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Thermal and dynamic-mechanical properties of new chiral smectic networks

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Summary

The thermal and dynamic-mechanical behavior of two chiral liquid-crystalline networks are described. Both polymer networks formed a smectic mesophase whose isotropization temperature and enthalpy decreased with increasing crosslinking degree. The dynamic-mechanical behavior was studied in the linear viscoelasticity range. Three main relaxation regions were assigned to the β relaxation, the α network relaxation and the isotropization. Thus, it was possible to monitor the dynamic-mechanical response of the networks in both the anisotropic and isotropic states. Values of the storage and loss dynamic moduli in the range 10^6-10^7 Pa were detected in the isotropic state. Above the α relaxation temperature, either an elasticity or viscosity dominant state was observed depending upon the crosslink density of the network.

Introduction

Liquid-crystalline networks combine high dimensional stability and mechanical orientability typical of polymer networks with the unique anisotropic behavior of liquid crystals[1]. In this respect, great attention is addressed to the preparation of chiral liquid-crystalline networks which can exhibit special properties such as ferroelectricity or piezoelectricity[2,3]. Major contributions in this field are concerned with chiral dopants included in networks with low[4,5] or high[6] crosslink density. However, a few examples of liquid-crystalline networks with the chiral groups placed at the end of the side-chains[7-9] or in the spacer[10] were reported.

The preparation of slightly crosslinked polyacrylate networks can be achieved in one step by the copolymerization of monofunctional and di- or poly-functional monomers,[11-13] or in a two-step procedure involving first the formation of a linear polymer or copolymer containing reactive groups and then a crosslinking reaction.[12,14,15]

In this work, two liquid-crystalline networks **1a** and **1b** with different crosslink density were prepared by the former method starting from mesogenic acrylate (**2**) and diacrylate (**3**) monomers. Both monomers were based on the biphenyl mesogenic group, the former possessing the chiral (*S*)-2-methylbutoxy substituent in the 4'-position of the aromatic moiety. We describe the thermal and unsual dynamic-mechanical behavior of the networks. In particular, it was possible to monitor their viscoelastic behavior well into the isotropic state.

Experimental

Materials. 4-((6-Acryloyloxy)hexyloxy)-4'-((*S*)-2-methylbutoxy)biphenyl (**2**) was prepared

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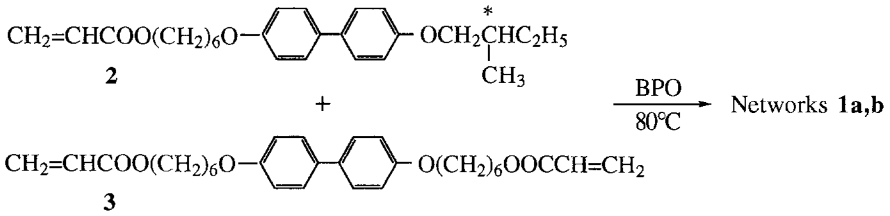
according to the general procedure previously described.[16]

4,4'-Bis((6-acryloyloxy)hexyloxy)biphenyl (**3**) was synthesized by alkylation and acryloylation of 4,4'-biphenol following a literature procedure.[17]

Synthesis of the networks. Networks **1a,b** were prepared by the one step procedure outlined in Scheme 1. Suitable proportions of **2** and **3**, with a total monomer weight of 0.3 g, were finely ground together with 1 wt.% of benzoyl peroxide (BPO) at room temperature and this mixture was introduced into a rectangular mould. The entire assembly was placed between press plates with a nominal pressure of 5 tonn·cm^{-2} and let to stand at room temperature for 20 min. The temperature was then raised to 80°C, the pressure released to 0.5 tonn·cm^{-2} and the polymerization reaction let to proceed for 48 h. At the end of the reaction, the networks were recovered as rectangular 18x5x1 mm sheets suitable for the DMA measurements. The content of the diacrylate monomer **3** was 4 mole % in **1a** and 14 mole % in **1b**.

Scheme 1. Synthetic procedure for the preparation of networks **1a,b**.



Physicochemical characterization. IR analysis was performed with a Perkin-Elmer 1600-FTIR spectrophotometer. The thermal and liquid-crystalline properties of the polymers were studied by DSC (Perkin Elmer DSC-7, at a scanning rate of 10 K·min^{-1}) and polarized light microscopy (Reichert Polyvar microscope equipped with a programmable Mettler FP52 stage at a scanning rate of 10 K·min^{-1}). Dynamic-mechanical measurements were performed with a dynamic-mechanical analyzer (Perkin Elmer DMA-7, at a scanning rate of 4 K·min^{-1}) at 1 Hz frequency using the three-point bending geometry.

Results and discussion

Networks **1a,b** were synthesized by a one-step procedure (Scheme 1) which involves the free-radical copolymerization of 4-((6-acryloyloxy)hexyloxy)-4'-((*S*)-2-methylbutoxy)-biphenyl (**2**) and 4,4'-bis((6-acryloyloxy)hexyloxy)biphenyl (**3**), at 80°C in bulk using PBO as the free-radical initiator. In both cases, a relatively low concentration (4 and 14 mole %) of the diacrylate monomer **3** was employed. The networks **1a,b** were opaque, macroscopically homogeneous and therefore suitable for dynamic-mechanical tests. When observed at the polarizing microscope, they were birefringent in the whole temperature range (25-150°C), although their birefringence was definitely more intense at temperatures lower than the isotropization. Above this temperature, a slight birefringence was still seen probably due to residual stress induced by the crosslinks. No characteristic textures could, however, be detected by microscopy.

The transition temperatures and relevant phase transition parameters (Tab.1) were taken from the DSC heating traces of samples that had been annealed by cooling at 10 K·min^{-1} from the isotropic melt.

Table 1. Thermal properties[a] of networks **1a,b**.

Network	**3** content (mole %)	T_g (K)	T_i (K)	ΔH_i ($J \cdot g^{-1}$)
1a	4	373	413	7.5
1b	14	374	406	5.2

[a]By DSC, at 10 $K \cdot min^{-1}$ heating rate.

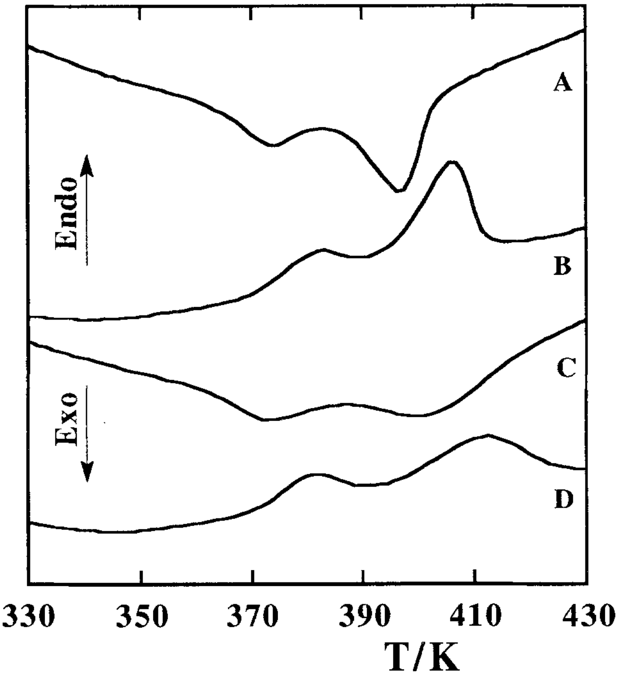


Figure 1. DSC first cooling and second heating curves of networks **1b** (A, B) and **1a** (C, D).

The DSC heating curves for **1a** and **1b** are reported in Fig.1. Both samples showed a stepwise increase in specific heat at about 370 K, due to the glass transition and an endothermic peak centered at 413 K for **1a** and at 406 K **1b** associated to the smectic A-isotropic transition analogous to the liquid-crystalline behavior of the homopolymer of monomer **2**. An intermediate transition was seen at about 380 K for both networks. While X-ray measurements suggest the formation of an additional partially ordered phase, this did not fully develop due to the close proximity to the glass transition. On cooling, the transitions were reversible with a supercooling of a few degrees. For both networks the isotropization transition extended over a rather broad range of temperatures (≈ 30 K). However, the isotropization temperature and enthalpy (T_i, ΔH_i) of **1a** were greater than the ones of **1b**. These findings suggest that the increase in the crosslink density in going from **1a** to **1b** caused a decrease of the overall degree of order and stability of the mesophase, in agreement with other observations on the phase transition behavior of different liquid-crystalline networks.[18]

The dynamic-mechanical behavior of networks **1a,b** was studied in the linear viscoelasticity range at 1 Hz frequency. The transition temperatures of the dynamic-mechanical processes, estimated as corresponding to the maxima of the relevant loss tangent (tan δ) peaks, are collected in Tab.2. Figs.2 and 3 illustrate the trends of tan δ as well as of the storage (G') and loss (G'') components of the dynamic modulus as functions of temperature for **1a** and **1b**, respectively. In both samples, G' decreased with increasing temperature with definite drops corresponding to the main relaxation regions. In particular, a slightly pronounced decrease of G' at about 200 K, due to the β relaxation, preceded a significant drop of two orders of magnitude at about 360 K associated to the α network relaxation. The magnitude of this drop was greater for **1a** which has a lower crosslinking degree. With further increasing temperature in the 390-450 K region, a complex viscoelastic behavior was observed involving a modulus decrease then an increase up to a plateau value which was at $G' = 1.2\ 10^6$ and $1.0\ 10^7$ Pa for **1a** and **1b**, respectively. This latter relaxation was due to the isotropization relaxation and closely corresponded to the same transition as evidenced by DSC and optical microscopy. The minimum in the modulus around the smectic-isotropic transition may result from two conflicting tendencies, i.e., an usual modulus decrease with increasing temperature and a rather unusual modulus increase due to the increase in the internal friction among adjacent polymer segments, or to the increase in the constraints on the mesogens at the transition from a locally organized to a locally random chain arrangement.

The plateau values of the isotropic modulus are one to two orders of magnitude greater than those reported for other acrylate networks[12].

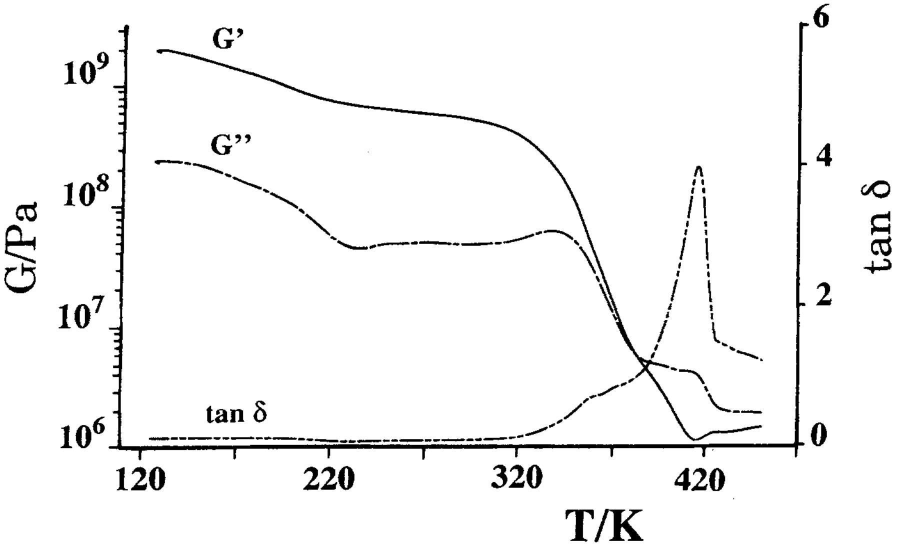


Figure 2. Plots of the dynamic storage modulus (G'), dynamic loss modulus (G''), and loss tangent (tan δ) versus temperature for network **1a** at 1 Hz.

Table 2. Temperature of maximum loss[a)] (tan δ) for the α, β, and isotropization relaxations of networks **1a,b**.

Network	T_β (K)	T_α (K)	T_i (K)
1a	198	363	411
1b	203	363	403

[a)] By DMA, at 1 Hz and 4 K·min^{-1} scanning rate.

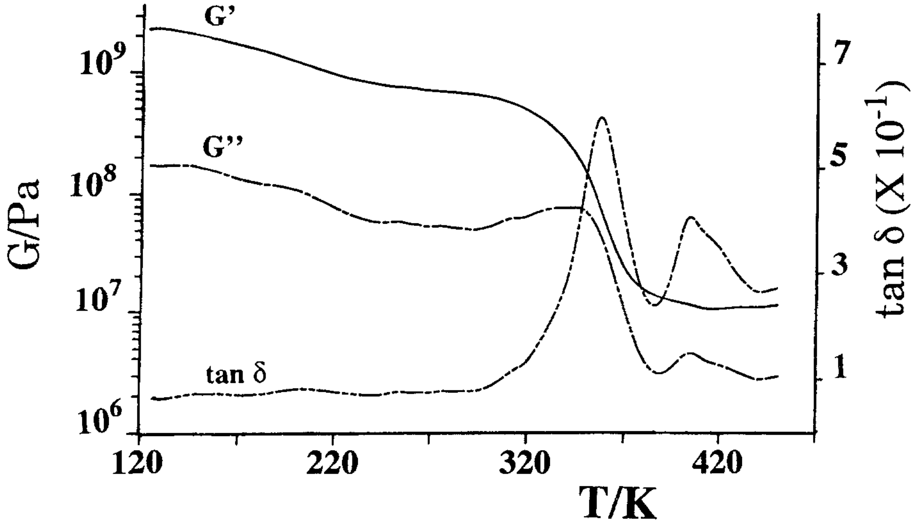


Figure 3. Plots of the dynamic storage modulus (G'), dynamic loss modulus (G''), and loss tangent (tan δ) versus temperature for network **1b** at 1 Hz.

This suggests the formation of a well developed continuous network structure. At temperatures corresponding to the β, α and isotropization relaxation regions definite maxima were observed in the G'' and tan δ curves for both samples.

The tan δ curve relevant to network **1a** at temperatures above 320 K presented two strongly overlapping peaks, corresponding to the α network relaxation and isotropization relaxation, whereas two well resolved peaks were seen for **1b** in correspondence to the same processes. The tan δ peak associated to the α network relaxation of **1a** was less intense than the one relevant to the isotropization process, whereas the opposite occurred for **1b**, thus indicating a more liquid-like nature of the former sample consistent with its lower crosslinking degree. It is interesting to note that for the more crosslinked **1b**, the value of G' was higher than that of G'' in the whole temperature range, in analogy to what had been reported for other liquid-crystalline polymer networks[19]. In contrast, for the less crosslinked **1a** a cross-over point with the inversion of the trends of *G'* and *G"* was observed around 360 K. Therefore, a change from an elasticity dominant state (*G'* > *G"*) to a viscosity dominant state (*G"* > *G'*) occurs at this temperature.

Conclusions

Liquid-crystalline chiral networks **1a,b** present a smectic mesophase, whose stability and order decrease with increasing crosslink density. Their complex and peculiar dynamic-mechanical behavior involves three main relaxations, namely the β, the α network, and the isotropization relaxations. Thus, it was possible to monitor the dynamic-mechanical responses of the networks in both the anisotropic and isotropic states. The β process, which probably reflects the relaxation modes of the mesogenic units, seems to be quite insensitive to the crosslink density according to its local scale nature. In contrast, the magnitude of the α network relaxation is evidently influenced by crosslinking, in agreement with its long range cooperative character. The smectic-isotropic transition is also mechanically active and results in the appearance of a complex relaxation process in which the dynamic storage modulus goes through a minimum value at temperatures within the smectic-isotropic transition region and then rises again. This rather anomalous viscoelastic behavior may reflect the difference in constraints on the mesogens or the chain segments in the isotropic and smectic phases, and is being presently investigated in more detail.

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