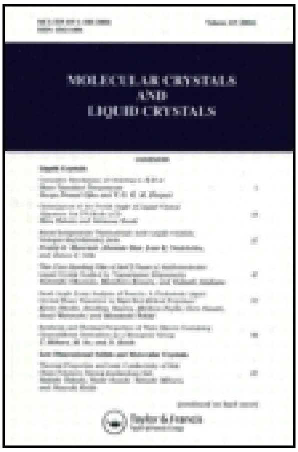

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Functional Liquid Crystalline Polymers: Ferroelectric Polymers and Liquid Crystalline Elastomers and Ionomers

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FUNCTIONAL LIQUID CRYSTALLINE POLYMERS: FERROELECTRIC POLYMERS AND LIQUID CRYSTALLINE ELASTOMERS AND IONOMERS

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Abstract The incorporation of different functional groups in liquid crystalline polymers opens the way to a variety of interesting new materials, which may be used for non-linear optics, as piezo-elements or as two-phasic composite materials.

INTRODUCTION

It is one of the specialities of polymeric systems that different molecular structures, which give rise to different material properties, can be linked covalently to one polymer chain. This allows a combination of material properties, which often can not be achieved in low molar mass materials. The resulting materials can show very special physical properties. *Functionalized* liquid crystalline (LC) polymers belong to this class of materials, because they combine different physical properties or *functions*, which are related to different molecular structures linked by one polymer chain.

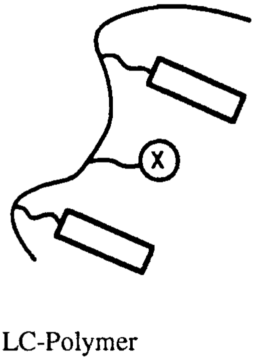


FIGURE 1 Functionalized LC-Polymer

The functionalization of liquid crystalline materials with chiral groups, which leads to chiral LC phases, is one example [1]. These phases show, both for low molar mass and for polymeric systems, special physical properties, which are e. g. ferroelectricity in the chiral smectic C* (s_C*) phase. Now for (chiral and achiral) polymeric liquid crystals additional property combinations are possible that take advantage of the ***combination of the properties of liquid crystals with typical polymer properties.*** The most common polymer property to be introduced is the glass transition, which allows a "freezing in" of the LC phase at low temperatures. Other examples involve: i.) the combination of ferroelectricity with the presence of "NLO-chromophores" to prepare materials, which can be used for non linear optical (NLO) effects like frequency doubling of laser light, ii.) the combination of the ferroelectric properties of the chiral smectic C^* phase with the mechanical orientability of polymer networks to prepare piezoelements, iii.) the combination of the tendency of ionomers to gel reversibly with the presence of LC phases in LC ionomers. These different possibilities will be discussed in the following.

S_C^*-POLYMERS FOR SECOND HARMONIC GENERATION

The precondition for the suitability of materials for second harmonic generation (SHG) is a noncentrosymmetric structure. S_C^*-Polymers fulfill this condition, once their helical superstructure is unwound. Consequently, SHG experiments with chiral smectic C* liquid crystals were performed several years ago [2], proving the possibility of second order nonlinear optical effects in these materials. The magnitude of the effect, on the other hand, was rather disappointing (d values of about 0.01 pmV^{-1}), which is a consequence of the chemical structure of conventional s_C^*-materials. They don't have a donor and acceptor substitution pattern in their aromatic system along the direction of the polar axis, i. e. perpendicular to the long axis of the mesogen. First experiments with low molar mass FLCs gave evidence that the SHG efficiency can be strongly increased by using mesogens with a suitable structure (d values up to 5 pmV^{-1}) [3].

It is our attempt to synthesize polymers for this purpose [4], since they may offer advantages in processibility (stable thin films etc.). As already mentioned, copolymers of chiral mesogens and achiral chromophores were prepared. In these materials, it should be possible to use the high internal electric field of the ferroelectric matrix to orient the chromophores in a noncentrosymmetric way.

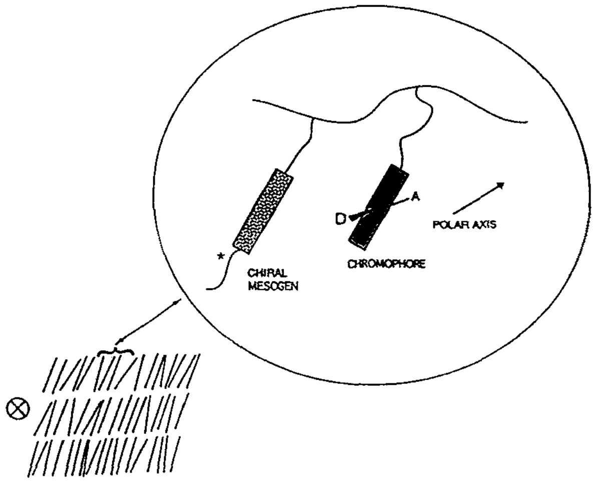
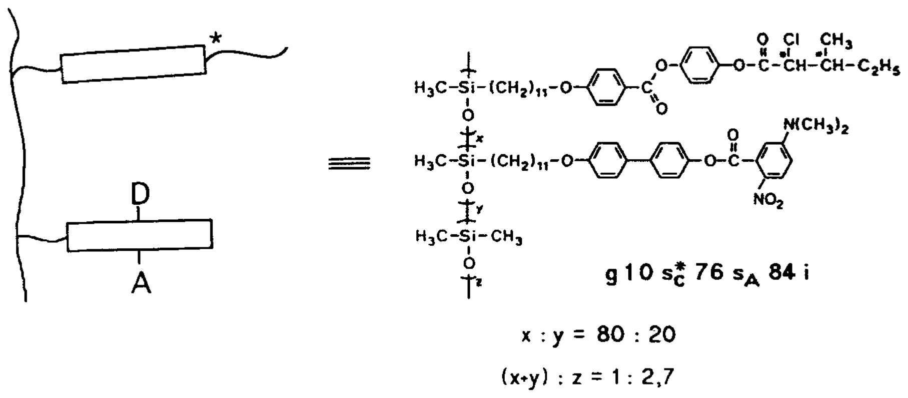


FIGURE 2 Orientation of the achiral chromophores in the ferroelectric matrix

This is in contrast to poled polymers for nonlinear optical applications, where external electric fields are needed for the orientation, often involving relaxation problems.

Depending on the mesogenic group, up to 30 to 50 % of chromophore could be incorporated in the polymer without loosing the s_C*-phase. Incorporation of higher amounts of chromophore leads only to s_A-phases. In scheme I the structure and phase transition temperatures of one selected copolymer are shown, which shows a considerably higher SHG activity than the homopolymer without chromophores.



SCHEME I Ferroelectric LC Polymer for Second Harmonic Generation

Figure 3 shows the dependency of tilt angle and SHG output on the temperature. Both decline with rising temperatue, which indicates the SHG relies on the symmetry breaking in the s_C*-phase in the same way as the ferroelectric properties.

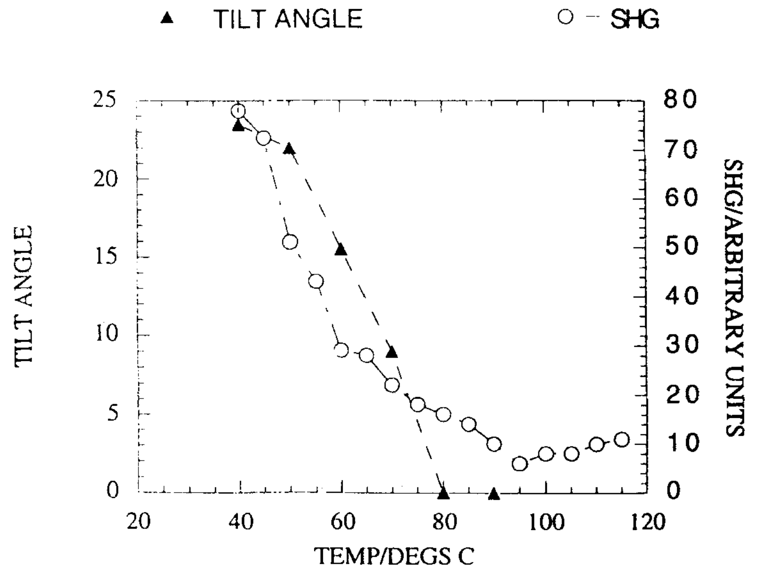
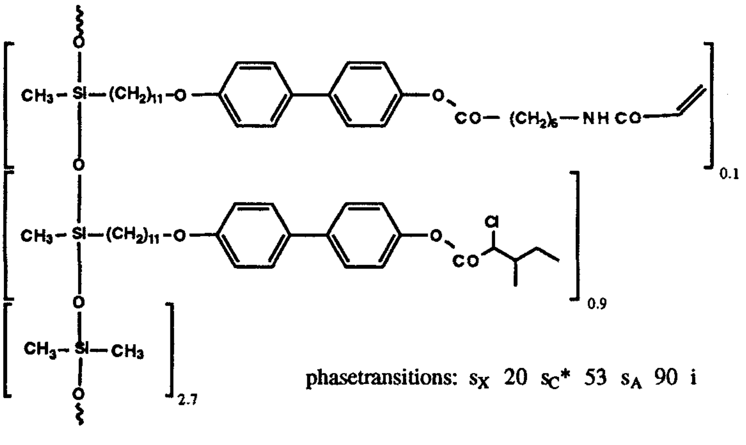


FIGURE 3 Temperature dependency of tilt angle and SHG output

CHIRAL LC-ELASTOMERS

The crosslinking of LC-polymers leads to LC-elastomers, which combine the mechanical orientability of elastomers with LC-phases[5,6]. In addition the information of the orientation during crosslinking is stored in the arrangement of the netpoints. Chiral LC-elastomers and especialy elastomers derived from ferroelectric LC-polymers show additional interesting properties like piezoelectricity [5].

The material used for this investigation is a ferroelectric copolysiloxane (see scheme II), synthesized in analogy to ref. [7].



phasetransitions: s_X 20 $s_C{}^*$ 53 s_A 90 i

SCHEME II Crosslinkable ferroelectric copolysiloxane

Together with the photoinitiator (2,2-dimethoxy-2-phenylacetophenone, 0.5 wt. %) the polymer can be filled in EHC-cells (10 μm) by capillary forces. Electric fields (5 Hz, 400 V_{pp}, rectangular, 30-60 °C) can be used to obtain a polar monodomain (see Fig 4).At this stage the polymer behaves like a typical ferroelectric LC-polymer (P_S: 45 nC/cm^2, 10 K below the clearing point). The crosslinking can be done within the $s_C{}^*$-phase by illumination with UV-light (365 nm) for one hour, under an electrical field of 200V DC. This leads to a disappearance of the IR absorption of the unsaturated amide (1698 cm^{-1}). After the crosslinking the orientation of the LC-director is fixed, which can be demonstrated by heating the sample up into the isotropic phase and cooling back into the $s_C{}^*$-phase. The original orientation of the LC-phase is retained after this treatment.

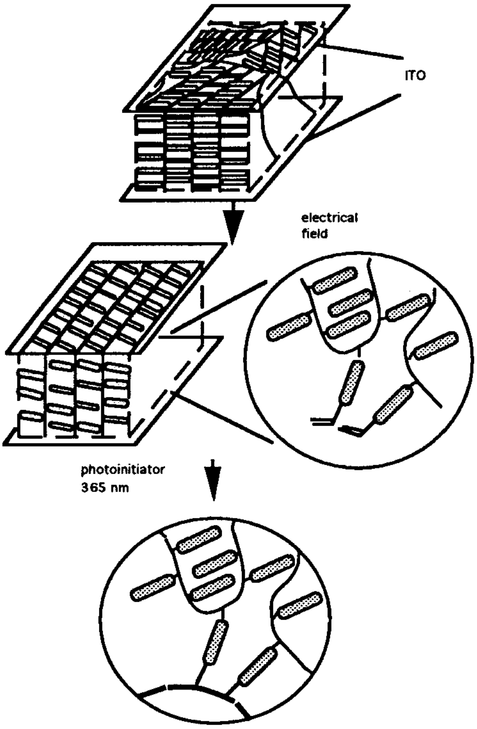


FIGURE 4 Crosslinking of an oriented s_C^*-sample

The switching characteristics of the s_C^*-phase are strongly changed by the photocrosslinking, which stabilizes one of the switching states . While both switching states with the polarisation up or down were isoenergetic for the uncrosslinked polymer , attempts to change the orientation of the director create now elastic stress in the network. This leads to an incomplete switching, which is strongly asymmetric [8]. If the applied field is strong enough, the second ferroelectric switching state can be reached.

The macroscopic polar structure of LC-elastomers crosslinked in the oriented state (monodomain), can be proven by piezoelectric measurements (Fig.5) [8-11]. The rise of the signal with temperature is due to the higher deformability. Piezocoefficients up to 1.4 pC/N are found for the device used (LC-elastomer in EHC-cell). This value represents a lower limit for the piezocoefficient of the LC-elastomer, since most of the stress is taken up by the EHC glass cell.

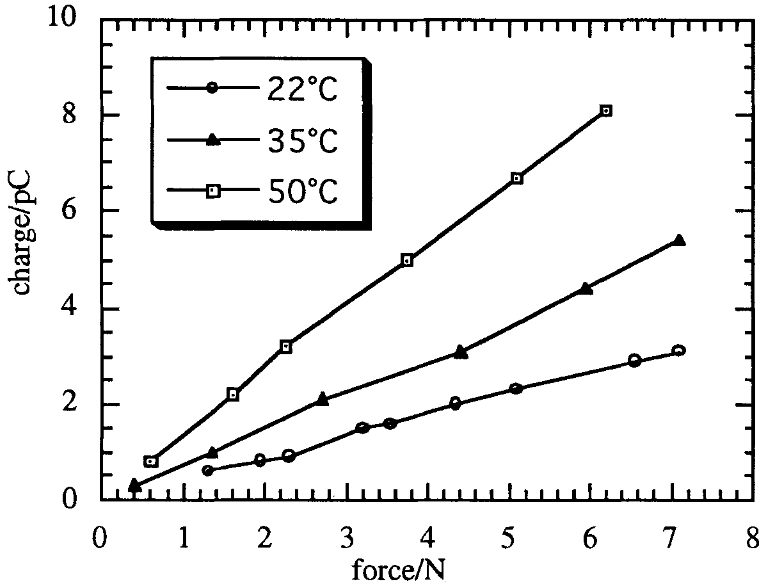


FIGURE 5 Electrical response of the network in EHC-cell on deformation at different temperatures

BLENDS FROM LC-IONOMERS AND AMORPHOUS IONOMERS

The incorporation of ionic groups in LC-polymers leads to a micro phase separation of ionic groups and LC-matrix forced by the tendency of the ionic groups to segregate from the apolar polymer. Because of this phase separated situation, the liquid crystalline behaviour of the LC-Ionomer is not influenced by the presence of ionic groups, but it shows additional properties caused by the presence of ionic clusters.

The formation of ionic clusters in the LC-matrix leads to a physical crosslinking in the LC-phase and in the isotropic state as it is well known from classical ionomers[12] (see Fig. 6).

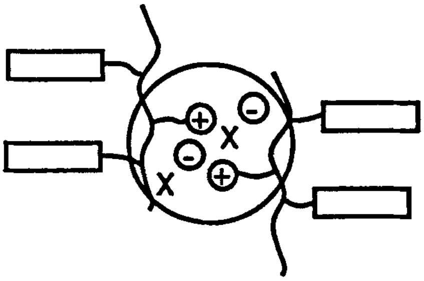
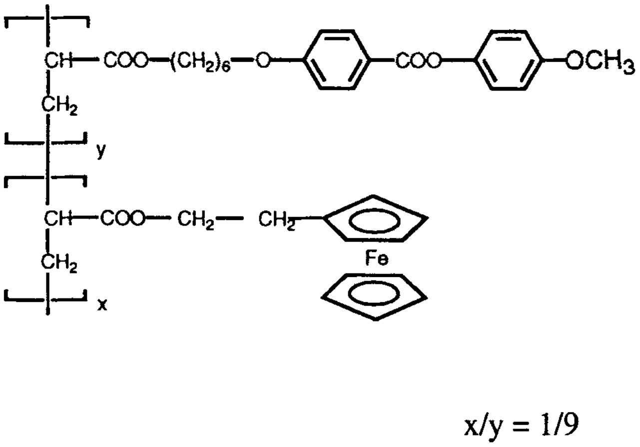


FIGURE 6 Schematic representation of physical crosslinking by cluster formation

In blends consisting of LC-ionomers and amorphous ionomers (molar ratio of ionic groups up to 10 %) the microphase separated ionomer structure (Clusters and LC-matrix) gives the chance to combine special properties of both blend constituents. In this case ionic interactions occur at the phase boundaries and this leads to a decrease of surface tension and a drastic increase of adhesion between the two phases.

To introduce ionic groups in LC-polymers, we functionalized LC side group (see Scheme III) and main chain polymers with neutral redoxactive units (ferrocene). These polymers can be converted into LC-ionomers with different counterions by a redoxreaction (oxidation with benzoquinone/acid).

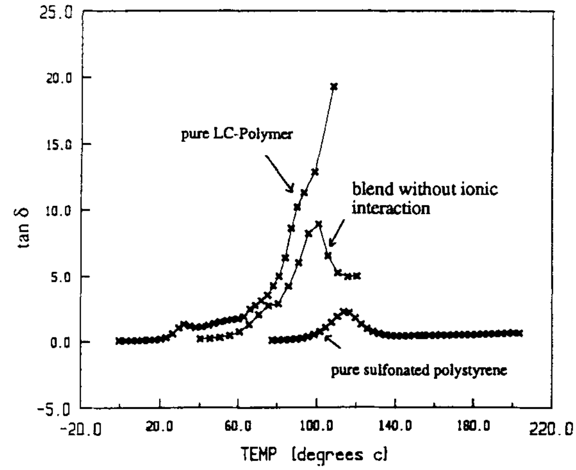


SCHEME III Ferrocene containing LC-side group polymer

Results from small angle X-ray scattering measurements on LC side group ionomers lead to the conclusion that large ionic clusters [13] are formed. Dynamic mechanical measurements on these ionomers show that they behave like slightly crosslinked polymers [13]. The results obtained from the different measuring methods verify that ionic clusters are formed in the LC-matrix and that they are effective as crosslinking points.

Blends of reduced and oxidized LC-polymers (ionomers) with partially sulfonated polystyrene and polystyrene (50 weight %) show the two glass transitions of the pure components and are therefore phase separated [14]. In Figure 7 the dynamic mechanical behaviour of a blend consisting of a LC-polymer and partially sulfonated polystyrene (no ionic interaction) and a blend consisting of the corresponding LC-ionomer and partially sulfonated polystyrene (ionic interaction) is presented in comparison with the pure components.

7a) Blend without ionic interaction



7b) Blend with ionic interaction

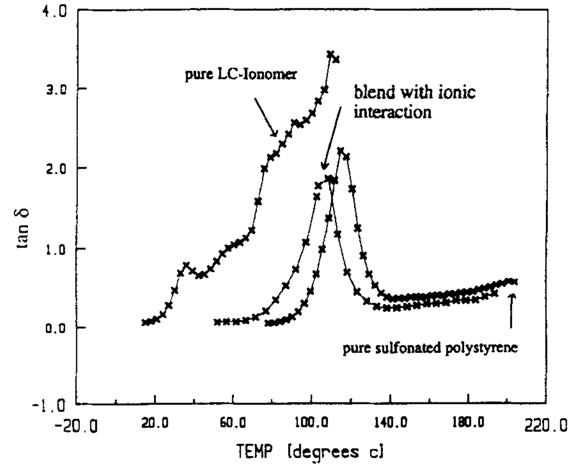
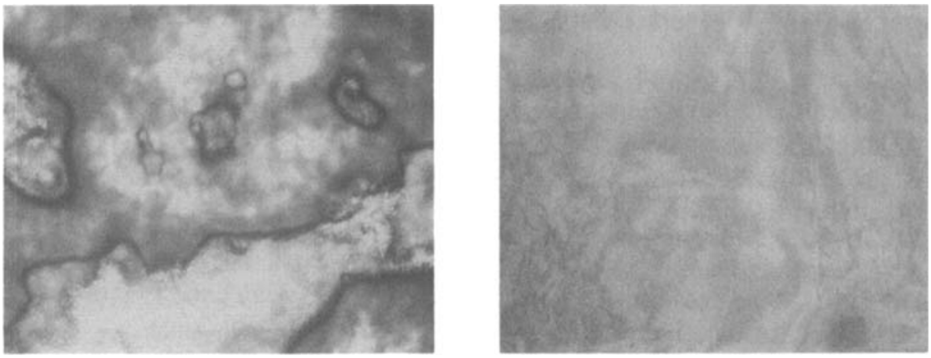


FIGURE 7) Teperature dependence of tan ∂ of polymer blends and components

The loss factor tan ∂ (ratio of dissipative and elastic components of the complex shear modulus) of the blend without ionic interactions exhibits a strong increase with increasing temperature (see Fig. 7a). This behaviour is very similar to the flow behaviour of the pure LC-Ionomer and shows that the elastic blend component is free to flow in the surrounding LCP matrix. The blend with ionic interactions shows a very different behaviour (see Fig. 7b). The low values of tan ∂ demonstrate the elastomeric behaviour of this blend. The mechanical behaviour is nearly identical to the behaviour of pure sulfonated polystyrene.

In accordance with the observed flow behaviour of the blend without ionic interactions, the optical micrograph shows a coarse phase separation (see Fig 8a) whereas the blend with ionic interaction is exhibiting a homogeneous LC-texture without any phase separation on a macroscopic scale despite the fact that the blend consists of weight % of a non LC-component (see Fig. 8b).



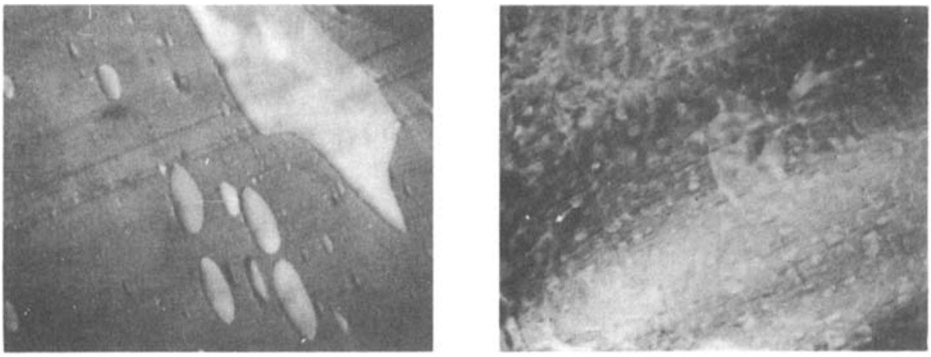
8a) Blend without ionic interaction

8b) Blend with ionic interaction

FIGURE 8) Textures of polymer blends See Color Plate IV.

So, depending on the measuring method the blend with ionic interactions shows the property of only one component. In optical microscopy the liquid crystalline properties of the pure LC-component is observed whereas the mechanical behaviour is dominated by the amorphous ionomer.

The change from a coarse phase separated to a homogeneous texture is caused by a drastic change of the superstructure. The transmission electron micrographs of ultra thin sections of these blends show that the blend without ionic interaction (see Fig. 9a) is phase separated on a micrometer scale whereas the blend with ionic interactions (see Fig. 9b) shows a very fine dispersion (100-200 nm) of each phase in the other.



9a) without ionic interaction

9b) with ionic interaction

FIGURE 9 TEMs of polymer blends, magnification: 13 500

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