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Dynamic mechanical properties of cyclohexane-based glass-forming liquid crystals and a linear side chain polymer analogue

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A nematic and a cholesteric liquid crystal, both derived from *trans*-1,3,5-cyclohexanetricarboxylic acid, and a linear side chain polymer analogue were characterized in terms of storage (G') and loss (G'') moduli as functions of frequency and temperature. It was found that all three model compounds show a shear shinning flow behaviour with zero shear viscosities of the low molar mass systems significantly less than that of the polymer system at the same reduced temperature, T/T_g. With shift factors prescribed by the WLF equation, both the G' and G'' data of all three compounds are adequately represented by master curves. Furthermore, within the framework of the stretched exponential model, the relaxation behaviours of the low molar mass systems are well described by a single Maxwell element, whereas the polymer system shows a relatively broad distribution of relaxation times. The observed viscoelastic properties suggest a relative ease of material processing of the low molar mass systems compared to the polymer analogue due to a lower zero shear viscosity and a single relaxation time characterizing the dynamics of response to a mechanical or thermal stimulus.

1. Introduction

Low molar mass glass-forming liquid crystals with a glass transition temperature, T_g, above ambient have emerged as a class of advanced organic materials potentially applicable to a diversity of linear and non-linear optical technologies [1–7]. Intensive recent research [8–16] has produced numerous material systems with a varying degree of morphological stability as assessed by the tendency of the quenched glass to crystallize upon heating beyond its T_g. Nonetheless, fundamental understanding of vitrification in low molar mass organics in general is still lacking at present; it remains challenging to design molecular systems representing a subtle balance between encouraging liquid crystalline mesomorphism and discouraging solid crystallinity. At the same time, the ability to design functional materials is critical to the development of advanced optical technologies. In a recent series of publications [17–19], we have reported a number of glass-forming liquid crystals based on a novel molecular design approach in which mesogenic groups are attached to alicyclics as a way to depress crystallization. In addition, morphological stability and its dependence on stereochemistry [20] have been quantitatively evaluated through the measurement of spherulite growth rate as a function of temperature. An ultimate objective is to establish a sound basis for designing morphologically stable, glass-forming functional materials including liquid crystals.

Understanding of the flow behaviour of liquid crystalline polymers (LCPs) and their dynamic response to an external stimulus, either mechanical or thermal, is crucial to the development of effective processing methodologies. A typical optical device fabrication process may involve mechanical shearing of a melt above T_g to maximize mesogenic ordering followed by quenching to below T_g to ensure long-term stability of the ordered structure. The use of side chain LCPs has been reported for potential optical applications. However, their high

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molecular weight results in a high viscosity which can cause difficulty during the shear processing of the material into thin films. In addition, a broad distribution of relaxation times associated with polymers in general can lead to nonuniform alignment across the device area. To circumvent these problems, it would be desirable to use a material that exhibits low viscosity yet retains the glass-forming ability and that possesses a single relaxation time to ensure uniformity when subjected to thermal annealing. From a fundamental standpoint, there has been a continuing interest in the rheology of ordered liquids because of the potential effect of liquid crystalline order on relaxation dynamics [21].

Here we report the results of a rheological investigation where we have examined the potential for using low molar mass cyclic LCPs as an alternative to high molecular weight linear side chain LCPs for optical applications. In our approach we employed dynamic mechanical methods to determine the relaxation behaviour of cyclohexane-based liquid crystals above T_g and compared their rheological behaviour to a linear polymeric analogue. Rheological parameters such as the storage (G') and loss (G'') moduli, complex viscosity (η^*), zero shear viscosity (η_0), and distribution of relaxation times will be presented for evaluating relative ease of material processing.

2. Experimental

2.1. *Materials and characterization*

The chemical structures of two low molar mass liquid crystals, (**I**) and (**II**), and one nematic liquid crystal polymer, (**III**), are as depicted in figure 1. The synthesis and characterization of these three model compounds have been reported in a recent series of papers [17, 18, 22]. Glass and thermotropic transition temperatures were determined with differential scanning calorimetry and hot-stage polarized optical microscopy. In addition, the molecular weight distribution of (**III**) was determined with gel permeation chromatography with reference to polystyrene standards, from which the weight-average molecular weight, $\overline{M_w}$, and the polydispersity index, $\overline{M_w}/\overline{M_n}$, were calculated. All these characterization data are also included in figure 1.

2.2. *Rheological measurements*

Dynamic shear moduli, G' and G'', of (**I**) were measured on a Rheometrics Dynamic Spectrometer RDSII and (**II**) and (**III**) were measured on a Rheometrics Dynamic Spectrometer RDS 7700 upgraded with operating software and transducer from AIC Inc. Parallel plates with a diameter of 25 mm were used for all samples. The temperature was controlled by heated nitrogen which was circulated within the environmental chamber. The sample gaps used for measurements ranged from 0·4 to 0·8 mm.

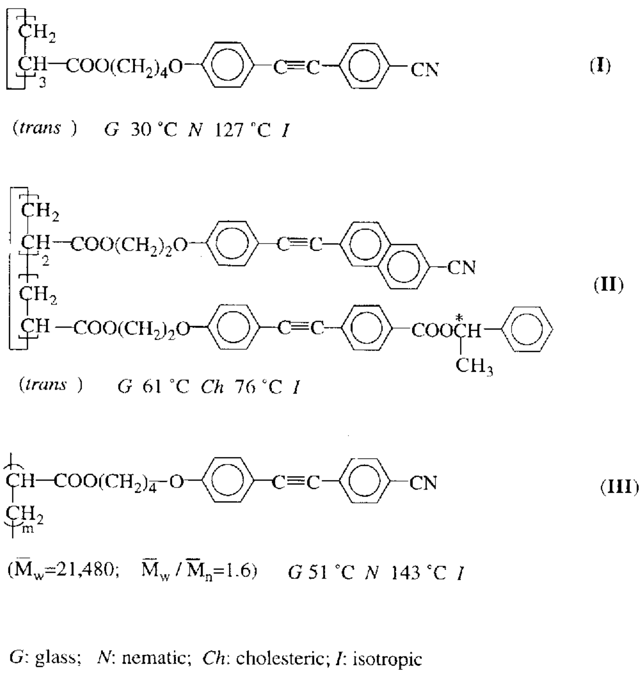

Figure 1. Chemical structures and thermotropic properties of compounds (**I**), (**II**), and (**III**).

Press-molded samples were placed on the bottom plate and then softened by heating them to at least 30°C above T_g. Once the material was softened, the top plate was brought down and the material was squeezed between the plates until the gap was completely filled. Samples were then annealed at a temperature a few degrees above the clearing temperature for 15 min. The temperature was then lowered to the initial measuring temperature at a cooling rate of approximately 3°C min^{-1}. Once the desired temperature was reached, a rate sweep was performed from 1–100 rad s^{-1}. After completing one measurement, the temperature was decreased to the next temperature and another rate sweep was performed. At cooler temperatures, the frequency window was increased to 0·01–100 rad s^{-1} in order to capture the long-time low frequency behaviour. Strain levels of $0{\cdot}10 < \gamma < 0{\cdot}20$ were used at higher temperatures in order to generate sufficient torque on the transducer. As the temperature was lowered, strains of $\gamma < 0{\cdot}05$ were employed. All strain levels used were found to be in the linear viscoelastic region. All data were analysed by standard IRIS software.

3. Results and discussion

For the sinusoidally imposed shear strain, the complex modulus is given as (see p. 12 in [23])

$$G^* = G' + iG'' \tag{1}$$

where G' and G'' are the storage and loss modulus, respectively. Note that G' is a measure of the energy stored per cycle of deformation and represents the portion of the stress that is in phase with the strain and that G'' is a measure of the energy dissipated per cycle of deformation and represents the portion of the stress that is 90° out of phase with the strain. An example of G' and G'' as a function of frequency, ω, for compound (**I**) is presented in figure 2.

The magnitude of the complex viscosity is given in terms of the dynamic moduli as (see p. 44 in [23])

$$|\eta^*| = \frac{(G'^2 + G''^2)^{1/2}}{\omega} = \frac{|G^*|}{\omega} \qquad (2)$$

which is shown at varying temperatures for compounds (**I**), (**II**), and (**III**) in figure 3. In light of the analogy between $|\eta^*|$ as a function of ω obtained from dynamic measurement and η, shear viscosity, as a function of $\dot{\gamma}$, shear rate, from steady-state measurement [24], all three compounds exhibit a shear shinning flow behaviour. The values of the zero shear viscosity, η_0, can be evaluated from the low frequency response (see p. 43 in [23])

$$\eta_0 = \lim_{\omega \to 0} \frac{G''(\omega)}{\omega} \qquad (3)$$

as shown in figure 4 for all three compounds. It was found that the values of η_0 of (**I**) and (**II**) are an order of magnitude less than that of (**III**) at the reduced temperature of $T_g/T = 0{\cdot}94$. We propose that the lower shear viscosity is a manifestation of the small size of the core backbone in the case of the cyclics compared to the linear analogue. Hence, low molar mass glass-forming liquid crystals are expected to be more readily processable into highly ordered films than the side chain polymer analogue in view of the lesser viscous resistance that molecules have to overcome in the process of molecular alignment.

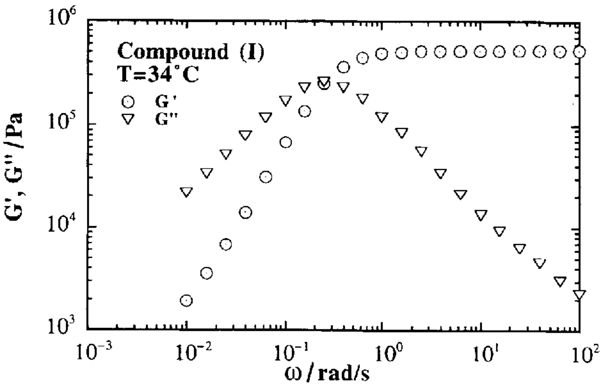

Figure 2. G' and G'' as functions of radian frequency ω illustrated with compound (**I**) at 34°C.

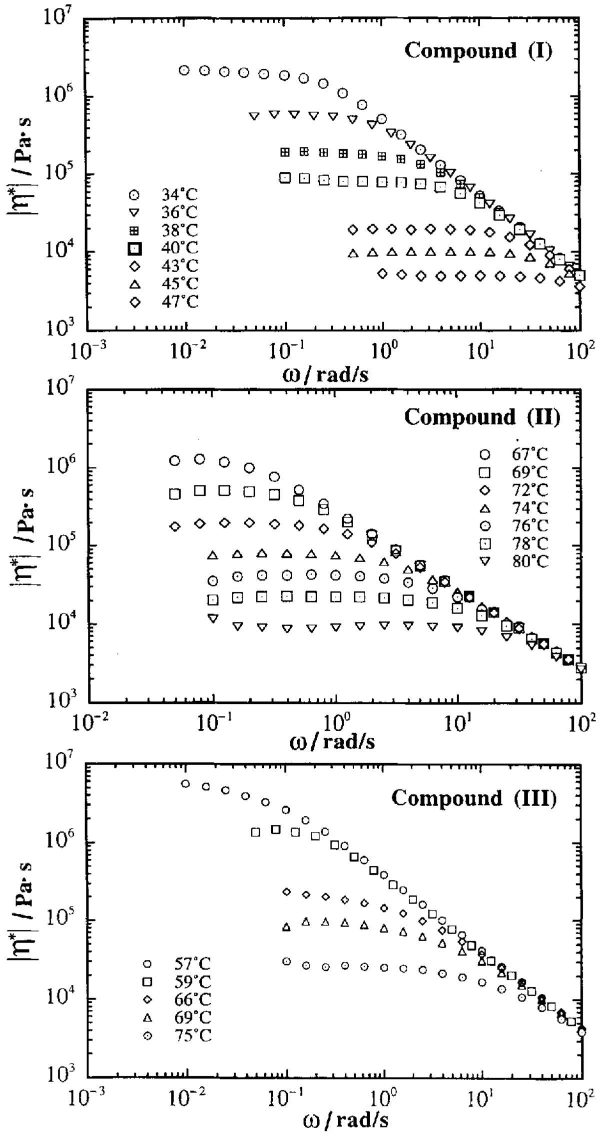

Figure 3. $|\eta^*|$ as functions of ω and T for compounds (**I**), (**II**), and (**III**).

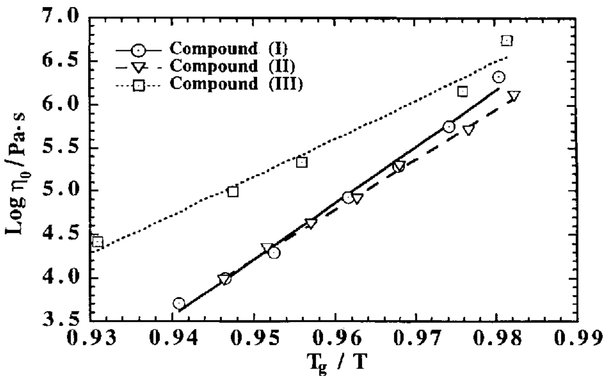

Figure 4. η_0 as a function of T_g/T for compounds (**I**), (**II**), and (**III**).

An attempt was made to construct master curves using the G' and G'' data as functions of frequency and temperature as a way to test the applicability of the time–temperature superposition principle. In the construction of master curves for the three model compounds, the shift factor, a_T, evaluated as the ratio $\eta_0/\eta_{0,\mathrm{ref}}$, is fitted to the WLF (Williams, Landel and Ferry) equation [25]:

$$\log a_T = \log\frac{\eta_0}{\eta_{0,\mathrm{ref}}} = -\frac{C_1(T-T_{\mathrm{ref}})}{T-T_{\mathrm{ref}}+C_2} \qquad (4)$$

with reference temperatures and fitted values of parameters as listed in table 1. Solid curves in figure 5 represent a_T as a function of temperature, which permit the G' and G'' data to be shifted into master curves shown as dashed curves in figure 6. Note that in the case of (**II**), the temperature range for G' and G'' measurements covers both sides of T_c, and single smooth curves emerge covering both the cholesteric and isotropic regimes.

Table 1. Parameters determined for the WLF equation, equation (4).

Compound	T_{ref}/°C	C_1	C_2/°C
I	34	8·09	27·26
II	67	9·94	49·61
III	57	7·50	38·76

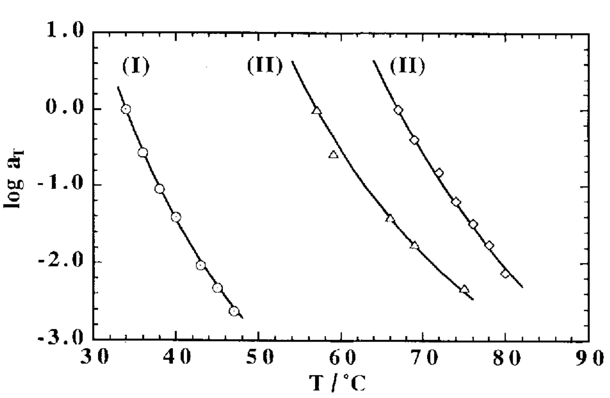

Figure 5. a_T as a function of T for compounds (**I**), (**II**), and (**III**).

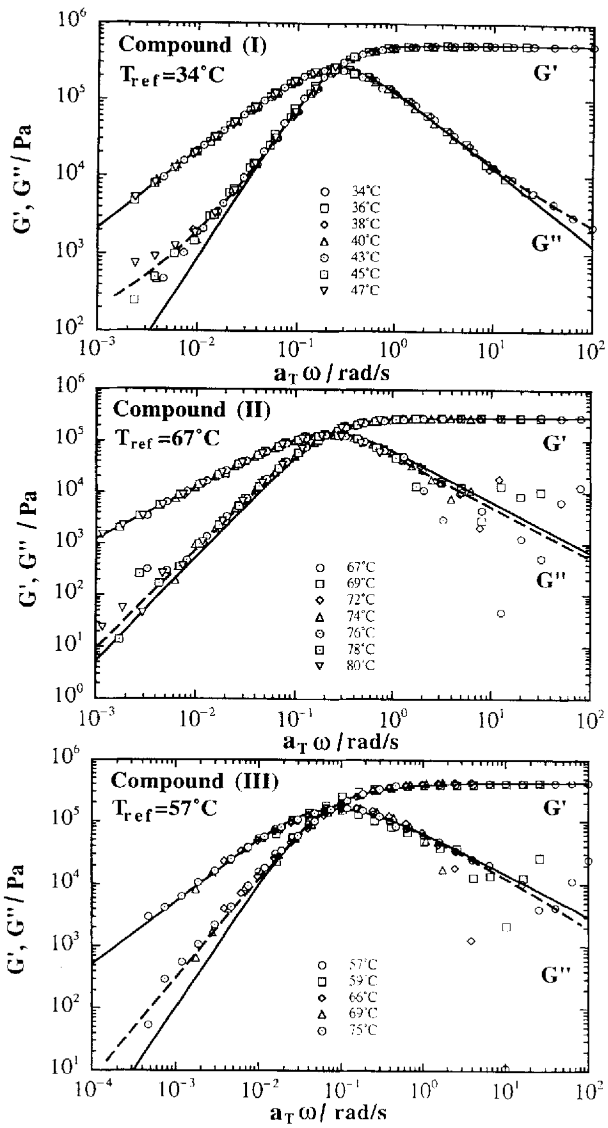

Figure 6. G' and G'' as functions of $a_T\omega$ and T for compounds (**I**), (**II**), and (**III**): master curves shown as dashed curves, and predictions by the stretched model as solid curves with $\beta = 1$ for (**I**) and (**II**) and $\beta = 0{\cdot}69$ for (**III**).

A further attempt was made to interpret G' and G'' as functions of $a_T\omega$ to reveal the relaxation behaviours of all three model compounds. Specifically, we employed the Kohlrausch–Williams–Watts function (i.e. the stretched exponential function) for dynamic shear moduli [26]:

$$G'(a_T\omega) = a_T\omega\int_0^\infty G(t)\sin(a_T\omega)\,\mathrm{d}t, \qquad (5)$$

$$G''(a_T\omega) = a_T\omega\int_0^\infty G(t)\cos(a_T\omega)\,\mathrm{d}t, \qquad (6)$$

with

$$G(t) = G_0\exp\left[-\left(\frac{t}{\tau_0}\right)^\beta\right] \qquad (7)$$

in which G_0 is the unrelaxed modulus with a value equal to G' as $\omega\to\infty$, τ_0 is the shear relaxation time, and the stretch exponent, β, has a value between 0 and 1. Note that equations (5) and (6) have been modified to establish G' and G'' as functions of $a_T\omega$ across a range of temperature instead of ω as normally accomplished. It follows that the existence of a master curve ensures that β is temperature independent. Moreover, equations (5) and (6) are reduced as follows for a single Maxwell element with $\beta = 1$:

$$G'(a_T\omega) = G_0 \frac{(a_T\omega)^2\tau_0^2}{1+(a_T\omega)^2\tau_0^2} \tag{8}$$

and

$$G''(a_T\omega) = G_0 \frac{(a_T\omega)\tau_0}{1+(a_T\omega)^2\tau_0^2} \tag{9}$$

in which τ_0 can be calculated from

$$\tau_0 = \frac{\eta_0}{G_0}. \tag{10}$$

In the case of $\beta < 1$, the relaxation behaviour deviates from a single Maxwell element and can be described by a distribution of relaxation times [27]

$$G'(a_T\omega) = a_T\omega \int_0^\infty \int_0^\infty G_0 \exp\left(-\frac{t}{\tau}\right) \sin(a_T\omega)p(\tau)\,\mathrm{d}t\,\mathrm{d}\tau \tag{11}$$

and

$$G''(a_T\omega) = a_T\omega \int_0^\infty \int_0^\infty G_0 \exp\left(-\frac{t}{\tau}\right) \cos(a_T\omega)p(\tau)\,\mathrm{d}t\,\mathrm{d}\tau \tag{12}$$

A comparison of equations (11) and (12) to equations (5) and (6) leads to

$$\exp\left[-\left(\frac{t}{\tau_0}\right)^\beta\right] = \int_0^\infty \exp\left(-\frac{t}{\tau}\right) p(\tau)\,\mathrm{d}\tau \tag{13}$$

where $p(\tau)$ is the relaxation time distribution function, which has been related to β [27]: the smaller the β value, the broader the relaxation time distribution. In the process of parameter estimation, G_0 in equation (7) was predetermined to be G' ($\omega \rightarrow \infty$) in all cases. A single Maxwell element was tested for the low molar mass systems, (I) and (II), by stipulating that $\beta = 1$ and that $\tau_0 = 1/a_T\omega$ at $G''_{\max}$. In the case of the polymer system, (III), both β and τ_0 in equation (7) where evaluated via fitting the G'' data to equation (6). The resultant parameters are compiled in table 2.

The solid curves in figure 6 represent the prediction of G' and G'' as functions of $a_T\omega$ on the basis of the stretched exponential model using parameter values given in table 2. It is clear that the low molar mass systems, (**I**) and (**II**), are well represented by a single Maxwell element, whereas the polymer system, (**III**), shows a significant deviation with a β value of 0·69, suggesting a rather broad distribution of relaxation times. The average relaxation time, $\langle\tau\rangle$, can be calculated using [27]

$$\langle\tau\rangle = \frac{\tau_0}{\beta}\Gamma\left(\frac{1}{\beta}\right) \tag{14}$$

where Γ is the Gamma function.

To compare the relaxation behaviour at a specified reduced temperature, T/T_g, the relaxation time at 1·019 T_g was calculated from τ_0 at T_{ref} using the WLF equation with parameters listed in table 1. The calculated values of τ_0 and $\langle\tau\rangle$ at 1·019 T_g are included in table 2. It is noted that at the reduced temperature of $T/T_g = 1{\cdot}019$, the average relaxation time of liquid crystal polymer, (**III**), is much longer than those of low molar mass systems, (**I**) and (**II**). A shorter relaxation time of low molar mass liquid crystals means that a shorter annealing time is needed to achieve a given degree of mesogenic ordering. Furthermore, a single relaxation time characterizing the low molar mass systems suggests a relative ease of processing into a uniform thin film via thermal annealing as part of the optical device fabrication process.

4. Summary

The storage and loss moduli, G' and G'', of a low molar mass nematic and a cholesteric glass-forming liquid crystal, (**I**) and (**II**), plus a nematic side-chain polymer, (**III**), were characterized as functions of frequency and temperature above T_g. The main points emerging from the present study are recapitulated as follows: (1) All three compounds show a shear thinning flow behaviour, and the zero shear viscosities of low molar mass systems were found to be an order of magnitude less than that of the polymer analogue at $T/T_g = 0{\cdot}94$. (2) Based on shift factors expressed in the WLF equation, master curves were constructed for the G' and G'' data across ranges of temperature for all three

Table 2. Parameters evaluated for the stretched exponential model, equation (7).

Compound	T_{ref}/T_g	G_0/Pa	β	τ_0/s at T_{ref}	τ_0/s at $T/T_g = 1{\cdot}019$	$\langle\tau\rangle$/s at $T/T_g = 1{\cdot}019$
I	1·013	$5{\cdot}24 \times 10^5$	1·00	4·1	1·3	1·3
II	1·018	$2{\cdot}86 \times 10^5$	1·00	4·3	3·7	3·7
III	1·019	$4{\cdot}28 \times 10^5$	0·69	9·5	9·5	12·2

compounds. (3) The G' and G'' data adjusted by the shift factor were successfully interpreted by the stretched exponential model with $\beta = 1$ for low molar mass systems, and with $\beta = 0{\cdot}69$ for the polymer analogue. Thus, it is concluded that the relaxation behaviour of the low molar mass systems is well represented by a single Maxwell element and that a relatively broad relaxation time distribution prevails in the polymer system. (4) The observed viscoelastic properties suggest a relative ease of material processing of the low molar mass systems in comparison to the polymer analogue on accounts of a lower zero shear viscosity and of the absence of relaxation time distribution.

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