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Blends from redox active liquid crystal ionomers and amorphous ionomers

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Biphasic blends (mixtures) of liquid crystal ionomers (prepared from ferrocene containing liquid crystal polymers by a redox reaction) and partially sulfonated polystyrene combine the constituent properties in a way, which is dependent on the measuring method. Polarizing microscopy shows homogenous textures similar to the pure liquid crystal polymer. Mechanical measurements show however the elastomeric behaviour of sulfonated polystyrene. The phase separated structure of these blends is proved by differential scanning calorimetry measurements.

1. Introduction

Biphasic mixtures allow the combination of constituent properties, which is not possible in homogeneous mixtures. Polymer dispersed liquid crystals [1] enable, for example, the combination of the unchanged properties of a liquid crystalline (LC) mixture (the LC order and the mobility in electric fields) with the form stability of a polymer matrix. More examples for such a desirable combination of properties are known from the field of block copolymers and polymer blends [2]. In this case rubber modified polymers may result, which combine the hardness of one phase with the possibility of a soft phase to dissipate energy during deformation. Generally, the properties of such (biphasic) blends depend strongly on their morphology and the adhesion at the interface between the phases.

In this work we attempt to evaluate one aspect arising from a combination of LC polymers and amorphous polymers [3]. In order to vary the adhesion and the morphology, LC ionomers [4], in which the concentration of ionic groups can be varied by a redox reaction, were used. In blends with amorphous ionomers [5], mixed ionic clusters may form at the interface, thereby reducing the interfacial tension and increasing the adhesion (see figure 1). The concentration of these mixed clusters can be modified by a redox reaction. This may lead to drastic changes in the morphology.

2. Experimental

The synthetic route to the reduced (**1a**) and oxidized (**1b**) LC polymer is presented in Scheme 1. Polymer **1a** (M_w: 46000 determined by GPC in chloroform calibrated against polystyrene standards) was prepared as described in [4]. However, the oxidation to polymer **1b** was achieved with 4-benzoquinone [6]. This method has the advantage, that different counterions (for example halogenids and sulphate) can be used. The amount of ferrocene units in the copolymers was determined by

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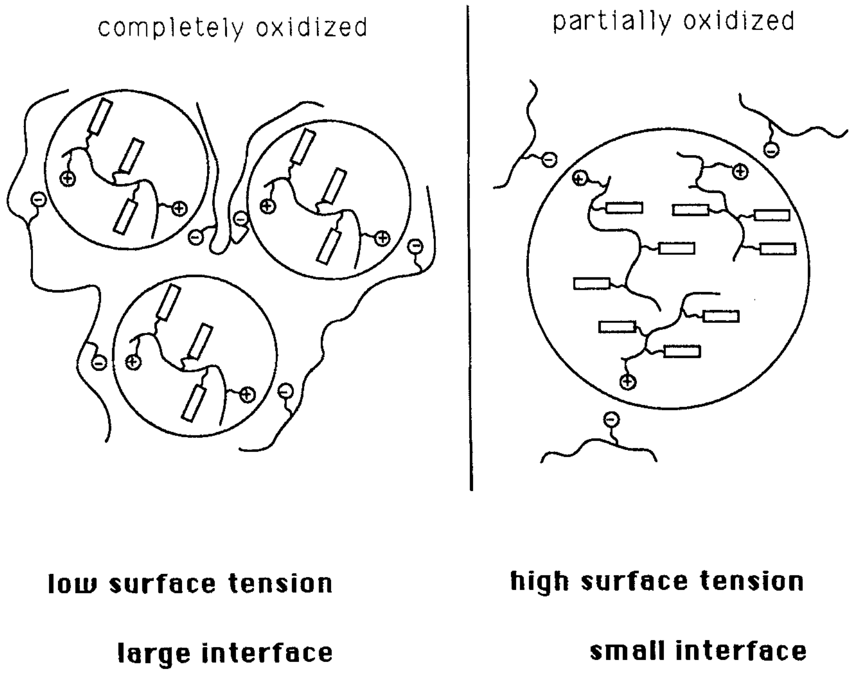


Figure 1. Variation of the amount of ionic groups in a polymer blend consisting of a LC ionomer and an amorphous ionomer. Proposed influence on the size of microphase-separated regions.

potentiometric titration with $Cu(ClO_4)_2$ (see [4, 7] and found to be 10·2±0·5 per cent).

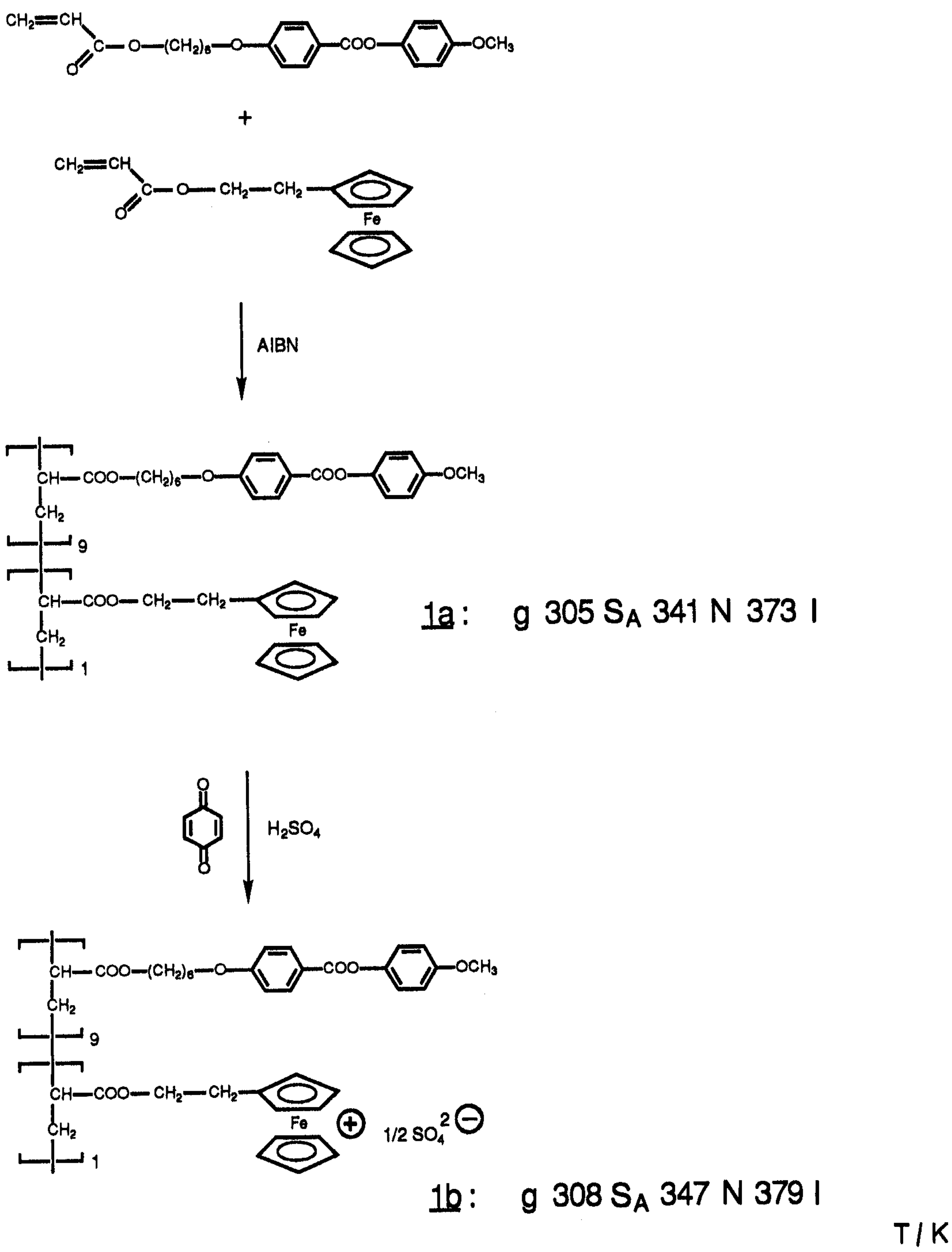
2.1. *Synthesis of ionomers*

2.1.1. *Synthesis of redox active LC ionomer* **1b**

1 g of the ferrocene containing copolymer **1a** ($2{\cdot}63 \times 10^{-4}$ mol ferrocene equivalents) and 40 mg of 4-benzoquinone ($3{\cdot}7 \times 10^{-4}$ mol) were dissolved in 10 ml of chloroform. Then a solution of concentrated sulphuric acid (5 drops) in 1 ml of methanol was quickly added under stirring. The colour of the solution changes at once from yellow to deep blue. The polymer was precipitated two times into cold methanol and dried at 40°C under reduced pressure. Reprecipitation has to be done very fast because charged ferrocene groups tend to decompose in solution. Yield: 820 mg (79·5 per cent).

2.1.2. *Poly-(styrene-co-sodium-4-styrenesulphonate)*

Poly-(styrene-co-sodium-4-styrenesulphonate) [8] was prepared according to Scheme 2. 5 g of polystyrene (0·05 mol styrene equivalents, $M_w = 166\,000\,\mathrm{g\,mol^{-1}}$) was dissolved in 100 ml of dichloromethane and cooled to a temperature of 0°C. Then a solution of 0·53 g (0·0045 mol, calculated for a degree of sulfonation of 4·5 per cent) of freshly distilled chlorosulphonic acid in 5 ml of dichloromethane was added dropwise to the stirred polymer solution over half an hour. After stirring the reaction mixture for additional 2 hours at room temperature, the polymer was precipitated in a mixture of methanol/water (9 : 1). The product was isolated by

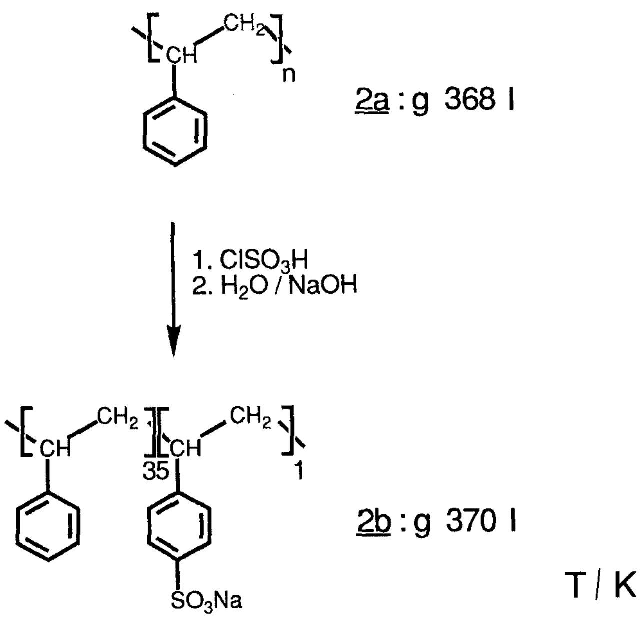


1a: g 305 S_A 341 N 373 I

1b: g 308 S_A 347 N 379 I

T / K

Scheme 1



Scheme 2

filtration and washed with methanol. The obtained product was dissolved in a mixture of 70 ml chloroform/25 ml methanol/5 ml water and heated under reflux for half an hour. Thereafter the solution was made basic by adding concentrated aqueous sodium hydroxide solution. The polymer solution was added dropwise to 800 ml of methanol/water (9 : 1) and cooled to 0°C. During the next 3 hours the ionomer precipitated and could be separated by filtration. To remove covalently cross-linked fractions (sulphones), the product was dissolved in chloroform and filtered. After removal of the solvent the ionomer was dried at 40°C under reduced pressure. The degree of sulfonation was determined by elemental analysis and found to be 2·8 mol%. Yield: 1·1 g (22 per cent). Elemental analysis: found C: 89·98 per cent, H: 7·77 per cent, S: 0·835 per cent.

2.1.3. *Preparation of polymer blends*

Four polymer blends were prepared from 50 wt% mixtures of the constituents as presented in the table. 100 mg of the blend components were dissolved in 5 ml chloroform and mixed under stirring. The solvent was removed rapidly under reduced pressure at 40°C and the mixtures were annealed at 170°C for 10 min. Potentiometric, DSC and mechanical measurements were performed according to the procedures reported in [4].

3. Results and discussion

The DSC curves of polymers **1a** and **1b** are presented in figure 2. It follows from them that the liquid crystalline behaviour of ferrocene containing side group polymers **1a** and **1b** is similar to the behaviour of the corresponding homopolymer [4]. The mesophase width ΔT (smectic A and nematic) decreases with increasing ferrocene content and is reduced from 88°C for the homopolymer [4] to a value of 68°C for the reduced form and 71°C for the oxidized form. The glass transition and phase transition temperatures of the oxidized polymer **1b** are shifted by a few degrees to higher values compared to the corresponding reduced form (**1a**).

Generally, oxidation of ferrocene containing polymer **1a** with 4-benzoquinone/H_2SO_4 leads to LC ionomers with high thermal stability in the melt (no decomposition up to 250°C). Similar LC ionomers with perchlorate counterions did decompose above 100°C caused by the action of perchlorate as a strong oxidation agent [4].

In all blends prepared from reduced and oxidized liquid crystalline polymers (LCP) with polystyrene and partially sulfonated polystyrene (see the table), the glass transition of the LCP (T_{g1}) and the phase transition smectic A to nematic and nematic to isotropic of the LCPs occur at nearly the same temperatures as for the pure LCPs (see figure 3). The DSC curves exhibit also the glass transition of pure polystyrene and pure partially sulphonated polystyrene (T_{g2}). For miscible blends a single composition-dependent glass transition would be expected whereas biphasic blends show the two characteristic glass transitions of the pure components. Thus, the observed thermal behaviour of the four polymer mixtures proves, that all of them are completely phase separated, independent of the fact that ionic interactions between the blend components are possible (see blend IV in the Table) or not (blend I). In contrast to the similar thermal behaviour, the optical micrographs of the four blends (see figure 4(*a*)–(*d*)) show that the blend consisting of two ionomeric components exhibits no phase separation on a macroscopic scale, whereas all other

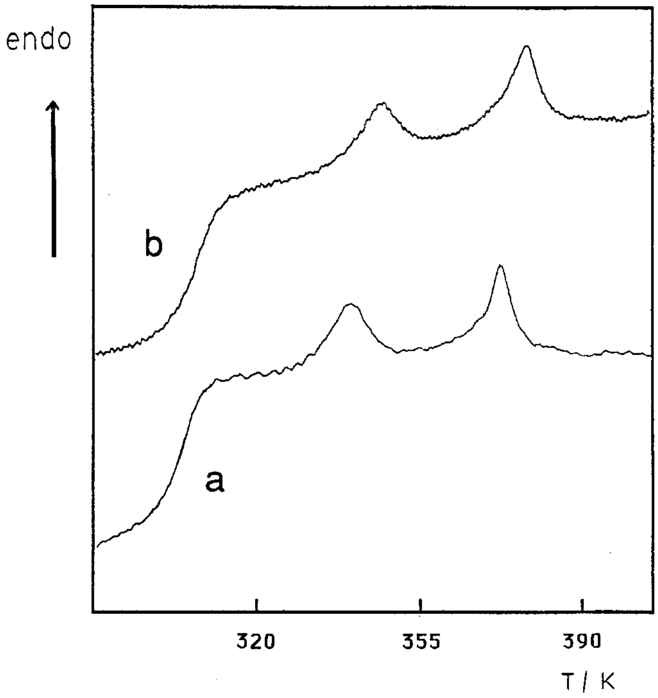


Figure 2. DSC thermogram of polymers **1a** (reduced form) (*a*) and **1b** (oxidized form) (*b*).

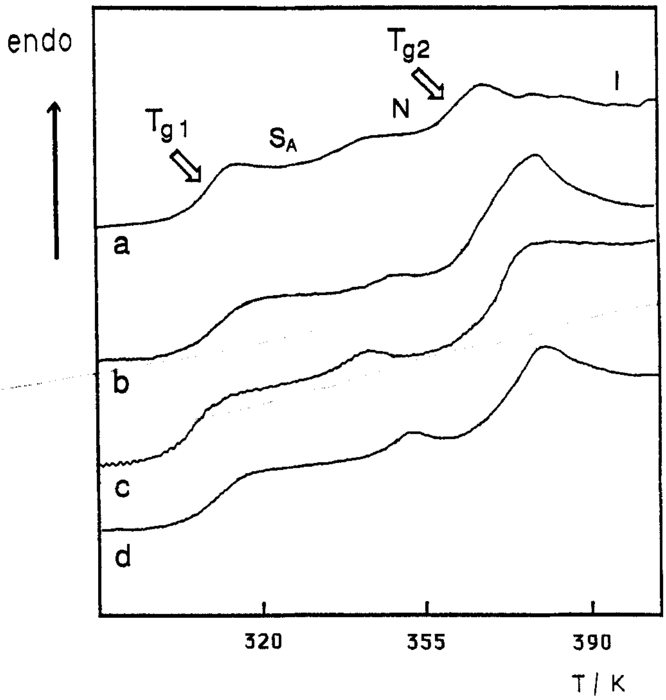


Figure 3. DSC thermogram of polymer blends *I* (*a*), II (*b*), III (*c*) and IV (*d*).

Assignment of the blends I–IV (50% mixtures of the constituents).

	Polystrene **2a**	Sulphonated polystyrene 2b
LC polymer **1a**	Blend I g_1 309 K S_A 343 K N (g_2 363 K) 373 K I	Blend III g_1 306 K S_A 344 K N 372 K I (g_2 374 K)
LC ionomer **1b**	Blend II g_1 310 K S_A 350 K N (g_2 370 K) 379 K I	Blend IV g_1 310 K S_A 352 K N (g_2 376 K) 382 K I

combinations show a coarse phase separation. Figure 4 (*d*) shows a homogeneous texture which looks similar to the texture of the pure polymer **1b**. The results from the DSC measurements and polarizing microscopy lead to the conclusion, that mixing ionomeric LCP **1b** with the amorphous ionomer **2b** induces a microphase separation, the super-structure of which allows a macroscopically uniform alignment of the director.

A further interesting point is the mechanical behaviour of this microphase-separated blend in comparison with a coarse phase-separated blend. In figure 5 the dynamic mechanical behaviour of the pure LCPs is presented. The $\tan\delta$ (ratio of loss modulus G'' and storage modulus G') increases for the neutral polymer **1a** with increasing temperature (flow behaviour) but remains a nearly constant value for the

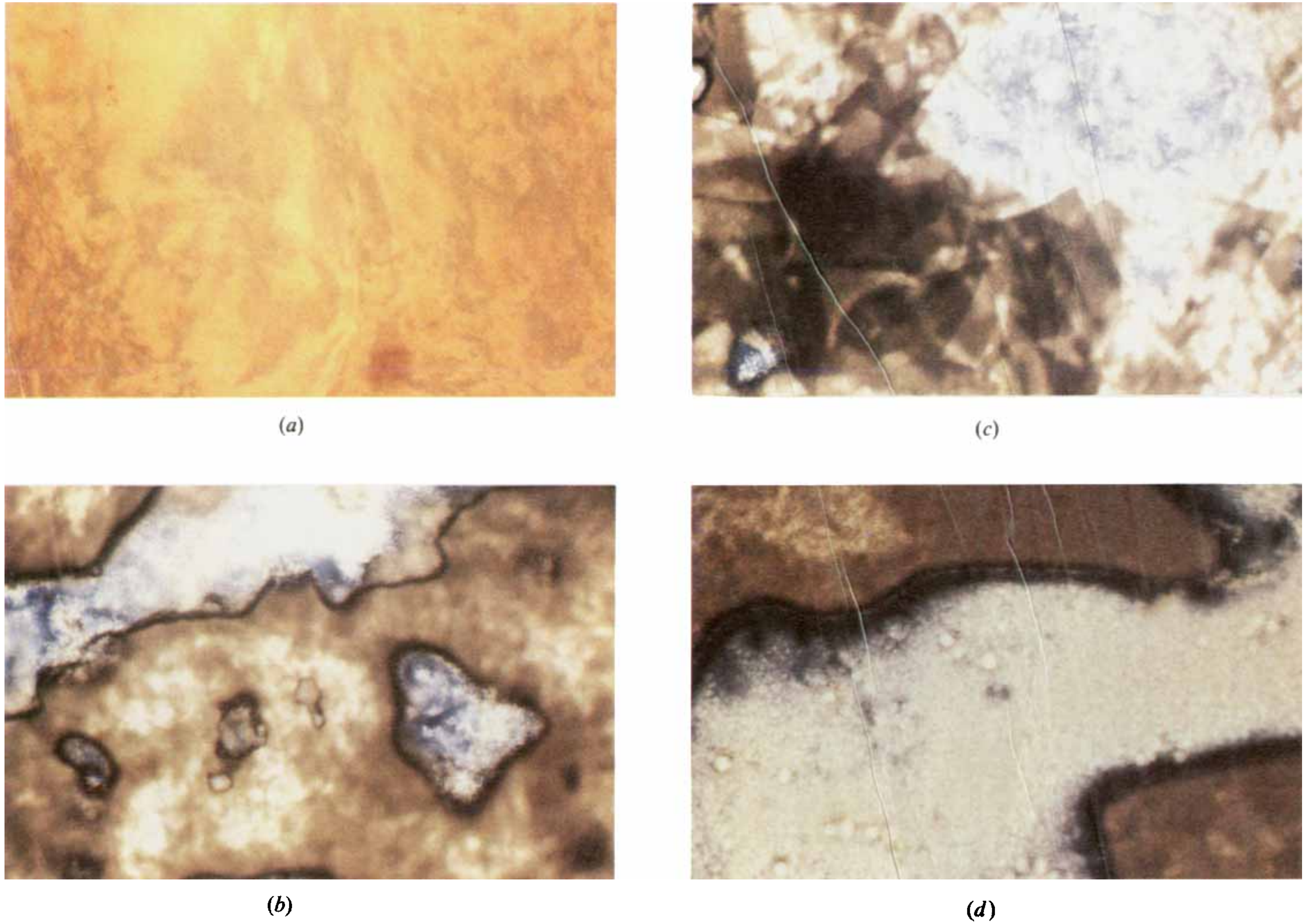

(a)
(c)
(b)
(d)

Figure 4. Optical micrographs obtained by polarizing microscopy, crossed polarizers, temperature: 70°C. (*a*) Blend I, (*b*) blend II, (*c*) blend III, (*d*) blend IV.

oxidized form **1b**. In accordance with previously reported results [4], the LC ionomer **1b** exhibits the elastic behaviour of a slightly cross-linked polymer caused by the formation of ionic aggregates in the liquid crystalline matrix.

In figure 6(*a*) the dynamic mechanical behaviour of blend III (consisting of reduced LCP and partially sulphonated polystyrene) and its pure components is presented. Blend III shows nearly the flow behaviour of the pure reduced LCP **1a**. In this phase-separated blend no ionic interaction (adhesion) occurs between the two phases and the elastic phase (ionomer **2b**) is free to flow in the surrounding LCP matrix above T_{g1}. Blend IV exhibits a very different behaviour (see figure 6(*b*)) consisting of two charged components. The low values of tan δ above T_{g2} demonstrate that both blend IV and sulphonated polystyrene **2b** behave like elastomers. The ionic interactions at the phase boundaries lead in this case to a strong coupling between the mobility of the liquid crystalline phase and the polystyrene containing phase and to nearly identical mechanical properties. As a consequence this blend exhibits the elastomeric behaviour of pure sulphonated polystyrene.

So it is possible to combine the LC properties of LC ionomers and the elastomeric properties of amorphous ionomers in such a way that, depending on the measurement, only one of these properties may be found. For polarizing microscopy this blend resembles the pure LC polymer, for mechanical measurements it resembles the pure amorphous ionomer.

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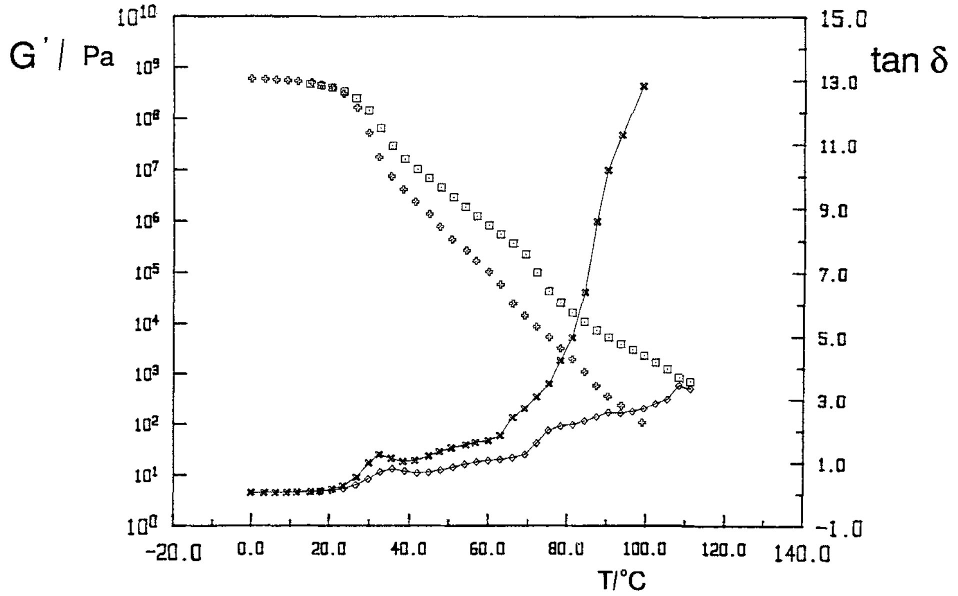
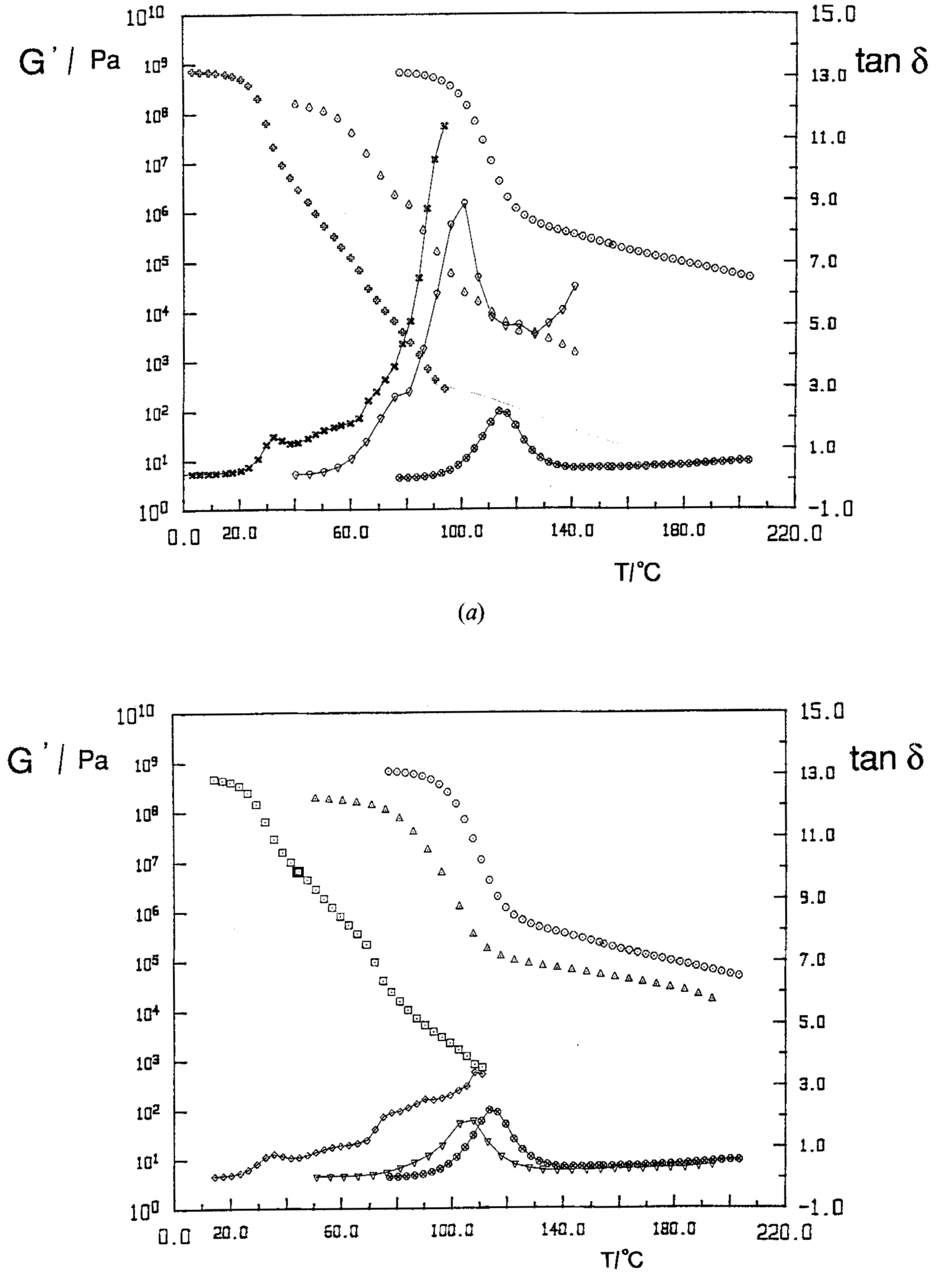


Figure 5. Dynamic mechanical behaviour of polymer **1a** (◈, G', ✱, tan δ) and polymer **1b** (□, G'; ◇, tan δ), temperature dependence of G' and tan $\delta = G''/G'$, G'', loss modulus; G', storage modulus, frequency: 10 rad s^{-1}.



(*a*)

(*b*)

Figure 6. (*a*) Dynamic mechanical behaviour of blend III (◊, *G*′; ▽, tan *δ*) and its components: polymer **1a** (✣, *G*′; ✖, tan *δ*) and polymer **2b** (⊙, *G*′; ⊗, tan *δ*), temperature dependence of *G*′ and tan *δ*, frequency: 10 rad s^{-1}. (*b*) Dynamic mechanical behaviour of blend IV (△, *G*′, ▽, tan *δ*) and its components: polymer **1b** (⊡, *G*′; , tan *δ*) and polymer **2b** (⊙, *G*′; ⊗, tan *δ*), temperature dependence of *G*′ and tan *δ*, frequency: 10 rad s^{-1}.

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