specific orientation of the nanodomains of a block copolymer subsequently deposited on the said surface.

[0027a] In another aspect, there is provided a composition intended to be used for the implementation of the process for controlling the surface energy described above, characterized in that it comprises a homogeneous blend of copolymers, each copolymer comprising at least one functional group which allows it to be grafted to or crosslinked on the surface of a substrate, so that, once grafted to or crosslinked on the surface of the said substrate, the said composition neutralizes the surface energy of the said substrate and makes possible a specific orientation of the nanodomains of a block copolymer

subsequently deposited on the said surface.

[028] In another aspect, there is provided a process for nanostructuring a block copolymer, characterized in that it comprises the stages of the process for controlling the surface energy of a substrate described above, then a stage of depositing a solution of the block copolymer on the surface of the said pretreated substrate and an annealing stage which makes possible nanostructuring of the said block copolymer by generation of nanostructured patterns oriented along a specific direction.

[029] In another aspect, there is provided the use of the process for controlling the surface energy of a substrate described above in lithography applications.

[030] Other distinctive features and advantages of the invention will become apparent on reading the description, made as illustrative and nonlimiting example, with reference to the appended figures, which represent:

- Figure 1, a diagram of an example of a polymerization installation which can be used,
- Figure 2, photographs taken with a scanning electron microscope of samples

CLAIMS

1. Process for controlling the surface energy of a substrate in order to make it possible to obtain a specific orientation of the nanodomains of a film of block copolymer subsequently deposited on the said surface, the said process being characterized in that it comprises the following stages:

- preparing a homogeneous blend of copolymers, each copolymer comprising at least one functional group which allows it to be grafted to or crosslinked on the surface of the said substrate,
- depositing the said homogeneous blend thus prepared on the surface of the said substrate,
- carrying out a treatment which results in the grafting to the surface of the substrate or the crosslinking on the surface of the substrate of each of the copolymers of the blend.

2. Process according to Claim 1, in which the treatment resulting in the grafting or the crosslinking is carried out at a temperature of less than 280°C in a time of less than or equal to 10 minutes.

3. Process according to either of Claims 1 and 2, characterized in that the stage of grafting or crosslinking each of the copolymers of the blend is carried out by at least one of the following treatments: heat treatment, organic or inorganic oxidation/reduction treatment, electrochemical treatment, photochemical treatment, treatment by shearing or treatment with ionizing rays.

4. Process according to one of Claims 1 to 3, characterized in that the number n of copolymers in the blend is such that it is $1<n\leq5$ and preferably $2\leq n\leq3$.

5. Process according to one of Claims 1 to 4, characterized in that the constituent copolymers of the blend are statistical and/or gradient and/or block and/or alternating copolymers.

6. Process according to one of Claims 1 to 5, characterized in that the proportions of each copolymer in the blend are between 0.5% and 99.5% by weight of the final blend.

7. Process according to one of the preceding claims, characterized in that each copolymer of the blend comprises a variable number x of comonomers, with x taking whole values, preferably $2 \leq x \leq 7$, and more preferably still $2 \leq x \leq 5$.

8. Process according to one of the preceding claims, characterized in that the relative proportions, in monomer units, of each constituent comonomer of each copolymer of the homogeneous blend are between 1% and 99%, with respect to the comonomer(s) with which it copolymerizes.

9. Process according to one of the preceding claims, characterized in that the number-average molecular weight of each copolymer of the homogeneous blend is between 500 and 250 000 g/mol and more preferably still between 1000 and 150 000 g/mol.

10. Process according to one of the preceding claims, characterized in that the polydispersity index of each copolymer of the homogeneous blend is less than 3 and more preferably still less than 2.

11. Process according to one of the preceding claims, characterized in that, when the homogeneous blend comprises block copolymers, at least one of the comonomers of each block copolymer carries the chemical functional groups which make it possible for the copolymer to be grafted to or crosslinked on the surface of the substrate.

12. Process according to one of the preceding claims, characterized in that the homogeneous blend of copolymers can additionally comprise one or more homopolymers comprising at least one functional group which makes it possible to graft it to or to crosslink it on the surface of the said substrate.

13. Process according to one of the preceding claims, characterized in that the substrate is chosen from one of the following substrates: an inorganic substrate, a metallic substrate or an organic substrate.

14. Process according to Claim 13, characterized in that, when the substrate is inorganic, it is chosen from substrates composed of silicon or germanium exhibiting a layer of native or thermal oxide, or of aluminium, copper, nickel, iron or tungsten oxides.

15. Process according to Claim 13, characterized in that, when the substrate is metallic, it is chosen from substrates composed of gold or of metal nitrides.

16. Process according to Claim 13, characterized in that, when the substrate is organic, it is chosen from substrates composed of tetracene, anthracene, polythiophene, PEDOT (poly(3,4-ethylenedioxythiophene)), PSS (sodium poly(styrene sulphonate)), PEDOT:PSS, fullerene, polyfluorene, polyethylene terephthalate, crosslinked polymers, graphenes or anti-reflecting organic polymers.

17. Composition intended to be used for the implementation of the process for controlling the surface energy of a substrate according to one of Claims 1 to 16, characterized in that it comprises a homogeneous blend of copolymers, each copolymer comprising at least one functional group which allows it to be grafted to or crosslinked on the surface of a substrate, so that, once grafted to or crosslinked on the surface of the said substrate, the said composition neutralizes the surface energy of the said substrate and makes possible a specific orientation of the nanodomains of a block copolymer subsequently deposited on the said surface.

18. Process for nanostructuring a block copolymer, characterized in that it comprises the stages of the process for controlling the surface energy of a substrate according to one of Claims 1 to 16, then a stage of depositing a solution of the block copolymer on the surface of the said pretreated substrate and an annealing stage which makes possible nanostructuring of the said block copolymer by generation of nanostructured patterns oriented along a specific direction.

19. Use of the process for controlling the surface energy of a substrate according to one of Claims 1 to 16 in lithography applications.