Synthesis and properties of functionalized polymers*

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This paper describes the rational design of four different types of functionalized polymers with interesting material properties. (i) Liquid crystalline (LC) side-group polymers with a high spontaneous polarization in the ferroelectric chiral smectic C^* phase can be prepared by a proper selection of the chiral groups. The additional functionalization with non-linear optical chromophores makes these materials interesting for non-linear optics. (ii) Chiral LC polymers, which are functionalized with crosslinkable groups, can be converted into LC elastomers. The mechanical orientability of these elastomers leads to new piezoelectric materials. (iii) The incorporation of ferrocene units into a LC matrix allows the reversible formation of LC ionomers by a redox reaction. This leads to a gelation of the LC polymer system. (iv) The curing (dense crosslinking) of a polymer matrix is one possibility to stabilize the polar order of dye molecules, which is necessary for frequency doubling. This can lead to large and stable non-linear optical coefficients.

(Keywords: liquid crystalline polymers; elastomers; redox-active polymers; non-linear optical polymers; ferroelectricity; piezoelectricity)

INTRODUCTION

In materials science it is important to understand the relationship between the molecular structure and the resulting macroscopic material properties, because this is the precondition for a rational design of materials with complex physical properties. In order to reach this goal it is necessary to optimize the molecular properties and, in a second step, to orient the molecules in such a way that the molecular properties transform into the macroscopic properties of a condensed phase. Thereby supramolecular structures become essential, which may be, for example, liquid crystalline (LC) phases[1,2]. Compared to crystals they have the advantage that they are less sensitive to the structural variations necessary to optimize the molecular properties, and there has been much research into the design of molecules to achieve a special LC phase. Another important concept in the rational design of materials with complex physical properties is the combination of different molecular fragments, which give rise to different properties, in one material. Functionalized polymers are important in this respect, because they allow the combination of different molecular fragments in one polymer and thus exclude demixing processes.

Here we will present four examples that demonstrate the possibility for a rational design of new materials by a combination of different functional groups in one polymer, while using LC phases or poled polymers as supramolecular structures.

1. Side group polymers with chiral smectic C^* (s_C^*) phases and a high spontaneous polarization (ferroelectricity) can be prepared by a combination of chiral end groups and bulky and highly polar lateral substituents[3]. The additional functionalization of these polymers with non-linear optical chromophores leads to materials of interest for non-linear optics (NLO).
2. Combined LC polymers with chiral smectic C^* (s_C^*) phases can be prepared in a convenient way by a polymer analogous reaction[4]. The molecular precondition for high spontaneous polarizations (P_s) can be created by a proper selection of chiral acids. The additional functionalization of these polymers with crosslinkable groups leads to the formation of LC elastomers, the mechanical orientability of which transforms the ferroelectricity discussed above into the piezoelectricity of new rubbery material[5–7].
3. An alternative method for the crosslinking of LC polymers is the formation of ionic aggregates in LC ionomers. The incorporation of ferrocene groups into various types of LC polymers allows the reversible formation of ionomers by a redox reaction[8].
4. The poling of dye containing polymers is widely used to create the polar non-centrosymmetric structure necessary for NLO applications, such as frequency doubling or the Pockels' effect[9–12]. The formation of a densely crosslinked network is one method to stabilize this structure[13–16]. The use of a high concentration of tolanes as non-linear optical chromophores leads to materials with high and stable non-linear optical coefficients[17].

STRUCTURE–PROPERTY RELATIONS IN CHIRAL SIDE-GROUP POLYMERS

The interest in side-group polymers with chiral smectic C^* phases is related to the fast switching times of these

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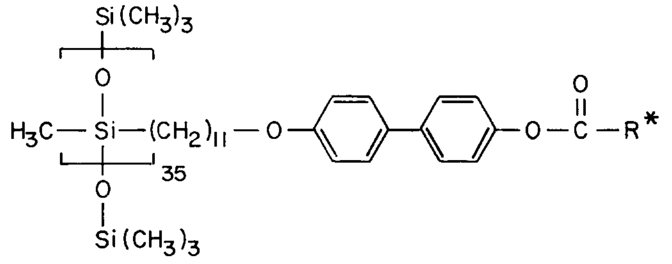
materials in electric fields[18–21]. This contrasts with the properties of the combined polymer discussed in the next section, which cannot be reoriented (switched) in electric fields, even if they show the typical X-ray pattern and ferroelectric modes. We have prepared chiral polysiloxanes via a polymer analogous reaction, which allows an easy variation of the chiral centres. The polymers prepared in this way are listed in *Table 1*. All polymers form chiral smectic C^* phases, with spontaneous polarizations (P_s) varying from 18 to 420 nC cm^{-2}.

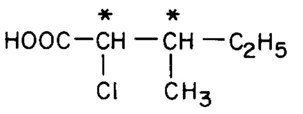
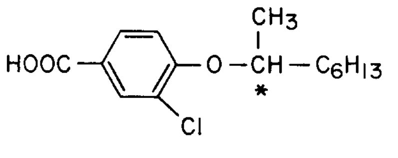
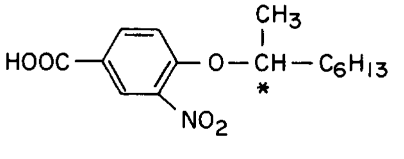
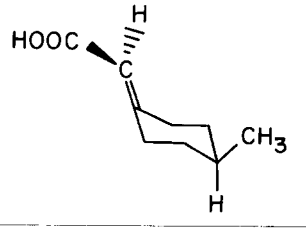
High frequency dielectric measurements[21], which measure the rotation of the mesogens around their long axis, are useful in understanding the molecular origin of these differences in P_s. These measurements show long relaxation times (10^{-9} s) for polymer *3*, which has high polarization and relaxation times, and relaxation times two orders of magnitude shorter (10^{-11} s) for polymer *4*, which has small polarization. Since dielectric relaxation gives no information about the mechanism of the motion, and since it allows no differentiation between a free rotation and a jumping motion, it is not possible to convert the information about the relaxation time into a prediction of P_s. However, following chemical intuition about the steric requirements of the chiral groups, the following point seems important. Bulky lateral substituents (the nitro group at the aromatic ring and the methyl group at the chiral centre of polymer *3*) seem to lead to a strong bias during the rotation of the mesogens around their long axis. This leads to a strong preference for one orientation and helps to increase P_s. At the same time the overall mobility is reduced, leading to a decrease of the relaxation time. However, if the chiral group is more rod-like, then the opposite happens: the bias for the rotation around the long axis of the mesogen is reduced and the overall mobility is increased. This seems to be the reason for the small P_s value of polymer *4*, which is chiral due to axial chirality[18]. Its chiral group, although chiral as a whole, is not very form-anisotropic.

In addition, we have been interested in exploring the possibility of using the macroscopic dipole of the chiral smectic C^* phase to orient molecules with a high non-linear optical hyperpolarizibility, in such a way that the resulting materials can be used for second harmonic generation. (In classical polymers this orientation is

Table 1 Characterization of the polysiloxanes *1–4*. Polymerization, P_s, the relaxation strength of the high frequency relaxation, $\Delta\varepsilon$, and the relaxation time, τ, were determined 10°C below the upper temperature limit of the s_C^* phase (see ref. 21)



1–4

Polymer	HOOC-R*	Phase transition temperatures (°C)[a]	P_s	$\Delta\varepsilon$	τ (s)
1	 $HOOC{-}\overset{*}{C}H(Cl){-}\overset{*}{C}H(CH_3){-}C_2H_5$	$k68\,s_C^*88\,s_A156\,i$	130	1.27	6×10^{-10}
2		$k62\,s_x128\,s_C^*170\,i$	120	1.19	6.7×10^{-10}
3		$g21\,k57\,s_C^*161\,s_A183\,i$	420	3.3	2.5×10^{-9}
4		$g51\,k118\,s_C^*151\,i$	18	0.56	7×10^{-11}

[a] g, glassy; k, crystalline; s_C^*, chiral smectic C^*; s_A, smectic A; s, smectic, not further specified; i, isotropic

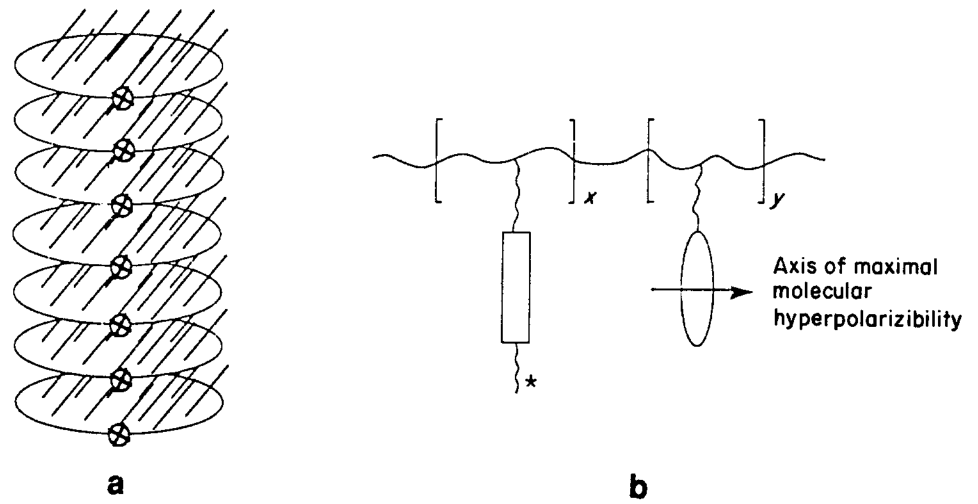
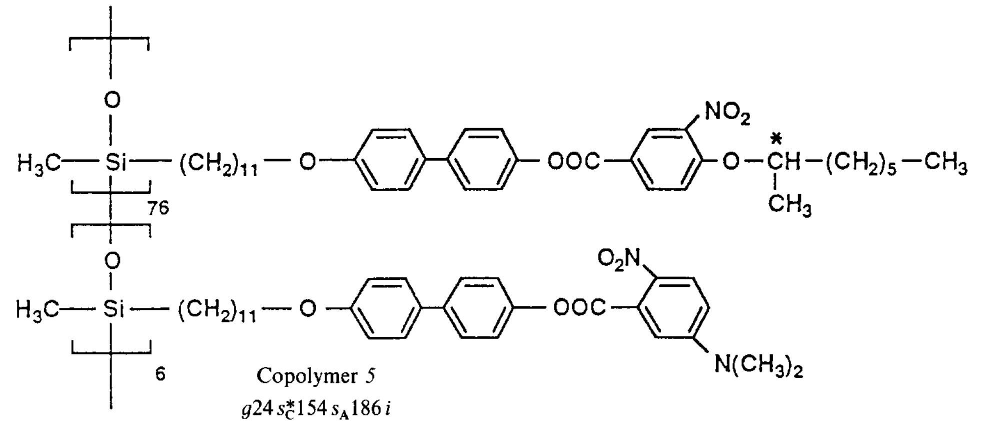


Figure 1 Schematic representation of the chiral smectic C^* phase: (a) with an untwisted helical superstructure (⊗, direction of the spontaneous polarization); (b) of a copolymer with chiral mesogens and a non-linear optical chromophore



Copolymer *5*
$g24\,s_C^*154\,s_A186\,i$

Scheme 1

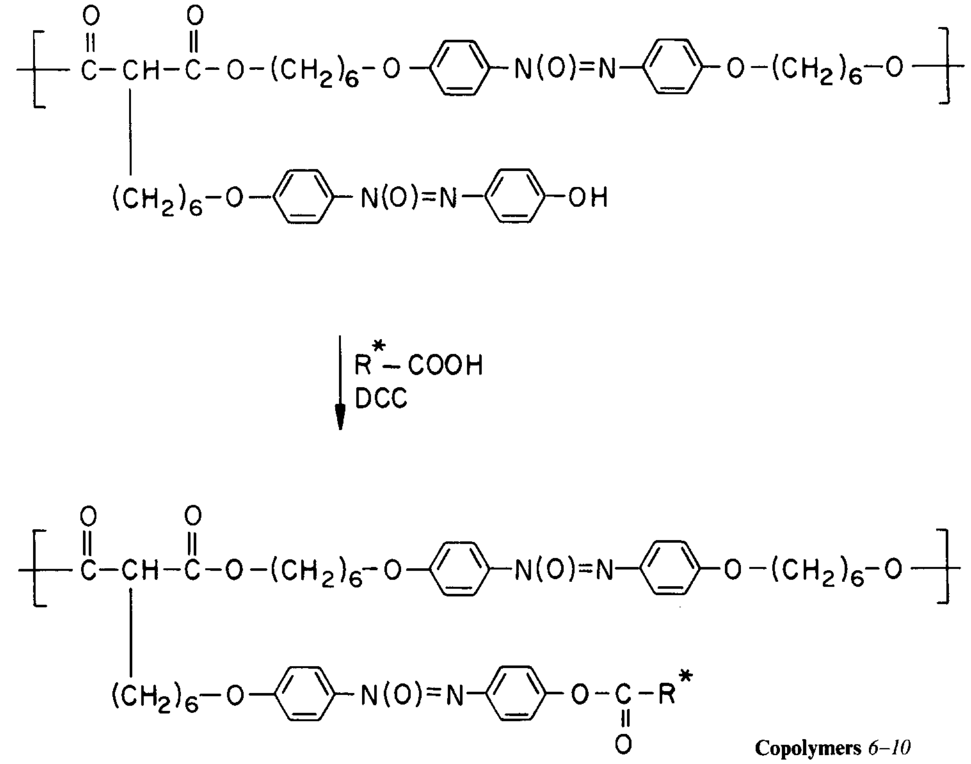
accomplished by poling these molecules in external electric fields.) The molecules normally employed for second order NLO are, however, not suitable for this purpose, because the axis of their maximum molecular hyperpolarizibility is oriented parallel to their molecular axis, while the macroscopic polar axis of chiral smectic C^* phases is oriented perpendicular to the long axis of the mesogens (*Figure 1*). In order to use side-chain polymers for frequency doubling in NLO, a copolymer was prepared (copolymer *5*), in which 6% of the mesogenic groups are esterified with a group which has an appreciable hyperpolarizibility component perpendicular to its long axis (2-nitro-5-dimethylamino benzoic acid). Introduction of this non-linear optical chromophore has almost no effect on the LC phase transitions, compared to the homopolymer (*Scheme 1*).

CHIRAL COMBINED POLYMERS AND LC ELASTOMERS

Chiral combined main-chain/side-chain polymers can be prepared by a polymer analogous esterification with the help of dicyclohexyl carbodiimide (DCC) (*Scheme 2*). According to ^1H n.m.r. measurements, this conversion proceeds nearly quantitatively. Compared to earlier synthetic routes to these polymers[22,23], this method has the advantage that the chiral group is introduced during the last step of the synthesis under mild conditions. This allows the introduction of many differently structured chiral acids[18] and thereby the evaluation of structure–property relations.

The polymers prepared in this way show cholesteric, smectic *A* and chiral smectic C^* phases, as well as higher ordered smectic and crystalline phases (*Table 2*). *Figure 2* presents the results of X-ray measurements performed on polymer *10* together with d.s.c. measurements and polarizing microscopy carried out to identify the LC phases.

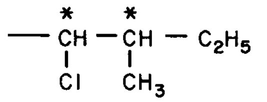
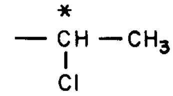
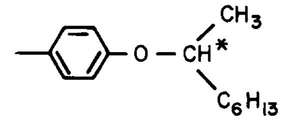
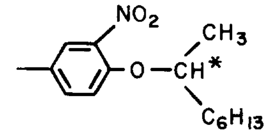
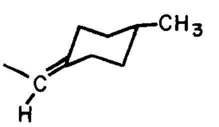
Crosslinking of chiral polymers of this type[5,6,23] leads to the formation of LC elastomers, the mechanical orientability of which transforms ferroelectricity into the piezoelectricity of new rubbery materials. Combined polymers may be ideally suited for this purpose (see *Figure 3* for a mechanically oriented network structure), because a part of the mesogenic groups is incorporated into the polymer chain, but all mesogens orient parallel to each other. If combined polymers are additionally functionalized with acrylate groups (*Scheme 3*), then this crosslinking reaction can be performed thermally. The LC elastomers prepared in this way (e.g. polymer *11b*, *Scheme 3*), show a piezoelectric response within the temperature range of the chiral smectic C^* phase[5] (*Figure 4*). It is noteworthy that chiral groups with a lateral nitro substituent, which give rise to a high spontaneous polarization (see polymer *3* in *Table 1*), can be used for this purpose.



Copolymers *6–10*

Scheme 2

Table 2 Phase assignments of the polyesters *6–10* (see *Scheme 2*)

Polymer	*R**	Phase transition temperatures (°C)[a]
6	 $-\overset{*}{C}H(Cl)-\overset{*}{C}H(CH_3)-C_2H_5$	$g19\,s100\,n^*128\,i$
7	 $-\overset{*}{C}H(Cl)-CH_3$	$g18\,s_C^*115\,s148\,n^*156\,i$
8		$g14\,s_C^*32\,s_A60\,n^*164\,i$
9		$g20\,s_C^*51\,s_A84\,n^*136\,i$
10		$g26\,s_C^*82\,n^*153\,i$

[a] See *Table 1* for abbreviations; n^*, cholesteric

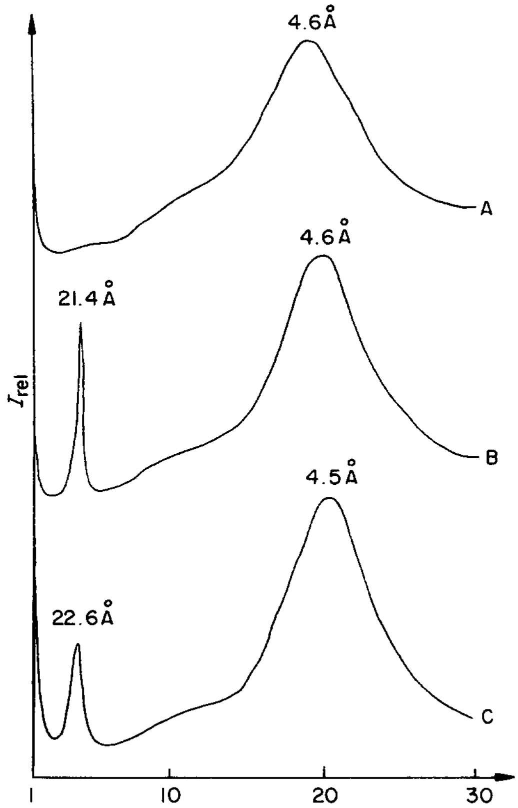


Figure 2 Temperature dependent X-ray measurements of polymer *10* (see *Table 2* and *Scheme 2*): A, cholesteric phase, $T = 140°C$; B, chiral smectic C^* phase, $T = 67°C$; C, glassy phase, $T = 25°C$

REDOX-ACTIVE LC IONOMERS

Ionomers have so far been prepared mainly by the neutralization (salt formation) of polymeric acids[24]. An alternative route to ionomers is the oxidation of polymers that have been functionalized with redox-active groups[25]. The advantage of the second method is that the neutral (not oxidized) reference polymers have no special interactions. In polymeric acids, however, strong hydrogen bonding is always observed. The reasons for interest in these ionomers are two-fold: on the one hand, the possibility of reversibly transforming a non-crosslinked

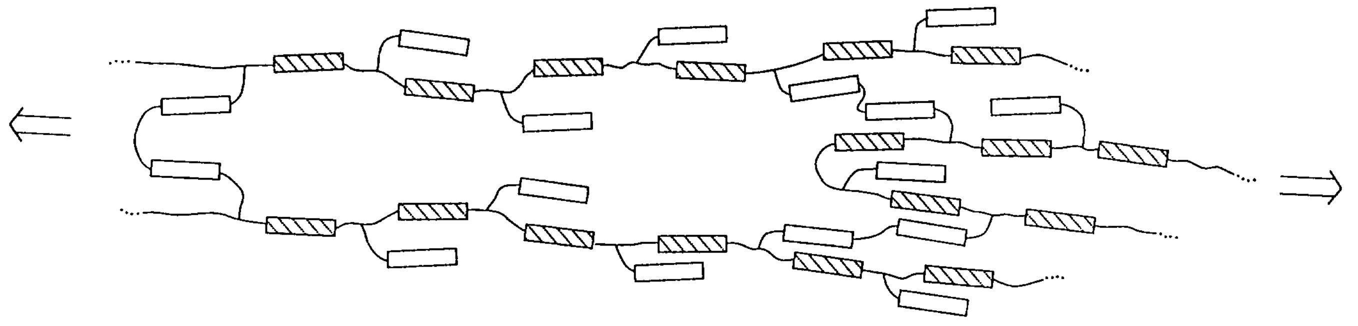
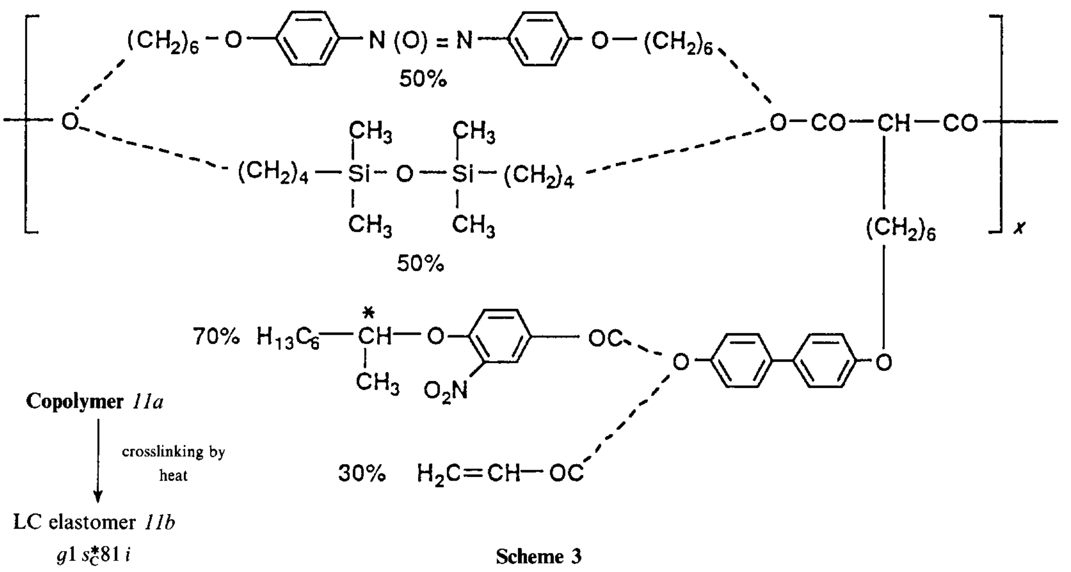


Figure 3 Schematic representation of an LC elastomer, which has been oriented by stretching



Scheme 3

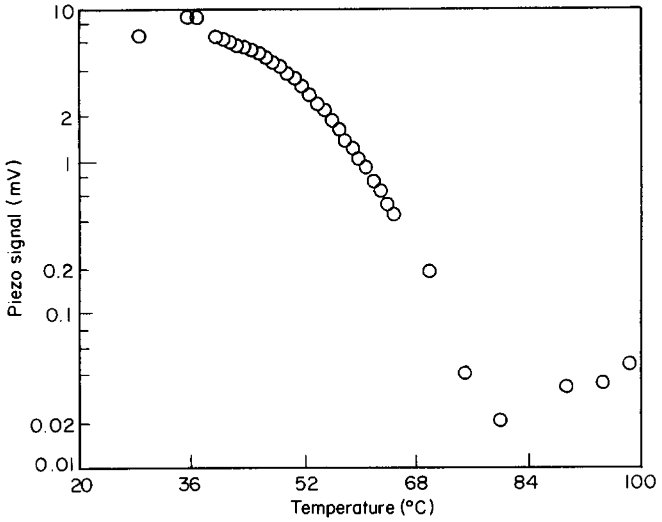


Figure 4 Piezo signal (in logarithmic scale) *versus* temperature for elastomer *11b* (see *Scheme 3*) with an amplitude of 10%

system via a redox reaction into a soft gel is fascinating; on the other hand the ionic groups incorporated into the polymer may help to stabilize a blend with a polymer with ionic groups of opposite charge.

We have prepared LC polymers with up to 10% ferrocene groups via copolymerization (see *Table 3*). The oxidation of these ferrocene groups is chemically reversible, as determined by cyclovoltagraphic measurements. It was done on a preparative scale with $Cu(ClO_4)_2$. For both the reduced (uncharged) and the oxidized (charged) polymers, LC phases were observed (see *Table 3*).

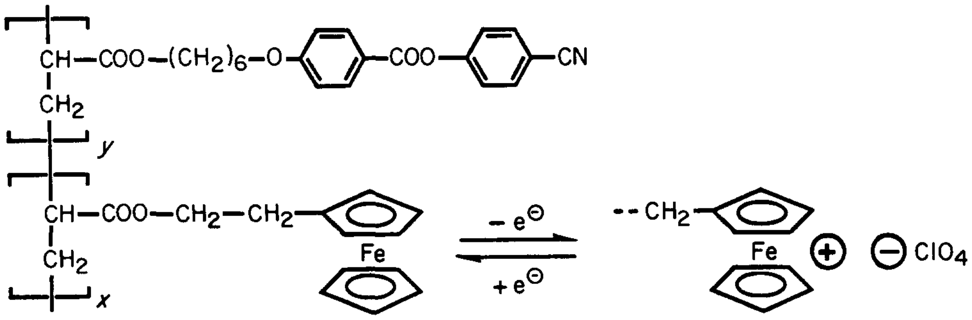
For the oxidized (charged) LC ionomers, the clustering of the ions could be observed by small angle X-ray measurements (*Figure 5*). Mechanical measurements performed on the same system show the formation of a soft gel (*Figure 6*). Investigations on the blending behaviour of these LC ionomers are in progress.

POLYMERS FOR NLO APPLICATIONS

In order to obtain a large and stable bulk optical non-linearity, it is desirable to introduce a concentration — as high as is feasible — of efficient non-linear optical chromophores into a crosslinking matrix$^{9-16}$. The tolanes *16* and *17* (*Scheme 4*) were prepared for this purpose. The polyaddition of two molecules of *16* to one molecule of *17* leads to a branched prepolymer (*Table 4*), which can be densely crosslinked during the poling procedure and which has an extremely high degree of loading (86 wt%) of non-linear optical chromophores. For comparison, the corresponding linear polymer (polymer *20*) was also prepared.

Both polymers form a smectic *A* phase if they are annealed above the glass transition temperature, T_g (see *Table 4*). However the LC phase can be suppressed quite easily to prepare non-scattering amorphous glasses, e.g. by spin casting. While spin-cast films of the linear

Table 3 Characterization of the ferrocene-containing copolymers *12–15* (see ref. 8)



Polymer	Ferrocene content (%)	M_w (g mol^{-1})	Reduced form T_g (°C)	Reduced form T_{ni} (°C)	Oxidized form T_g (°C)	Oxidized form T_{ni} (°C)
12	0	14 000	24	113	–	–
13	2.7	20 000	30	115	32	86
14	7.3	15 500	26	106	33	106
15	8.9	17 700	30	94	37	95

T_{ni} = clearing temperature

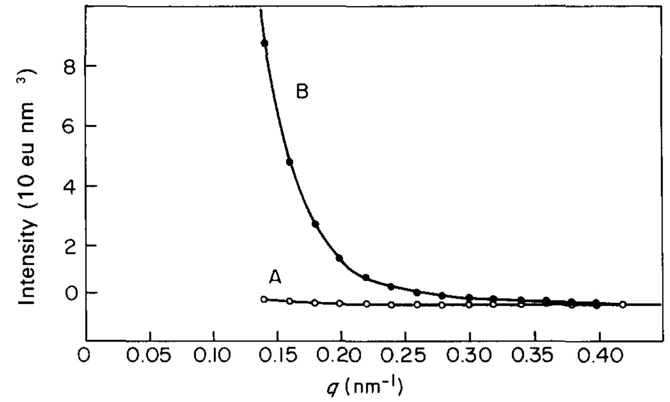


Figure 5 Small angle X-ray scattering of polymer *15* (see *Table 3*): A, reduced form; B, oxidized form

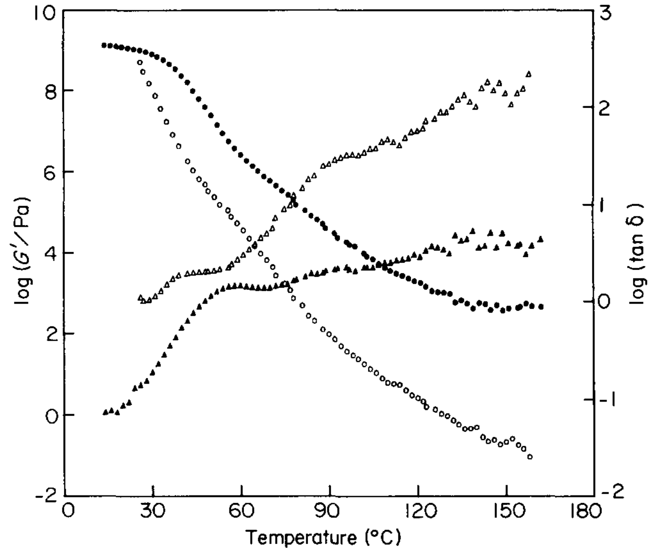
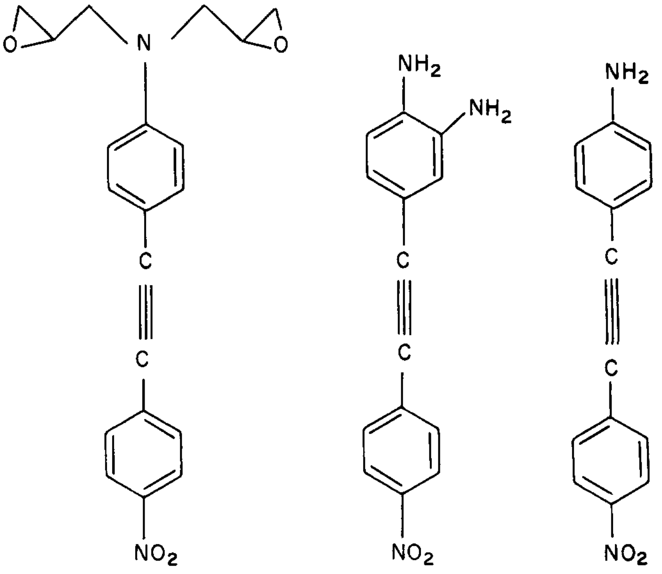


Figure 6 Dynamic mechanical behaviour of polymer *14* (see *Table 3*): reduced form (open symbols); oxidized form (solid symbols)



16 *17* *18*

16 + *17* → crosslinked polymer *19*

16 + *18* → linear polymer *20*

Scheme 4

Table 4 Thermal characterization of the crosslinked polymer *19* and the linear polymer *20* (see *Scheme 4* and ref. 17)

Polymer	Transition temperatures (°C)[a]	Layer thickness (Å)
19[b]	*g*73 s_A	18.7
[c]	*g*120 s_A170 dec	
20	*g*64 s_A155 dec	17.2

[a] See *Table 1* for abbreviations; dec, decomposition
[b] Fresh sample
[c] After curing at 147°C for 15 min

polymer *20* restore the LC phases upon heating above T_g, this is not observed for the crosslinked polymer *19*, where the crosslinking presumably inhibits the complete reformation of the LC phase. Thus, depending on the heat treatment, polymer *19* allows a poling process, during which mainly the short range order of the smectic *A* phase is active.

The poling of polymer *19* by corona poling techniques leads to a highly oriented non-scattering polymer film. Pockels' coefficients, r_{113}, up to 7.5 pm V^{-1} could be

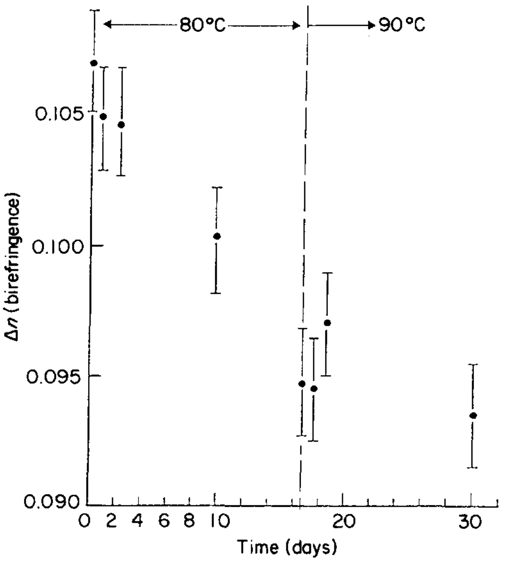


Figure 7 Stability of the birefringence induced by poling into a sample of the crosslinked non-linear optical polymer *19* (see *Table 4* and *Scheme 4*)

measured, proving the polar structure. The structure obtained is completely stable at room temperature and even at higher temperatures (80–90°C, see *Figure 7*) shows only a 13% decrease of the birefringence over 30 days. Measurements of the Pockels' coefficients showed no decrease during this time.

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