

Description

The invention relates to polymeric layers having optically non-linear or anisotropic properties in selected surface areas of arbitrary shape, such areas being defined relative to other regions of the layer having centro-symmetrical or isotropic structure or having different optically non-linear or anisotropic properties. The invention also relates to processes for the production of such layers and their use as optical components.

It is known that organic and polymeric materials with large delocalised π -electron systems may have non-linear optical coefficients which are larger than those of inorganic materials.

The properties of organic and polymeric materials can also readily be varied so that valuable secondary properties, such as mechanical and chemical stability, optical absorption, etc., can be set without having a negative effect on the non-linearity.

Thin films of organic or polymeric materials having considerable non-linearity of the second order have a great potential for use in the areas of optical communication, laser technology, electro-optics etc.

It is particularly significant that the non-linearity of these materials is due to the polarisability of the π -electron system and not to the shift or reorientation of atoms or molecules. Components having ultra-short response times can therefore be realised with these materials.

This field has been the subject of intensive research for many years and is documented, for example, in the following publications:

ACS Symposium Series 233, Washington D.C. 1983

Proceedings of SPIE Vol. 682 1986 Molecular and Polymeric Optoelectronic Materials: Fundamentals and Applications

Proceedings of SPIE Vol. 824 1987 Advances in Nonlinear Polymers and Inorganic Crystals, Liquid Crystals, and Laser Media

Proceedings of SPIE Vol. 1105 1989 Materials for Optical Switches, Isolators, and Limiters

Proceedings of SPIE Vol. 1147 1989 Nonlinear Optical Properties of Organic Materials 2

NATO ASI Series E: Applied Sciences Vol. 162 1989 Nonlinear Optical Effects in Organic Polymers

Springer Proceedings in Physics 36 1989 Nonlinear Optics or Organics and Semiconductors

Particularly important for these applications are side-chain polymers and liquid crystalline side-chain polymers doped with nlo-chromophores or having nlo molecules as side chains. For the purpose of this description, the term side-chain polymers also includes co-polymers and homopolymers. It is known that suitably selected representatives of this class of material can be given a dipolar orientation by heating above the glass temperature in a high electric field and retaining this non-centrosymmetrical order by cooling below the glass temperature T_g in the electric field. Frozen poled glasses of this kind represent nlo materials with high $\chi^{(2)}$ susceptibility (K. D. Singer et al. Appl. Phys. Let. 49, 1986).

A basis obstacle to the technical utilisation of these materials is the inadequate long-term stability of the dipolar order. It has been found that relaxation occurs even below the glass temperature of the polymer system and destroys the impressed non-centrosymmetrical structure.

There are various strategies for increasing stability of the dipolar order by modification of the polymer. Since the relaxation processes slow down with increasing distance from the glass temperature, one way is to select polymers having the highest possible glass temperature. Another method is to use polymer networks instead of linear polymers.

Much better long-term and temperature-stable nlo polymers have been obtained by using nlo chromophores with several (2 - 4) reactive substituents to act as cross-linking units in an epoxide system (M. Eich J. Appl. Phys. 66, 3241, 1989). In these epoxides, the cross-linking reaction takes place under the influence of an electric field and results in a partially dipolar-oriented network, which is retained after the field has been switched off, since the dipolar order is chemically fixed.

The simple and precise patterning of nlo-active polymer networks in complex components is of fundamental importance to

their technical use. Since, in previously known processes, the cross-linking was initiated thermally, it covers the entire layer and cannot thus be restricted to selected partial areas.

Patterning is possible only by the application of structured poling electrodes. However, this is accompanied by a number of disadvantages. Unavoidable electric stray fields at the edges of the electrodes cause the boundaries of the poled zones to become blurred. This is unacceptable for many applications, e.g. strip waveguides, periodic structures of poled and unpoled regions. Also, for most applications the electrode coatings have to be tediously removed again in additional process steps.

The object of the invention is to eliminate the described disadvantages. More particularly, it is an object of the invention to produce stable $\chi^{(2)}$ -active polymer layers which may have complex geometric structures. Another object of the invention is the production of stable liquid crystalline polymeric layers with complex geometric structures consisting of areas of different anisotropy, possibly combined with isotropic areas.

This is achieved in accordance with the invention in that the polymeric material referred to in the preamble has optically non-linear and/or mesogenic side chains and selective surface areas of the material being cross-linked by the action of light, whereby the side chains in the areas having optically non-linear or anisotropic properties are orientated under the influence of a electric DC field during cross-linking.

According to another aspect of the invention, the polymeric layer is characterized in that the transition between the optically different areas is limited to less than $10\text{ }\mu\text{m}$, preferably to less than $1\text{ }\mu\text{m}$.

The production of such layers according to the invention is characterized by the following steps: Application of a layer of a polymeric material having photo-cross-linkable side chains to a support, application of an electric field, irradiation of the layer areas to be for cross-linked with light of a wavelength which brings about cross-linking.

The process according to the invention is thus based on producing films which are stable thermally as well as with respect to time by photo-initiated cross-linking of suitable copolymers under the influence of a high electric DC field.

Under these conditions poling and cross-linking are independent. Poling takes place where the electric field operates; cross-linking takes place where irradiation is applied. The poled non-cross-linked (= non-irradiated) areas lose the dipolar orientation after the electric field is switched off while the cross-linked (= irradiated) poled areas retain it. Cross-linked and non-polar areas remain $\chi^{(2)}$ -inactive even when the electric field becomes operative.

Cross-linked poled areas retain their dipolar orientation even when an electric field is applied in the opposite direction.

These films can also be selectively $\chi^{(2)}$ -activated by photo-lithograph.

This enables complex optical components to be produced in a simple manner, e.g. strip waveguides, frequency-doubler waveguides (quasi-phase matching), optical correlators, two-beam interferometers, modulators, EO-switches.

The preparation temperature can in principle be freely selected since the photo-initiation is temperature-independent (in contrast to thermal initiation). This is important in respect of the use of temperature-sensitive nlo chromophores, increasing the order number by reducing the temperature, reducing the ion conductivity by temperature reduction and adjustment of the viscosity.

The fixed nlo-active areas are defined by irradiation. No structure-determining electrodes are required.

Different areas of a film can be cross-linked successively. This allows great freedom in respect of the construction of complex components.

Cross-linked and non-cross-linked areas can be produced selectively; the non-cross-linked areas can be removed by solvents and replaced by other materials without disturbing the cross-linked area (strip waveguides, cladding).

By adding small quantities of inhibitor molecules it is possible to produce sharp boundaries between cross-linked and non-cross-linked areas. Initiator radicals which diffuse into the non-irradiated area are deactivated by the inhibitor.

It is possible to expand the preparative and application possibilities by use of liquid crystalline side-chain polymers with photo-cross-linkable side chains.

Above T_c these have the same properties as the amorphous polymers already described. In addition, however, they are anisotropic below T_c , e.g. in the nematic phase. It is known that liquid crystalline polymers are axially orientable to a high degree in the nematic phase (e.g. by electric fields). This orientation can be selectively fixed by photolithograph as described. By increasing the temperature above T_c the non-cross-linked part of the layer is converted to the isotropic state and can be treated there like the described amorphous polymers, the area already cross-linked in the first step remaining anisotropic.

Materials which can be modulated both linearly and non-linearly optically have a high potential for use in integrated optics.

In particular, it is possible optically to write into the nlo material the coupling and decoupling grating for an nlo waveguide.

In addition to the previously described amorphous copolymers which have nlo-active and inactive side chains as well as the liquid crystalline co-polymers, the same structural and processing principle can also be applied to homopolymers, oligomers and monomers having a plurality of cross-linkable branches.

The object of the non nlo-active co-monomers is to influence secondary properties of the material, such as e.g. optical density, refractive index, hardness, brittleness, shrinkage on cross-linking, glass temperature, viscosity, etc.

Exemplified embodiments of the invention will be described below with reference to the accompanying drawings in which:

Fig. 1 is an illustration of the principle of cross-linking of selected surface areas.

Fig. 2 is a diagram showing an apparatus for producing an optically non-linear layer between electrode-coated glass plates.

Fig. 3 is a diagram showing an apparatus for the production of an optically non-linear layer on a substrate coated with a conducting layer.

Fig. 4 is a diagram illustrating a waveguide element.

Fig. 1 shows the principle of the area-specific or structured cross-linking of a polymeric material having a dipolar orientation. The material is provided in the form of a polymeric layer 1 between a bottom glass plate 2, the top surface of which has an ITO coating 4, and a glass plate 3 disposed parallel to the plate 2 at a distance of about 1-10 μm , the underside of the glass plate 3 also having an ITO coating 5. The arrangement consisting of ITO-coated glass plates is hereinafter referred to as the cell.

The ITO coatings are connected to a high-voltage supply HV. When the DC voltage is applied, a dipolar orientation is induced in the polymeric material which is as yet not cross-linked.

The cell is exposed to a parallel beam of light 6 in the ultraviolet range, a mask 7 limiting the beam to the surface areas 8 which are to be cross-linked. When the high-voltage is switched off after cross-linking, the dipolar orientation is retained only in the cross-linked areas. The material that is not cross-linked in the other areas can be removed by a suitable solvent. Alternatively, after removal of the mask 7 the material can also be cross-linked without an applied voltage to give a fixed centrosymmetrical structure there.

If the polymeric material 1 is liquid crystalline, it is axially oriented by known method in the electric field by the application of a voltage to the electrodes 4, 5. Depending on the voltage and dielectric anisotropy of the material, it is possible, for example, first to produce a homeotropic structure in the liquid crystalline polymeric material and to cross-link this in selective surface areas by means of the mask 7. The polymeric layer can then, for example, be removed in the areas which have not been cross-linked. Alternatively, cross-linking of the remaining areas can be effected with a different, for example planar, structure.

The principle shown in Fig. 1 can be performed with the apparatus shown in Fig. 2.

The material 1 intended for the production of an optically non-linear polymeric layer having a structured surface area is located in a cell 10 similar to that shown in Fig. 1. The cell consists of electrode-coated glass plates 11 additionally provided with an outer heating layer 12.

The cell 10 is located in an optical system which enables it to be irradiated with UV light 13 from two sides. The light passes from a UV lamp 14 via a thermal protection filter 15, a UG1 filter 16 and a lens or optical system 17 to a beam splitter 18. The latter splits the beam 13 into two equal sub-beams to give irradiation of the cell at the same intensity from both sides.

The transmitted beam passes to a prism 19 and is reflected by this through a mask 21 on to the cell 10. The beam deflected by the beam splitter 18 passes to a prism 20 from which it passes by double reflection through a mask 22 on to the opposite side of the cell 10.

The electrode plates 11 are connected to a high-voltage generator 44 controlled by a computer 45. The very low current through the cell is measured by a pico-ammeter 46. The current intensity recorded is the control parameter for the control of the high voltage. The voltage applied to the polymeric layer is selected such that the resulting current does not exceed a preselected value.

The heating layers 12 of the cell are connected to a temperature monitoring device 47. A temperature sensor 24 which gives the actual temperature is provided on the cell. The set-value for the temperature control is also delivered by the computer 45.

The procedure for making an optically non-linear layer is as follows.

Polymeric material having photo-cross-linkable side chains, some of which have nlo groups, is mixed with a small quantity (5% concentration) of photo initiator (e.g. by dissolution in a common solvent and subsequent evaporation of the solvent). The dried material is then pressed, above the glass temperature T_g , between glass plates coated with transparent electrodes, the layer thickness being defined by spacers. Alternatively, the material can be sucked into prefabricated cells.

The temperature of the layer is reduced so that a high electric field (1MV/cm) can be applied between the electrodes without high ion currents destroying the sample. The poling field induces a dipolar orientation of the nlo groups which possess a permanent dipole moment and hence eliminates the centrosymmetry of the original isotropic material.

At the same time, the layer is irradiated with light of a suitable wavelength to initiate the cross-linking reaction. Under the influence of the electric field the cross-linking results in a non-centrosymmetrical network. This is directly observable by measuring the SHG.

The cross-linking reaction results in continuous increase of the glass temperature and hence of the electric resistance, so that a higher voltage becomes permissible. The maximum voltage used depends on the breakdown strength of the polymeric material and is also pre-selectable. As soon as this maximum voltage has been reached, the cell temperature is increased, thus following the rising glass temperature of the polymer. As a result of the continuous increase in the reaction temperature the polymeric material remains sufficiently mobile so that the cross-linking reaction can be pushed to a high degree of cross-linking.

After an adequately high temperature has been reached, cross-linking has advanced to such an extent that a stable non-centrosymmetrical network has formed and is retained when the electric field is switched off.

An optically non-linear layer 25 is produced on a substrate 26 having an electrode layer as follows using the apparatus shown in Fig. 3.

Polymeric material having photo-cross-linkable side chains, some of which have no groups with a permanent dipole moment, is dissolved with a small quantity of photoinitiator in a suitable solvent. The concentration of the solution is adjusted such that its viscosity is suitable for spin layer. The solution is centrifuged in a spin coating apparatus on a support 26 coated with an electrode so as to form a homogeneous layer of 0.5 - 5 μm thickness. The film is then dried on a heat bench and preferably tempered to reduce the free volume.

In the corona poling apparatus shown in Fig. 3, the polymeric layer is poled in an inert gas atmosphere on a cooling/heating plate 27. The corona poling apparatus is known per se. It comprises a housing 28, the inside of which contains a heating table 27 on which the substrate 26 provided with the polymeric layer 25 is placed. A rotating high-voltage device 29 is disposed above the heating table and has downwardly projecting points 30

which generate a high electric field strength in the region of the polymeric layer 25 arranged thereunder.

The housing is covered by a window 31 and has an inlet 32 for inert gas. The apparatus is flooded with inert gas (N_2 , Ar) in order to keep away the oxygen which inhibits radical cross-linking. The layer is irradiated with uv light 33 of suitable wavelength through the window to initiate cross-linking. In the area of the corona discharge the chromophores have a dipolar orientation so that a permanent non-centrosymmetrical network forms. During the reaction the temperature follows the rising glass temperature T_g of the layer. The dipolar-orientated layer is fixed once the cross-linking reaction is complete.

By means of a downscaling projection it is possible to transfer fine structures to the polymeric layer. The exposed and unexposed areas are sharply separated from one another. By the addition of low inhibitor concentration it is possible to prevent the diffusion of the photoinitiator from initiating cross-linking in shaded areas.

In addition to the use of photo masks it is possible to use holographic processes.

As already partly stated, different combinations are possible in the polymeric layer according to the invention. Cross-linked poled areas and non-cross-linked poled areas can be combined in order to produce strip waveguides. In the cross-linked area the material is insoluble and in the non-cross-linked area it is soluble. The non-cross-linked material can be removed by means of a solvent. The free areas are covered with other polymeric material in the next operation (buffer coatings, cladding).

Alternatively, it is possible to combine cross-linked poled areas and cross-linked non-poled areas, e.g. for the production of frequency-doubler waveguides. In the first operation, strips of a width of the coherence length separated from non-cross-linked strips of the same width are cross-linked in the electric field by means of a grating mask in the path of the rays. After the electric field has been switched off, the non-cross-linked strips relax into the isotropic (non $\chi^{(2)}$ -active) state.

In the second operation the screen is removed so that the entire sample is cross-linked. A film forms which consists periodically of $\chi^{(2)}$ -active and inactive areas, the width of which

is precisely the coherence length. The refractive index of the poled and unpoled areas is substantially identical. Light propagated in this waveguide experiences only slight reflection at the interface layer (efficient frequency-doubler waveguides by realisation of the quasi-phase-matching condition).

Another combination consists of cross-linked poled areas and cross-linked areas of opposite polarity. This combination is similar to that described above, but in the second operation the sample is oriented in a field of opposite polarity. Under these conditions, the strips cross-linked in the first operation remain unaffected. Periodic strip systems form with a dipolar orientation of opposite directions. All the strips are $\chi^{(2)}$ -active. The strip width (= coherence length) is so selected that the second harmonic produced is amplified with phase matching over the entire sample length (quasi phase-matching). The refractive index of neighbouring strips is identical.

The waveguide element shown in Fig. 4 uses the anisotropic and the nlo properties of a liquid crystalline nlo polymeric coating 34. The waveguide element consists of a pair of parallel spaced glass plates 38, 39 coated with ITO electrodes 40 and 41. They have buffer coatings 42, 43 in addition. The liquid crystalline polymeric coating 34 is contained between them. The buffer coatings have a refractive index below that of the polymer. Light is coupled into the waveguide via a phase grating 35, 36 which is optically written into the polymer in accordance with the process described below. In the middle part 37 of the element, the coupled light traverses a $\chi^{(2)}$ -active zone which is produced by poling and cross-linking and in which the $\chi^{(2)}$ -process (SHG or Pockel's effect etc) takes place.

The following process steps are carried out for the production. The liquid crystalline material in the mesophase with $\Delta\epsilon > 0$ is given homeotropic orientation in the electric alternating field. In the zones 35 and 36 the photo-cross-linkable material is irradiated with ultraviolet light to form a strip pattern of suitable periodicity (e.g. by two-beam interference). Cross-linking takes place in the region of the exposed strips.

The polymeric layer is then heated to a temperature $> T_c$, so that it becomes isotropic except for the already cross-linked homeotropic strips. The areas 35 and 36 are irradiated uniformly with UV light through a mask so that the cross-linking taking

place in the entire area 35 and 36 fixes the isotropic condition here. As a result, strips having homeotropic orientation are obtained in an isotropic matrix.

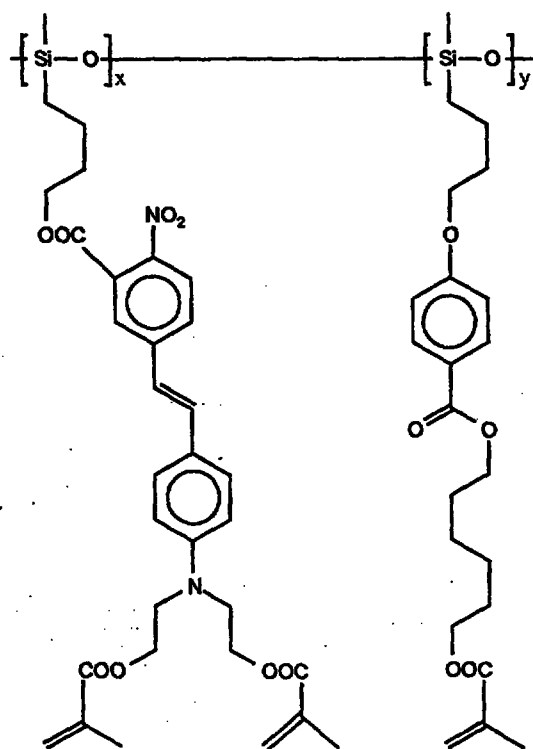
Area 37, which is still non-cross-linked, is now exposed to a high electric DC field. As a result, the side chains of the polymer in area 37 receive a dipolar orientation so that the coating becomes $\chi^{(2)}$ -active in this part. At the same time the sample is irradiated with UV light so that cross-linking occurs in area 37 as well and the dipolar orientation is fixed.

Suitable irradiation sources are lamps which emit in the range of absorption of the photoinitiator. Care must be taken to ensure that the spectral range of the chromophore absorption is not affected. Since conventional initiators are sensitive in the range between 200 and 400 nm, cold-light sources are suitable, such as Hg, D₂, Xe lamps, and also halogen lamps, and also lamp and filter combinations, and also laser systems such as dye lasers, excimer lasers, N₂ lasers, Nd:YAG 3rd harmonic.

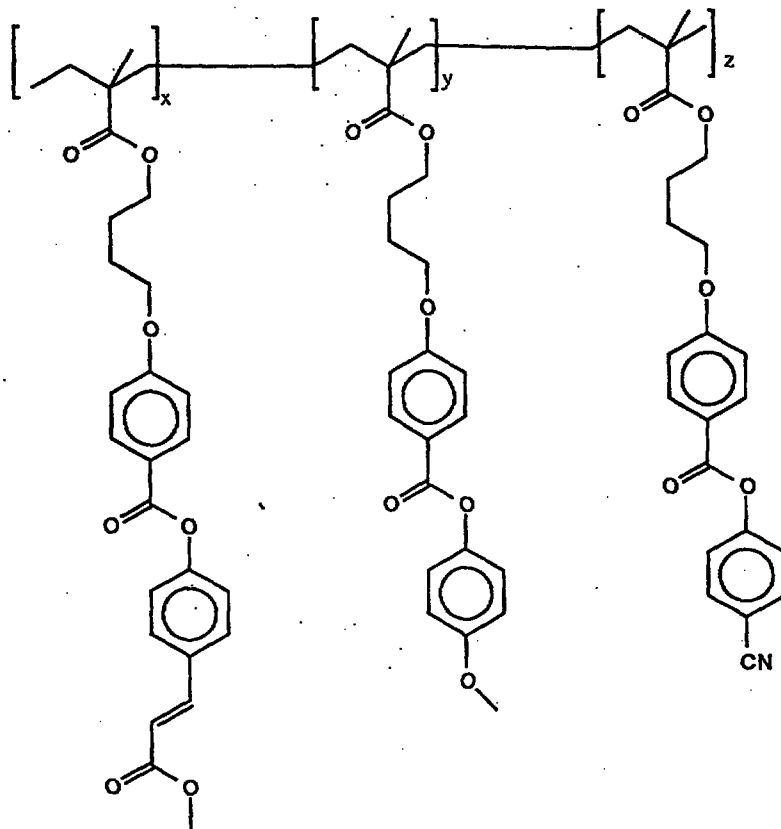
Pulsed excitation is particularly advantageous. Since cross-linking continues after excitation has been terminated, the photo-loading of the sample can be drastically reduced. Suitable light sources are flashlamps Xe, D₂, pulsed lasers N₂, excimer lasers Nd:YAG 3rd harmonic.

A number of known polymers with photo-cross-linkable side chains are suitable for the production of the layers according to the invention. For example the following typical substances are advantageously used.

An amorphous nlo polymer having photo-cross-linkable side chains has the following structural formula:



A liquid crystalline polymer with photo-cross-linkable side chains has the following structural formula



Conventional commercial initiators are e.g. phenone derivatives Darocur, Irgacure, isopropylthioxantones/H donor combinations (N-methyldiethanolamines). The absorption of the initiator must lie outside the chromophore absorption. When selecting the initiator care must be taken to ensure that the nlo chromophore does not act as a triplet quencher of the excited initiator and hence prevent the formation of radicals.

Claims

1. A polymeric layer (1) having optically non-linear or anisotropic properties in selected surface areas (8) of arbitrary shape, such areas being defined relative to other regions of the layer having centro-symmetrical or isotropic structure or having different optically non-linear or anisotropic properties, characterized in that the polymeric layer has optically non-linear and/or mesogenic side chains and selective surface areas of the layer being cross-linked by the action of light, the side chains in the areas having optically non-linear or anisotropic properties being orientated during cross-linking under the influence of one or more of the orientating forces of an electric field, a magnetic field, wall-orientation forces or shearing forces.
2. A polymeric layer according to claim 1, characterized in that the transition between the optically different areas is limited to less than 10 μm , preferably to less than 1 μm .
3. A polymeric layer according to any one of claims 1-2, characterized in that the defined areas form a pattern.
4. A polymeric coating according to any one of claims 1-3, characterized in that the defined areas consist of a cross-linked polymer.
5. A polymeric coating according to any one of claims 1-4, characterized in that the surfaces having a centrosymmetrical structure are non-cross-linked.
6. A polymeric layer according to any one of claims 1-5, characterized in that the polymer is a liquid crystalline side-chain polymer.
7. A polymeric layer according to any one of the preceding claims, characterized in that the photoinitiated cross-



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6. A polymeric layer according to any one of claims 1-5, characterized in that the polymer is a liquid crystalline side-chain polymer.
7. A polymeric layer according to any one of the preceding claims, characterized in that the photoinitiated cross-



linking of the side chains consists in a cross-linking radical polymerisation of methacrylates or acrylates.

8. A polymeric layer according to any one of claims 1-6, characterized in that the photoinitiated cross-linking of the side chains consists in a 2 + 2 cycloaddition of cinnamic acid derivatives.

9. A polymeric layer according to any one of claims 1-8, characterized in that homopolymers, oligomers or monomers are used as starting material.

10. A process for the production of a layer having optically non-linear or anisotropic properties in accordance with any one of claims 1-9, characterized by the application of a layer of a polymeric material having photo-cross-linkable optically non-linear and/or mesogenic side chains to a support, application of an electric field and irradiation of a layer with light of a wavelength which causes cross-linking.

11. A process according to claim 10, characterized in that for two-dimensional structuring of the coating the irradiation is restricted to partial areas of the layer.

12. A process according to claim 10, characterized in that the layer is cooled at the beginning of irradiation.

13. A process according to claim 12, characterized in that the temperature is continuously increased during irradiation.

14. A process according to any one of claims 10-13, characterized in that homopolymers, oligomers or monomers are used as starting material.