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Liquid-crystalline copolysiloxane system including side-on and side-end fixed mesogenic groups

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The work described here concerns new side-chain liquid-crystalline copolymers with different proportions of mesogenic groups attached laterally (side-on fixed) and terminally (side-end fixed) to a polysiloxane backbone. The mesomorphic properties, as well as structural and diamagnetic investigations, were studied as a function of the terminal–lateral ratio for each copolymer. In particular we show that equivalent proportions of both fixation types reduce significantly the orientational order of the nematic phase.

1. Introduction

Side-on fixed liquid-crystalline polymers, in which the mesogenic groups are laterally branched to the backbone, can exhibit certain specific characteristics which strongly differentiate them from the conventional side-end fixed liquid-crystalline polymers. In particular, whatever the backbone, the lateral attachment of the rod-like mesogenic groups favours the nematic state [1–4]. In contrast, the side-end fixed liquid-crystalline polymers are predominantly smectogenic [5]. In the side-on fixed polymethacrylates a biaxial character of the nematic phase has been claimed [6–8]. Moreover, for some side-on fixed polysiloxanes an anomaly of the diamagnetic anisotropy in the nematic domain has been found [2, 9]. These two previous features are also specific to this new class of liquid-crystalline side chain polymers. Finally, small angle neutron scattering studies underline the fundamental difference in the temperature dependence of the anisotropy of the chain conformation in side-on [10] and side-end [11–14] fixed liquid-crystalline polymers.

This stimulating situation made us undertake the study of a copolymer system including side-end and side-on attached mesogenic groups. Indeed, since blends generally appear immiscible, the only possible way to combine the physical properties of the two homopolymers is to use the two kinds of mesogenic groups via the preparation of copolymers [15, 16]. This method has been applied productively by Gray *et al.* in a lateral-terminal side-chain copolymer system [17]. The goal of the present work is to investigate a new copolysiloxane system in which the two homopolymers have been extensively studied and exhibit fundamental differences in their mesomorphic behaviour.

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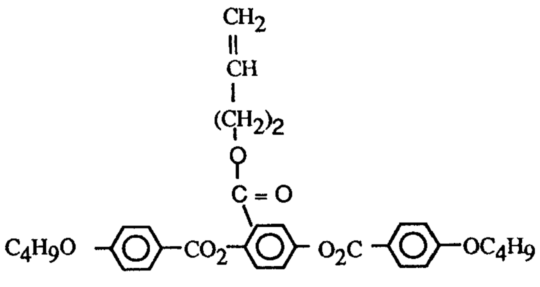
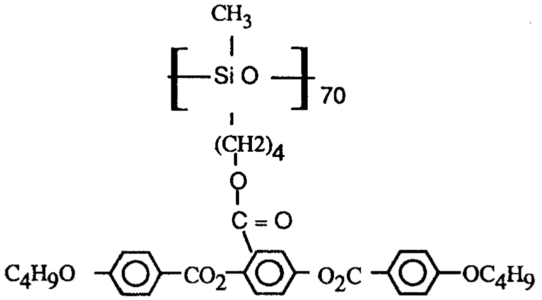
2. Materials

The side-on moiety **1** (C 100°C N 113°C I)

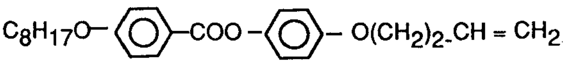


gives the homopolymer

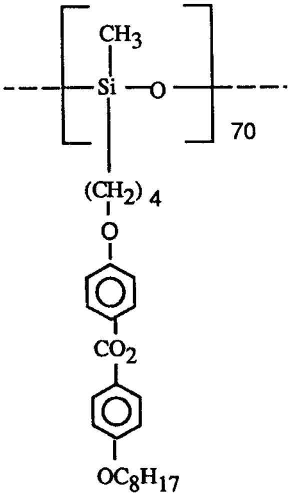


$P_{4,4,4}$ for short, which is nematic above the glassy state (g 36°C N 130°C I). Thermodynamic and magnetic properties [2, 9], X-ray analysis [9] and a SANS study [10] have been performed on this homopolysiloxane.

The side-end moiety **2** (C 56°C S_A 58°C N 72°C I)

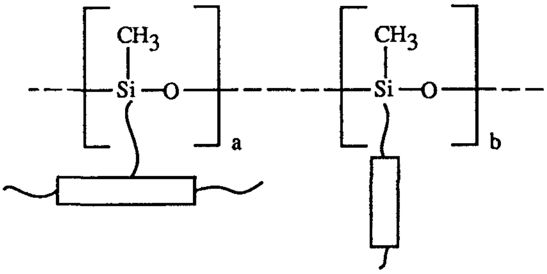


gives the homopolymer



$P_{4,8}$ for short, in which a smectic A–smectic B sequence is observed [5, 15]. This homopolysiloxane (or a very comparable one) has already been analysed by X-ray diffraction [18] and SANS experiments [19].

The copolymers were prepared by hydrosilylation of the alkenes **1** and **2** with an excess of the mixed alkenes



with $a+b=70$. The total substitution of the mesogenic moieties on the polymethylhydrogenosiloxane backbone was controlled by ^{1}H NMR.

Since the rate of reaction can differ for the terminal mesogen and for the lateral one, the effective proportion of the two mesogenic groups in the copolymer has to be determined. To this end, we use an original method: the phase diagram of alkene **1** and alkene **2** was first determined by accurate microscopic observations of some binary mixtures (see figure 1). After the hydrosilylation, the excess alkenes were separated from the copolymer by GPC. The measurement of the nematic–isotropic transition temperature for this mixture allows us to determine, via the phase diagram, the proportion of each alkene in the final excess. It is then easy to calculate, with good precision, the real proportion of each mesogen in the copolymer. In the following the weight fraction of the side-end fixed mesogen is called $x_{4,8}$. This fraction is systematically greater than the initial proportion: in other words, the fixation via an hydrosilylation reaction is easier for a side-end mesogen than for a side-on one.

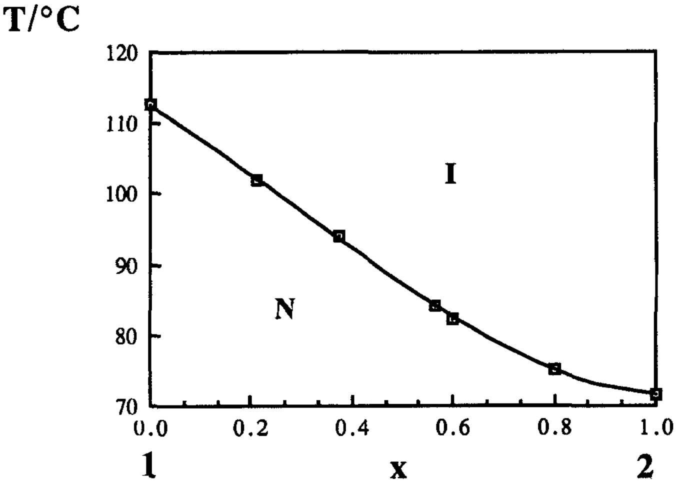


Figure 1. The binary phase diagram of alkene **1** and alkene **2**.

The phase behaviour of the various homo- and copolymers.

*x*4,8/%	*T*g/°C	*T*m/°C	S_B		S_A		N		I	ΔH_{NI}/J g^{-1}	ΔH_{S_AI}/J g^{-1}	$\Delta H_{S_BS_A}$/J g^{-1}
0	36						●	120	●	2·1		
12	33						●	115	●	2·1		
34·3	24						●	105	●	2·0		
48·9	17						●	91	●	1·5		
49·5	14						●	92	●	1·8		
59·6	10						●	99	●	2·0		
65·3	11				●	85	●	106	●	2·6		
75·3	10				●	106	●	110	●	3·0		
86·7	10		●	44	●	115	●	119	●		4·7	0·1
93·9	10	30	●	43	●			124	●		6·0	1·4
100		62	●	56	●			133	●		6·5	4·4

3. Results

3.1. Thermodynamic properties

The mesomorphic properties of the different copolymers were characterized by the usual methods: optical microscopy, differential scanning calorimetry and X-ray diffraction on powder samples. The transition temperatures and the enthalpies of transition are listed in the table. The temperatures were determined by optical microscopy with decreasing temperature ($1°C\,min^{-1}$) and they correspond to the appearance of the phase; the biphasic domain (isotropic–mesophase) is about 5°C in width. The following comments may be made on these results.

(i) The nematic state exists up to 86·7 per cent of side-end mesogenic groups. On the other hand, the smectic phases (S_A and S_B) relative to the homopolymer $P_{4,8}$ are strongly destabilized in the copolymer systems (see figure 2).

(ii) In the same way, the copolymers remain purely amorphous for $x_{4,8}=0$–86·7 per cent and the glass transition temperature decreases as $x_{4,8}$ increases.

(iii) Moreover a minimum of the clearing temperatures (T_{NI} or T_{S_AI}) as well as a minimum of the corresponding enthalpies (see the table) are clearly shown for $x_{4,8}=50$ per cent. Thus an equal proportion of side-end and side-on mesogens depresses the mesogenic potential.

3. Structural properties

We report in figure 3(*a*) the thermal evolution of the layer spacing, *d*, for the homopolymer $P_{4,8}$: in the S_A range *d* increases slightly as the temperature decreases and a clear jump is observed at the temperature which leads to the ordered smectic B phase. As shown in the table, the smectic A phase is preserved in the copolymers corresponding to the interval $x_{4,8}=65·3$–100 per cent. How is the layer spacing, *d*, influenced by the introduction of small amounts of side-on mesogens with the

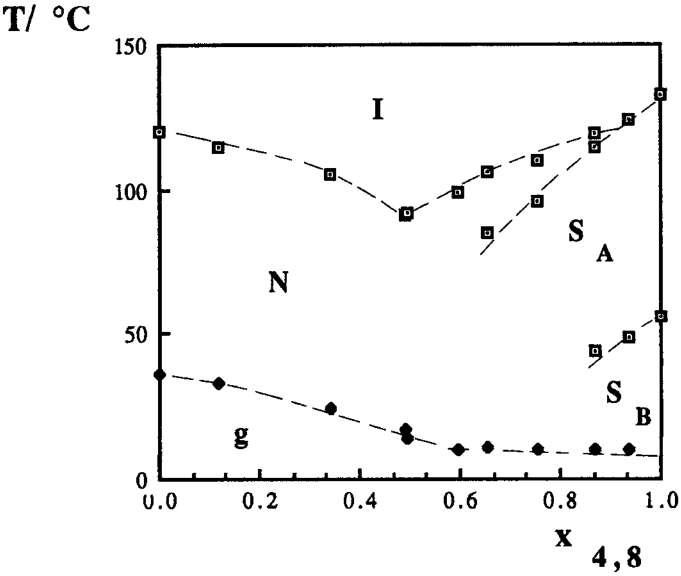


Figure 2. Thermal properties of the copolymers versus the proportion of side-end fixed mesogenic groups. The dotted lines serve as a guide for the eye.

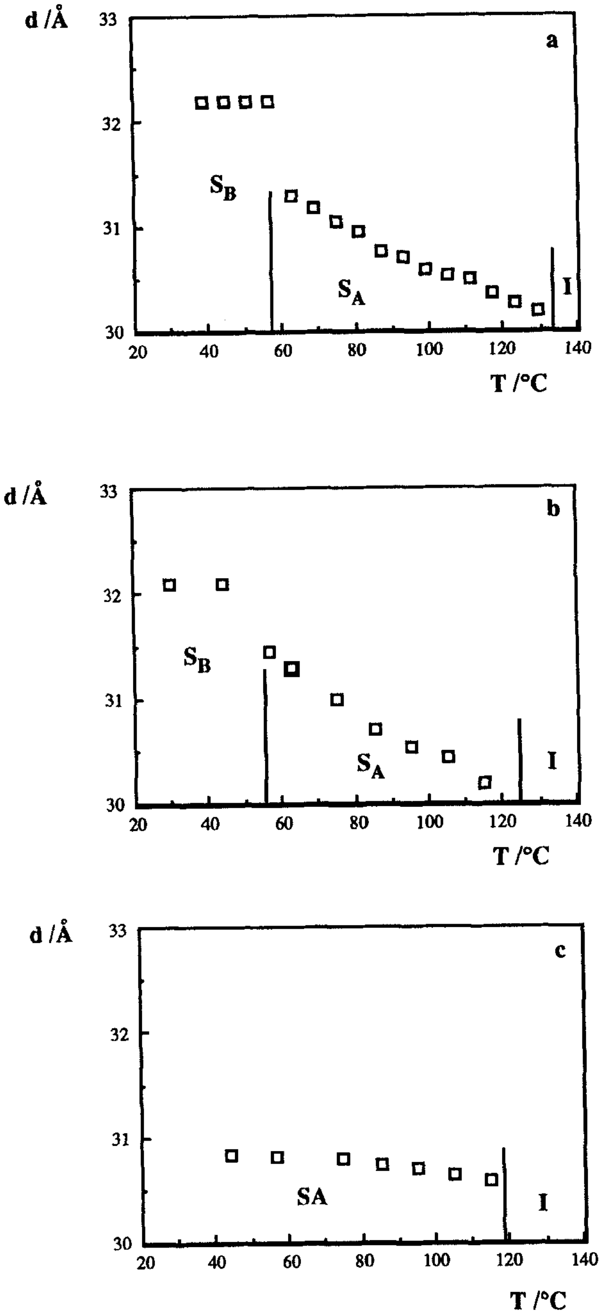
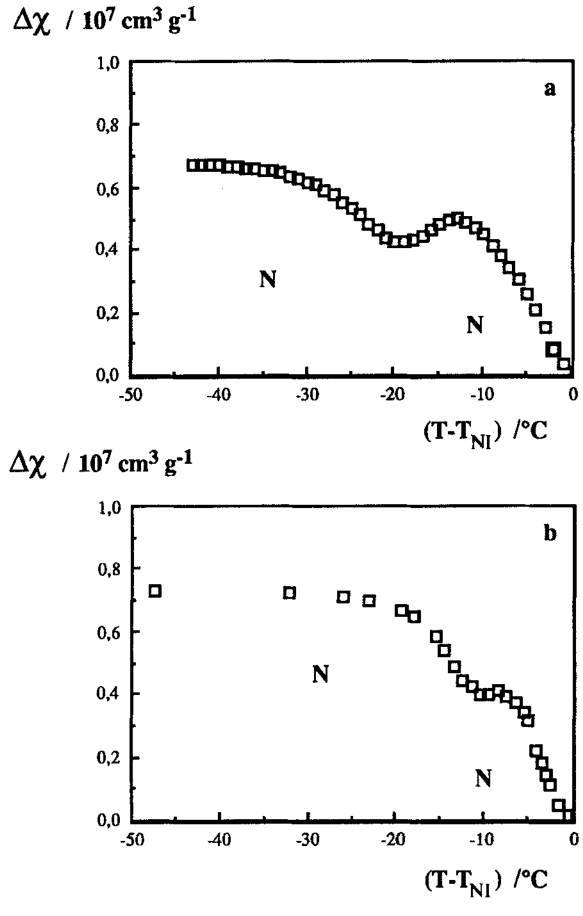


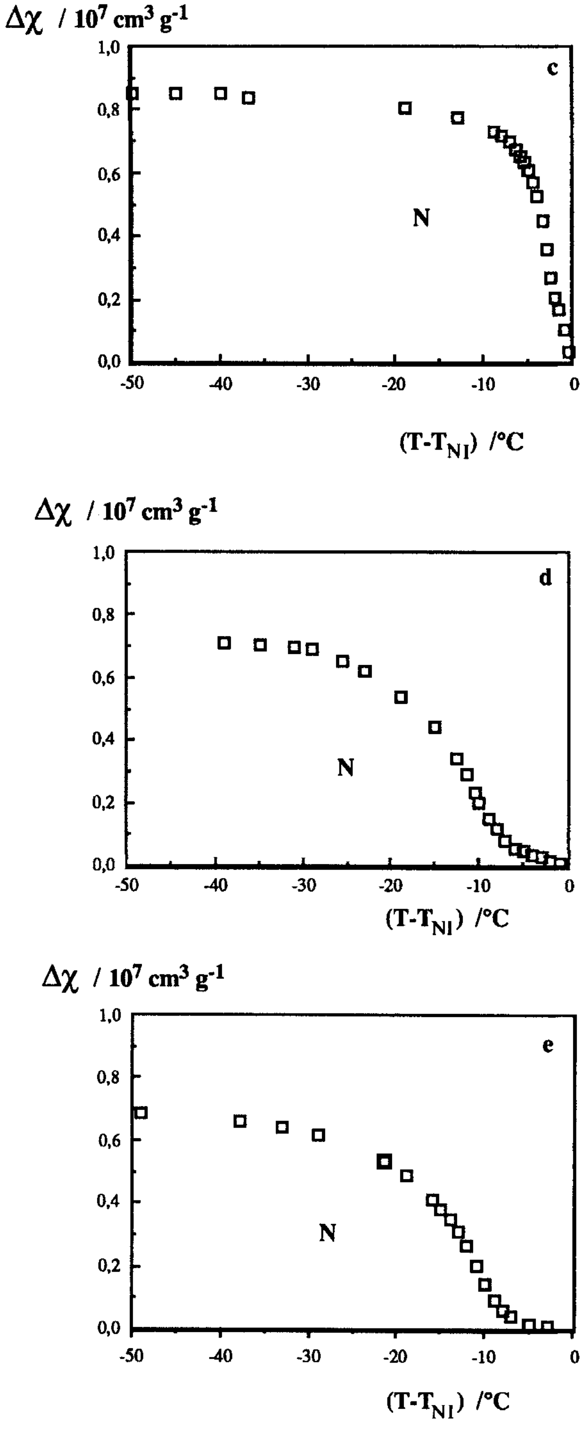
Figure 3. The temperature dependence of the layer spacing d in the S_A and S_B phases: (*a*) for the homopolymer $x_{4,8} = 100$ per cent and for the copolymers (*b*) $x_{4,8} = 93{\cdot}9$ per cent and (*c*) $x_{4,8} = 86{\cdot}7$ per cent.

predominantly side-end groups? Figure 3(*b*) ($x_{4,8}=93\cdot9$ per cent) and figure 3(*c*) ($x_{4,8}=86\cdot7$ per cent) reveal that the values of the *d* parameter in S_A or S_B phases are weakly affected by the presence of the laterally attached mesogens even if the slope of $d(T)$ varies with the proportions.

3.3. *Magnetic properties*

An anomaly has been detected in the thermal variation of the diamagnetic anisotropy, $\Delta\chi$, in the nematic range of the side-on fixed polymer $P_{4,4,4}$ [2], whereas under the same conditions, the temperature dependence of $\Delta\chi$ is regular for a side-end homopolymer [20]. We have found that this nematic–nematic anomaly is very sensitive to the molecular architecture; in particular a decrease of the amount of mesogenic groups laterally attached to the backbone leads to the disappearance of the anomaly [9]. Our aim is now to understand the influence of $\Delta\chi$ on the composition of the copolymers; the results are reported on figure 4. The anomaly revealed for the homopolymer $P_{4,4,4}$ (see figure 4(*a*)) exists up to the copolymer with 34·3 per cent of side-end mesogens (see figures 4(*b*) and (*c*)). For higher amounts of side-end ($x_{4,8}=65\cdot3$ or 75·3 per cent), we can observe a classical dependence on $\Delta\chi$ (see figures 4(*f*) and 4(*g*). Nevertheless, we can note the unusual behaviour of the copolymers bearing




Δχ / 10⁷ cm³ g⁻¹
1,0
0,8
0,6
0,4
0,2
0,0
-50
-40
-30
-20
-10
0
c
N
(T-T_NI) /°C
Δχ / 10⁷ cm³ g⁻¹
1,0
0,8
0,6
0,4
0,2
0,0
-50
-40
-30
-20
-10
0
d
N
(T-T_NI) /°C
Δχ / 10⁷ cm³ g⁻¹
1,0
0,8
0,6
0,4
0,2
0,0
-50
-40
-30
-20
-10
0
e
N
(T-T_NI) /°C

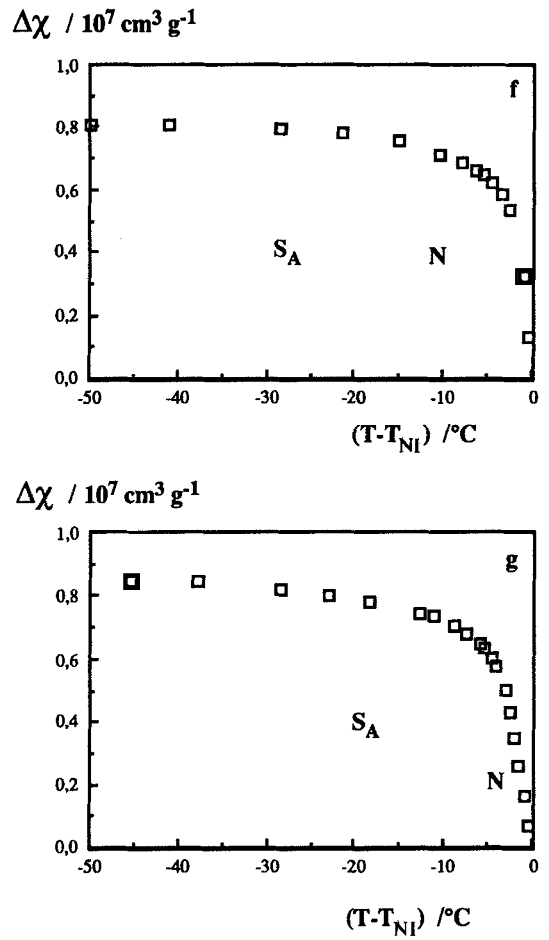


Figure 4. The temperature dependence of the diamagnetic anisotropy $\Delta\chi$: (*a*) for the homopolymer $P_{4,4,4}$ and for the copolymers (*b*) $x_{4,8} = 12$ per cent, (*c*) $x_{4,8} = 34{\cdot}3$ per cent (*d*) $x_{4,8} = 49{\cdot}5$ per cent, (*e*) $x_{4,8} = 59{\cdot}6$ per cent (*f*) $x_{4,8} = 65{\cdot}3$ per cent and (*g*) $x_{4,8} = 75{\cdot}3$ per cent.

approximately the same proportions of side-end and side-on mesogens ($x_{4,8} = 49{\cdot}5$ per cent and 59·6 per cent respectively). Indeed in figures 4(*d*) and (*e*) we note that the curvature of $\Delta\chi(T)$ is positive near the N–I transition. Compared with the dependence for the copolymers $x_{4,8} = 34{\cdot}3$ per cent and $x_{4,8} = 65{\cdot}3$ per cent this result together with weaker saturated values of $\Delta\chi$ appears to be the signature of a less ordered nematic medium.

This peculiar behaviour can originate from modifications of the global conformation of the polysiloxane backbone in the nematic phase with respect to the composition of the copolymers. We know that a backbone bearing side-end fixed mesogen exhibits an oblate shape imposed by the smectic fluctuations [11–14] while a backbone with side-on fixed mesogens possesses a prolate shape [10]. Probably the copolymers with equivalent proportions of side-end and side-on mesogens represent an intermediate case in which the shape of the chain nearly keeps a random-coil configuration. At this stage, the antagonism of the two kinds of attachment to the coupling backbone conformation–mesogens orientation makes the nematic ordering weaker as revealed by the thermodynamic data as well as by the $\Delta\chi$ measurements.

4. Conclusions

Finally, in this copolysiloxane system, we can distinguish roughly three regimes with respect to the composition of side-on and side-end fixed groups.

(i) A side-on nematic regime: starting from the homopolymer $P_{4,4,4}$, the addition of side-end fixed mesogens probably restricts the chain extension in the nematic phase of the copolymer even if the N–I transition temperature and enthalpy change are weakly reduced. Consequently the $\Delta\chi$ anomaly which is directly connected to this phenomenon tends to disappear.

(ii) A side-end smectic regime: at the opposite end, starting from the homopolymer $P_{4,8}$, the addition of side-on fixed mesogens tends to destabilize the smectic phases. Despite the fact that the side-end fixed mesogens are smaller, the layer spacing in the S_A phase is not composition dependent. Thus, the side-on fixed mesogens do not participate at all in the smectic arrangement and, in consequence, the clearing point and the S_A–I transition enthalpy are strongly reduced.

(iii) An intermediate nematic regime: due to equivalent proportions of both attachment types, the orientational correlations between mesogenic groups are the most affected at short range order. In other words, the percentages of mesogenic groups which give nematic ordering is hence a minimum but can also be quantitatively and qualitatively modified versus temperature. In addition to chain extension, it is shown here that this is another way to create a non-classical temperature dependence of $\Delta\chi$ on the nematic phase of liquid crystal polymers.

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