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## In-situ photopolymerization of oriented liquid-crystalline acrylates

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## Summary

Oriented polymers are of a long-standing theoretical and practical interest because of their highly anisotropic properties. Well-known features are (i) an anisotropic mechanical behaviour with a high modulus and a high strength in the direction of the molecular orientation, which is already widely applied in polymeric fibers and filaments, (ii) an anisotropic optical behaviour with a large difference in refractive index or optical absorption between the principal directions, which is useful for the manufacturing of optical components, and (iii) an anisotropic thermal behaviour with a low thermal expansion coefficient in the direction of the molecular orientation, which is desirable for coating and encapsulation of inorganic substrates in order to avoid thermal stresses.

The scope of this thesis concerns a new method to produce oriented polymers by the in-situ photopolymerization of oriented liquid-crystalline acrylates. The desired macroscopic molecular order is already accomplished in the monomeric state prior to the polymerization. Because of the combination of low-viscosity and anisotropic physical properties of the

mesogenic monomers, the molecules orient themselves instantaneously and with a low concentration of orientational defects under the action of an external field, e.g. an electric or a magnetic field, or by the interaction with a treated substrate, e.g. a thin rubbed polyimide coating. A subsequent short UV exposure generates free-radicals from a dissolved photoinitiator, initiating the chain-polymerization. During the bulk polymerization the liquid-crystalline ordering of the monomer persists and is frozen in as soon as the reacting medium passes a glass transition or crystallization temperature. The photopolymerization of diacrylates rather than monoacrylates leads to densely crosslinked oriented polymers in which the mesogenic moieties are anchored at both ends to the polymer network, yielding a permanent and temperature-insensitive molecular orientation.

The application of photo-initiated polymerization offers a number of advantages in comparison with for instance thermally-initiated polymerization. Firstly, it can be carried out in a broad temperature range and the reaction does not start before the exposure. This is very important since a particular liquid-crystalline ordering is often observed only in a relatively narrow temperature range. Consequently, one is able to successively heat the monomer to the desired temperature, shape it into the desired form and orient the monomer molecules without the occurrence of early polymerization which would fix a wrong type of ordering, e.g. another mesomorphic phase during heating to the appropriate temperature, or orientational defects, e.g. imposed during flow of the monomers during processing. Secondly, photopolymerization proceeds very fast which prevents phase segregation in case the polymer formed does not dissolve in its monomer. The latter is observed for instance when a smectic polymer is formed from a nematic monomer at low polymerization rates. Thirdly, by the use of photopolymerization one has the possibility to structurize the oriented polymer by pattern-wise irradiation, which might be useful especially in opto-electronic applications.

In Chapter 2 of this thesis the formation of liquid-crystalline side-chain polymers by photopolymerization of liquid-crystalline monoacrylates is discussed. In Chapter 2.1 it is shown that the macroscopic orientation of the monomer is preserved during polymerization, although both the order parameter and the type of mesogenic ordering of the polymer formed may be different from those of the monomer. During polymerization the liquid-crystalline transition temperatures shift to higher values. This means that for the monomer studied, an initially nematic monomeric ordering becomes smectic-A for the polymer-monomer mixture during the reaction, which can be observed by a step-wise increase of the birefringence. In the case of a polymerization below the melting temperature of the polymer, the sample crystallizes during the reaction. When a polymerization temperature is selected above the polymeric melting temperature, crystallization

takes place after polymerization and the sample is cooled to room temperature.

A kinetic study of the polymerization in the mesomorphic phase, as well as the effect of the polymerization temperature on the reaction rate, shows that the reaction proceeds faster at higher temperatures. The reaction proceeds faster at higher temperatures because of the faster crystallization of the reaction medium. At a low monomer diffusion coefficient, the mesomorphic monomer is not able to form a liquid crystalline during polymerization. The order parameter remains with mutually different values and, therefore, a decrease in the reaction rate and, therefore, a decrease in the order parameter as the light intensity decreases.

In Chapter 3 of this thesis the formation of liquid-crystalline side-chain polymers by photopolymerization of liquid-crystalline monoacrylates is discussed. In Chapter 3.1 it is shown that the macroscopic orientation of the monomer synthesized (C<sub>10</sub>H<sub>7</sub>O<sub>2</sub>) is preserved during polymerization in a temperature range between 88 and 100°C. The order parameter is high near the smectic phase transition temperature. Polymerization in the nematic phase leads to a polymer with a high order parameter. Polymerization in the nematic phase leads to a polymer with a high order parameter. The order parameter of the monomer is high near the smectic phase transition temperature. The order parameter of the monomer in case of a high order parameter it increases.

The attachment of a liquid-crystalline diacrylate moiety to the polymer backbone at high polymerization temperatures and low reduced temperatures leads to an equal reduced temperature. The order parameter of the monomer is high near the smectic phase transition temperature. The order parameter of the monomer in case of a high order parameter it increases.

A longer flexible aliphatic chain and the acrylate moiety stabilize the formation of the smectic-C phase. The order parameter of the monomer is high near the smectic phase transition temperature. The order parameter of the monomer in case of a high order parameter it increases.

takes place after polymerization during cooling from the polymerization temperature to room temperature.

A kinetic study of the polymerization of the monoacrylate in its mesomorphic phase, as described in Chapter 2.2, revealed that the polymerization proceeds fast both in the nematic and in the smectic state. The reaction proceeds until depletion of monomer. In the case of crystallization of the reaction mixture, complete conversion is hindered by a low monomer diffusion in the crystalline state. Polymerization of the mesomorphic monomer in an initially isotropic state gives a transition to liquid crystalline during the reaction. In that case the formation of domains with mutually different orientation directions causes light scattering and, therefore, a decrease of the overall polymerization rate since the UV light intensity decreases in the deeper sections of the polymerizing film.

In Chapter 3 of this thesis the formation of oriented polymer networks by photopolymerization of liquid-crystalline diacrylates is discussed. The monomer synthesized (Chapter 3.1) exhibits a broad nematic temperature range between 88 and 155°C and a monotropic smectic-C phase at lower temperatures. The order parameter in the nematic phase varies from 0.7 near the smectic phase transition to 0.4 near the isotropic phase transition. Polymerization in the nematic phase proceeds fast in the initial stage of the polymerization process and more slowly at higher conversions due to monomer depletion and a reduced mobility of the remaining vinyl groups. The order parameter of the polymer network formed is equal to that of the monomer in case of a high initial order parameter, e.g. 0.7. At lower initial order parameter it increases during polymerization.

The attachment of a lateral methyl group to the central moiety of the liquid-crystalline diacrylate (Chapter 3.2) is found to decrease the transition temperatures and to suppress the formation of smectic phases. At equal reduced temperature the methyl group does not affect the degree of orientation in the monomeric state. However, the increased packing density of the mesogens after polymerization leads to an enhanced steric hinderance due to the side-group and, as a consequence, to lower order parameters in the polymeric state. The mechanical properties of the networks hardly change by the substitution of the methyl group.

A longer flexible alkylene spacer between the mesogenic central group and the acrylate moiety (Chapter 3.3) decreases both the melting temperature and the nematic-isotropic transition of the diacrylate monomers and stabilizes the formation of a smectic-C phase. In the macroscopic oriented state the smectic-C phase is characterized by local director fluctuations which persist during polymerization. In the monomeric nematic state the degree of orientation is not influenced by the spacer length when studied at equal reduced temperatures. However, upon formation of the oriented networks the shorter alkylene spacers lead to somewhat lower order parameters of both the mesogenic unit and the spacer itself. It is proposed

that at short spacers the steric hindrance between the densely packed central units, as imposed by the periodicity in the acrylate main chains, leads to conformational changes of the mesogenic moieties, e.g. to a smaller angle between the para-axes of the benzene rings by a rotation of these moieties over the connecting ester groups.

From the studies presented in Chapters 3.1, 3.2 and 3.3 we conclude that the anisotropic optical properties of the polymer networks can be varied over a wide range by the variation of the spacer length, by the application of a lateral substituent or by influencing the degree of orientation by the polymerization temperature. This, and the fact that the network prohibits the formation of polymer crystallites as often observed for linear polymers which would enhance light scattering, makes the materials ultimately suited for various optical applications.

In the investigations discussed so far, only uniaxially oriented polymer networks are described. However, by the addition of chiral dopants to the liquid-crystalline monomers it becomes possible to produce polymeric networks with a helicoidal ordering of the mesogenic crosslinks. Chapter 3.4 has been dedicated to this technique which yields polymers with unusual optical properties. By the rubbed substrate orientation technique, a planar anchoring is achieved at both interfaces of the film and consequently the molecular helix lies perpendicular to the plane of the film. The total angle of rotation can be adjusted very accurately by the dopant concentration and the angle between the rubbing directions at both substrates. During the network formation or during temperature cycling afterwards, the pitch of the helix changes rather than the total angle of rotation due to thickness variations.

The anisotropic thermal expansion of both the uniaxially and the helicoidally ordered polymer networks are described in Chapter 3.5. In case of a uniaxial orientation, the thermal expansion coefficient in the direction of the orientation is low, but still positive, below the glass transition temperature of the networks. As soon as this transition sets in at increasing temperatures, the network starts to contract in the same direction. This process appeared to be reversible during repeated temperature cycling. Perpendicular to the molecular orientation, the thermal expansion is much higher and compensates for the anomalous thermal expansion along the molecular orientation such that the calculated overall volume expansion is comparable to that of conventional polyacrylates. The influence of the monomeric structure and the polymerization conditions on the anomalous thermal expansivity is discussed in terms of the small reversible decrease of the order parameter during temperature cycling. In case of a film consisting of a helicoidally ordered polymer network with the molecular helix perpendicular to the plane of the film, a low thermal expansion is measured for the principal directions in the plane of the film. As a result, this type of molecular arrangement is very promising for the coating or

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encapsulation of planar substrates where thermal stresses should be avoided in the plane of the substrate.

In the Appendix the influence of relatively high temperatures on the photopolymerization of isotropic di(meth)acrylates is discussed. Liquid crystalline diacrylates must be polymerized between 80 and 165°C because of the temperature range of their mesophases. However, little is known of the effects of these high temperatures on the kinetics of photopolymerization. Therefore, a high-temperature photopolymerization study is carried out using conventional isotropic monomers in order to get comparative matter for estimating the influence of liquid crystallinity on the polymerization behaviour. It is found for a dimethacrylate that the polymerization rate increases with temperature up to 160°C. At higher temperatures the propagation-depropagation equilibrium becomes increasingly important leading to lower overall polymerization rates. For isotropic diacrylates chain transfer via abstraction of the  $\alpha$ -hydrogen of the acrylate group enhances the rate of the termination reaction in the autoacceleration region of the polymerization. This leads to a decrease of the overall polymerization rate already above 90°C. In the liquid-crystalline ordered state chain transfer is suppressed, which results in high polymerization rates up to the isotropic transition temperature. At still higher temperatures this is followed by a rapid drop of the rate due to depropagation.

Gemiddelde polymeren vormen reeds lang een interessant onderzoekgebied vanwege hun sterk anisotrope eigenschappen die wettelijk zijn in tal van toepassingen. Voorbeelden zijn (i) een anisotroop mechanisch gedrag met een hoge modulus en sterkte in de richting van de moleculaire oriëntatie wat nuttig is voor kunststofvezels, (ii) een anisotroop optisch gedrag met groot verschil in brekingsindex en optische absorptie in de verschillende hooftrichtingen, wat toepasbaar is in diverse optische componenten, en (iii) een anisotroop thermisch gedrag met een lage uitzettingscoëfficiënt in de oriëntatierichting, hetgeen van belang is in coating- en behullings toepassingen.

De macroscopische ordening van de macromoleculen wordt meestal geïnduceerd tijdens de verwerking van de polymeren door viscoze stroming in de smelt of in oplossing. De resulterende ordening wordt vervolgens gefixeerd door afkleding beneden een glasovergang- of kristallisatietemperatuur of door verdamping van het oplosmiddel. Deze processen beperken echter de vormgeving van het polymer. Zo kan men