Dynamic Mechanical Relaxation Behavior of Low Molecular Weight Side-Chain Cyclic Liquid Crystalline Compounds near the Glass Transition Temperature

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ABSTRACT: In this paper, we report the mechanical relaxation behavior of low molecular weight glass-forming side-chain liquid crystalline compounds with cyclic cores and their linear polymeric analogues near the glass transition temperature. We examined two systems: one based on cyclic and linear siloxane backbones and one based on cyclic (cyclohexane) and linear aliphatic backbones. Dynamic mechanical spectroscopy is used to measure the dynamic shear moduli and the complex viscosity near but above T_g. The temperature dependence of the zero-shear viscosity of the cyclic compounds is well described by the Vogel−Tammann−Fulcher (VTF) equation. The strong temperature dependence of the viscosity along with the values of the fitted parameters of the VTF equation shows that the cyclic LC compounds are "fragile" liquids. All cyclic LC compounds, regardless of chemical structure, show identical relaxation behavior when viscosity is plotted versus normalized temperature (T_g/T), where T_g is the temperature obtained calorimetrically at a heating rate of 10 K/min. All cyclic compounds show lower viscosity than their linear analogues when plotted versus T_g/T. The difference in viscosity between the cyclic and linear siloxane compounds is much more pronounced than the difference observed in the aliphatic compounds. For the cyclic compounds, master curves of G' and G'' can be described by a single Maxwell mode. The linear compounds exhibit much broader mechanical spectra, suggesting a more complex relaxation phenomenon is taking place. Our results show that, while there is little difference in relaxation behavior among low molecular weight cyclic liquid crystalline compounds, the behavior of the linear polymeric systems is quite different.

Introduction

It is well known that low molecular weight organic compounds have the ability to form glasses upon cooling from the melt.[1] As these materials approach the glass transition temperature (T_g), their viscoelastic behavior becomes complex as molecular interactions become pronounced. Investigations of these interactions near T_g have been made by probing dynamic mechanical relaxation behavior and correlating the results to chemical structure for over a dozen low molecular weight organic compounds.[2−6] Interestingly, most of these compounds appear to display similar relaxation features just above T_g despite significant differences in chemical structure. One such feature includes storage (G') and loss shear moduli (G'') that closely resemble those prescribed by a single Maxwell element. Another feature is a strong temperature dependence of the zero-shear viscosity which can be described by the empirical Vogel−Tammann−Fulcher equation.[7−9]

Similarities in relaxation features among compounds with different chemical structures is not uncommon. The main factor that influences mechanical properties of a compound as T_g is approached is the type and strength of molecular interactions that are present in the system. Some compounds in these earlier studies mentioned were found to have different dynamic mechanical properties, and this was attributed to the presence of different types of bonding between molecules.[2,3] Recently, Angell[9,10] analyzed the temperature dependence of viscosity for a variety of inorganic and low molecular weight organic glass-forming materials and classified them as either strong or fragile liquids depending upon the strength of the intermolecular bonding of the glass network. Another study has just been reported by Kim and Karis[11] in which they present four mechanisms of molecular interaction and intramolecular motion which allow glass formation for a variety of organic monomers by observing viscosity−temperature relationships. They also presented their results in terms of strong and fragile liquids proposed by Angell. Therefore, determining the type of molecular interactions that take place in glass-forming liquids is important if one wishes to predict their flow behavior.

Over the last several years, reports have been made on a new class of low molecular weight liquid crystalline compound which also has the ability to form glasses like other small organic molecules reported in earlier studies. This new glass-forming compound consists of a low molar mass cyclic core with pendant side-chain liquid crystalline mesogens. Cyclic liquid crystalline compounds have received attention because they have the potential to be used for a variety of linear and nonlinear optical applications.[12−14] The main advantage of using cyclic side-chain compounds instead of side-chain liquid crystalline polymers (LCPs)[15,16] is that the cyclic compounds have much lower melt viscosities than LCPs, which makes side group orientation into desired ultrastructures during processing much easier.[17]

Much of the work reported to date on side-chain cyclic LCs focuses on their synthesis, phase behavior, and morphology.[18−21] At this time, little is known about this

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class of material's rheological behavior in the melt. The first report in this area was made by Ahuja et al.,[22] who examined the dynamic mechanical shear properties of a cholesteric cyclic siloxane LC which was well above the T_g (i.e., $T_g + 30$ K < T < $T_g + 100$ K). Rheological results were interpreted in terms of helical axis alignment and distortion during flow. The first study of the relaxation behavior near the glass transition of a cyclic siloxane LC has just been reported by Etienne et al.[23] We will discuss their results and compare them to those found in our study in greater detail later. Recently, we compared the dynamic mechanical shear measurements of a cyclohexane-based side-chain LC to its linear analogue in temperature ranges close to T_g.[17] At this time, more information about the relationship between chemical struture and relaxation behavior near T_g of this class of material as a whole is needed to optimize optical film processing conditions as well as obtain a molecular understanding of their glass-forming physics.

The purpose of this study is to obtain an understanding of why low molecular weight cyclic LC compounds form glasses and what the correlation is between chemical structure and their viscoelastic properties. Here we report the results of dynamic mechanical shear measurements in the linear viscoelastic range near T_g of two side-chain LC compounds with various chemical structures, mesophases, and backbone configuration (i.e., cyclic vs linear). Our results are compared to those found for other low molecular weight glass formers in an attempt to expand the knowledge of structure–mechanical property relationships in cyclic LCs.

Experimental Section

1. Materials. Siloxane-Based Backbones. Two cyclic siloxane liquid crystalline compounds were examined: One based on a five-membered siloxane ring (pentamethylcyclopentasiloxane) and the other on a four-membered ring (tetramethylcyclotetrasiloxane). Two types of mesogens were attached to the rings in statistical amounts via hydrosilation chemistry. The details of the synthesis are given elsewhere.[20,21] One of the mesogens was cholesterol based (cholesteryl 4′-(allyloxy)benzoate) and the other was biphenyl based (biphenylyl 4′-(allyloxy)benzoate). Both cyclic compounds contained a 50/50 statistical mesogen composition of biphenyl/cholesterol. A linear oligomeric analogue of the cyclic siloxane compounds with the same 50/50 mesogen composition was also examined. The molecular weight of the linear siloxane precursor without attached mesogens is ~1800 g/mol (DP ~ 29). All structures are given in Figure 1.

Thermal transitions were measured on a Perkin-Elmer DSC-2C or a Dupont 910. Measurements were made at a heating rate of 10 K/min. Data were taken from the second heating scans. Transition temperatures are given in Table 1.

Aliphatic-Based Backbones. Three aliphatic side-chain LCPs were examined: Two with cyclohexane cores and the third being a linear polymer. One of the cyclohexane compounds contained three pendant nematic mesogens (cyanotolan) and the other contained one chiral group and two nematic mesogens (1-phenyl-2-(6-cyanonaphth-2-yl)ethyne). A linear analogue of the nematic cyclohexane-based side-chain LCP, with $M_w = 21\,480$ g/mol (DP ~ 45), was also examined. All structures are given in Figure 2. The details of the synthesis and characterization of the cyclic[24] and linear compounds[25] are reported elsewhere.

Thermal characterization was performed on a Dupont 910 interfaced with Thermal Analyst 2100 system. The samples were measured under nitrogen at a heating/cooling rate of 10 K/min. Thermal transition data were taken from the second heating scan, and results are given in Table 1.

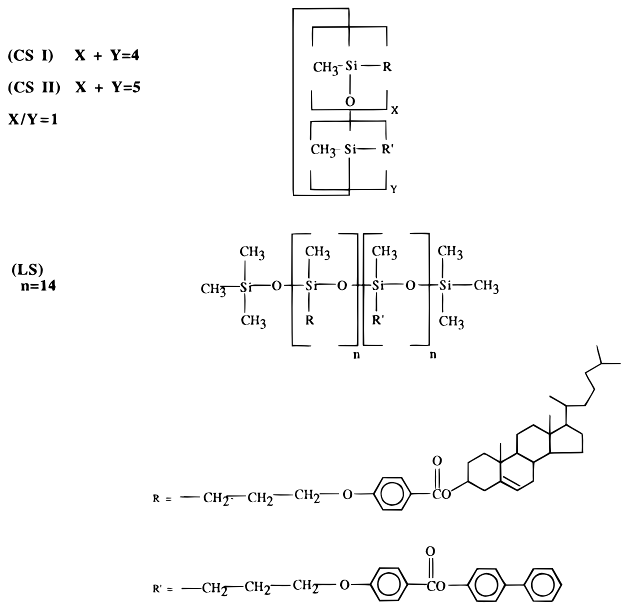

Figure 1. Cyclic siloxane (CS I) four-membered ring and (CS II) five-membered ring liquid crystalline compounds and linear siloxane (LS) analogue.

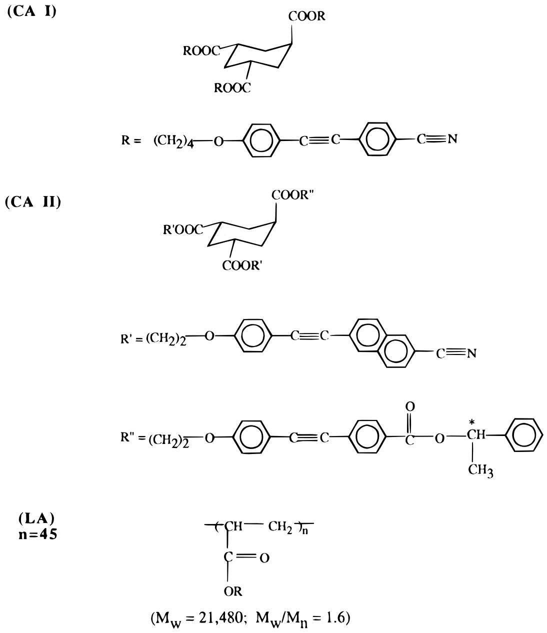

Figure 2. Liquid crystalline compounds with cyclohexane core (CA I, CA II) and linear aliphatic (LA) analogue.

Table 1. Thermal Transitions of Liquid Crystalline Compounds

sample	thermal transitions
	Siloxane-Based Backbones
cyclics	
CS I	g 62 n* 236 i
CS II	g 57 n* 237 i
linear	
LS	g 62 n* 230 i
	Aliphatic-Based Backbones
cyclics	
CA I	g 31 n 127 i
CA II	g 63 n* 76 i
linear	
LA	g 52 n 143 i

2. Rheological Measurements. Dynamic shear moduli (G', G'') were measured on a Rheometrics RDS 7700 dynamic spectrometer upgraded with operating software and transducer from AIC Inc. The nematic cyclohexane compound was measured on a Rheometrics RDSII upgraded with operating software by AIC. Parallel plates having a 25 mm diameter were used for all samples. The sample gap between the plates used for measurements ranged from 0.4 to 0.8 mm. The temperature was controlled by using heated nitrogen which was circulated throughout the environmental chamber.

Press-molded cyclic LCP samples were placed on the bottom plate and then softened by heating them up to temperatures 30−50 K 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. Linear samples had to be heated to temperatures >50 K above T_g, which allowed the sample to be squeezed to completely fill the gap. Samples were then annealed by heating them to a temperature 3−5 deg above the clearing point and then holding the temperature in the isotropic region for 15 min. The temperature was then lowered to the initial measuring temperature at a cooling rate of approximately 3 K/min. Once the desired temperature was reached, a rate sweep was performed from 1 to 100 rad/s. After the measurement was completed, the temperature was decreased to the next desired temperature and another rate sweep was performed. At the lowest temperatures, the frequency window was increased to 0.01−100 rad/s in order to capture the long-time behavior. Strain levels of $0.10 < \gamma < 0.20$ were used at higher temperatures in order to generate sufficient torque on the transducer. As the temperature was lowered, strains of $\gamma < 0.05$ were used. All strain levels were found to be in the linear viscoelastic region.

All data were analyzed by using IRIS software (IRIS Development). Dynamic data were shifted into master curves by time−temperature superposition.

Results and Discussion

Complex viscosities ($|\eta^*|$) of all siloxane and aliphatic compounds at different temperatures are shown in Figures 3 and 4, respectively. All cyclic and linear compounds display a Newtonian region at low frequencies. The zero-shear viscosity (η_0) is reported as the value of $|\eta^*|$ in the Newtonian region where $|\eta^*|$ is independent of frequency (ω). The values of η_0 for the linear siloxane compound were taken at the lowest frequency available since a true Newtonian region was never quite reached on the time scale of our measurements. All samples exhibited a strong shear thinning region at frequencies above the Newtonian region. This effect is more pronounced at lower temperatures as the temperature approaches T_g.

The dynamic viscoelastic behavior of our cholesteric cyclic siloxane compound was first reported by Ahuja et al.[22] They conducted measurements from 80 to 110 °C and did not observe strong shear thinning at these elevated temperatures. However, they did observe a slight decrease in $|\eta^*|$ as a function of frequency. The decrease in complex viscosity with increasing frequency became more pronounced at higher temperatures, and this was attributed to distortion and ultimate alignment of the cholesteric helical axis during flow. In our study, we were not able to observe such behavior because the viscosity at these temperatures was so low that the levels of torque fell below the sensitivity of the transducer. In the study of Ahuja et al., they did not make measurements close to T_g and consequently their report did not contain information about the glassy behavior of the cyclic compound, which is the focus of our study.

The values of η_0 versus temperature for the siloxanes and aliphatic compounds are plotted in Figures 5 and 6, respectively. Both sets of compounds show a strong temperature dependence of the viscosity near T_g. This will be discussed in detail later.

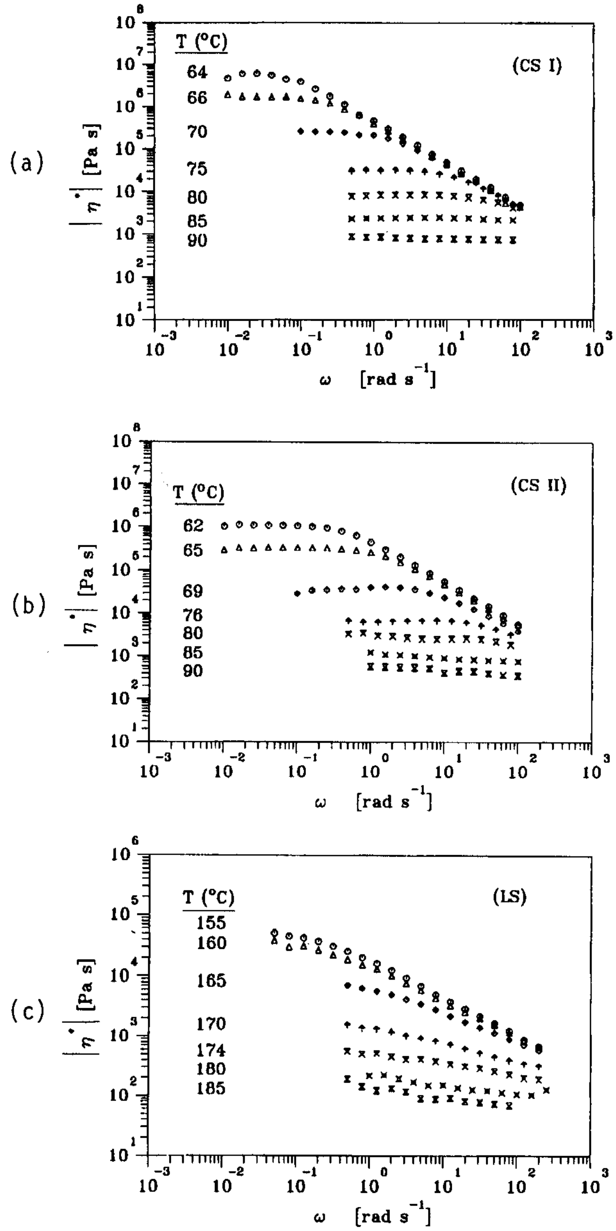

Figure 3. Complex viscosity ($|\eta^*|$) versus frequency (ω) at different temperatures for sample (a) CS I, (b) CS II, and (c) LS.

The viscosity data of Figures 5 and 6 are plotted versus the measured temperature normalized by T_g. This allows us to compare the rates of relaxation as a function of the distance from the glass transition temperature. Figure 7 shows the viscosity plotted versus reduced temperature (T_g/T), where T_g is the calorimetric glass transition temperature[26] of samples taken at a constant heating rate of 10 K/min. Other studies have plotted viscosity versus reduced temperature temperature where T_g is the temperature at which $\eta_0 = 10^{12}$ Pa s[9−11,23] or the time at which the relaxation time τ_s (where $\tau_s = \eta/G_\infty$) = 100 s.[9,10] Regardless of the method chosen, the patterns will almost always show departure from Arrhenius behavior and provide information about the structure of the glass network as will be discussed in the next section. However, when η_0 is plotted as a function of T_g/T, where T_g is the temperature at which $\eta_0 = 10^{12}$ Pa s, the results for samples CS I and CS II are in agreement with those reported by Etienne et al.[23]

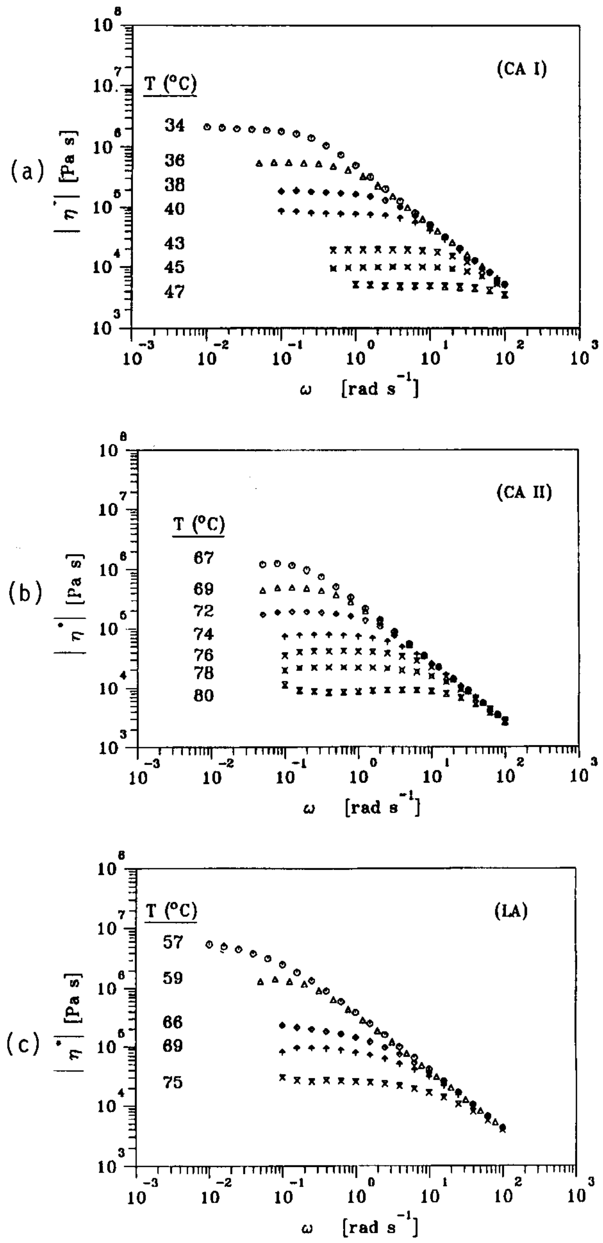

Figure 4. Complex viscosity ($|\eta^*|$) versus frequency (ω) at different temperatures for sample (a) CA I, (b) CA II, and (c) LA.

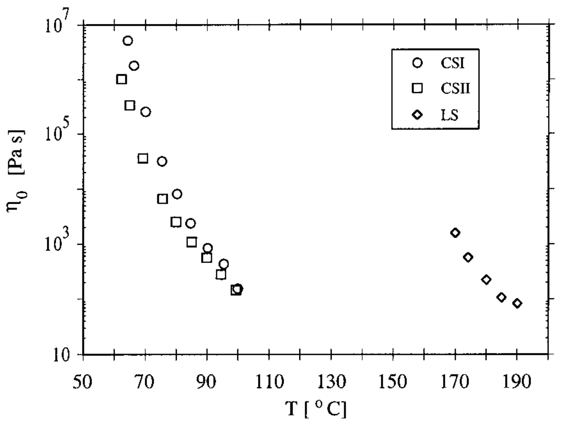

Figure 5. Viscosity (η_0) versus temperature for liquid crystalline samples with siloxane backbones.

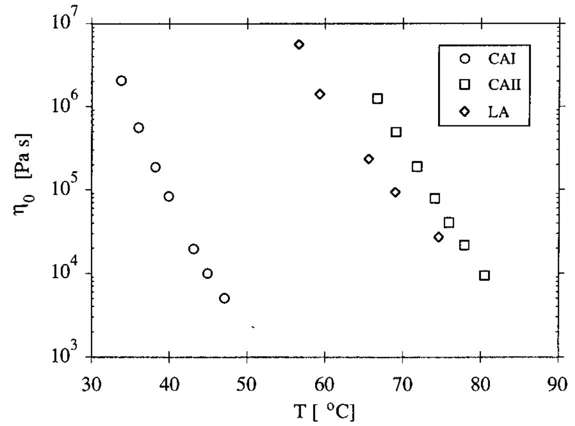

Figure 6. Viscosity (η_0) versus temperature for liquid crystalline samples with aliphatic backbones.

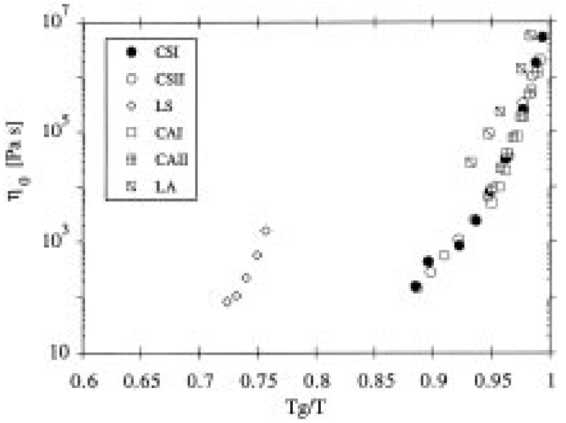

Figure 7. Viscosity versus normalized temperature for all liquid crystalline compounds. T_g is the glass transition temperature obtained calorimetrically at a heating rate of 10 K/min.

The data plotted in Figure 7 reveal something important about the relative rates of relaxation above T_g. First, all of the cyclic compounds display almost identical flow behavior even though they are of different chemical structure, ring size, and mesophases. This suggests that these molecular parameters have little effect upon the relaxation behavior in the vicinity near but above T_g. This observation has also been made for many other low molecular weight organic compounds that have different chemical structures.[2,3,11,26] The materials in these earlier studies, however, were not liquid crystalline.

Second, the linear compounds show higher viscosities than their cyclic analogues when they are compared at the same distance above T_g. In the case of the siloxanes, the difference between the cyclics and linear samples is much larger than in the case of the aliphatic-based backbone compounds. Nevertheless, it is clearly evident that the cyclics, even though they have identical chemical structure and similar values of T_g as their linear counterparts, have faster rates of relaxation above T_g. This is to be expected and can most likely be explained by the fact that the linear compounds are much larger than the cyclic compounds due to their polymeric structure and thus have longer terminal relaxation times. The lower viscosity of the cyclics means it would be easier to orient side chains during processing, which will ultimately produce higher quality optical films. We recently reported this observation for the cyclohexane compounds.[24]

Glass Network Structures from Viscosity Data Analysis. The data shown in Figure 7 can provide

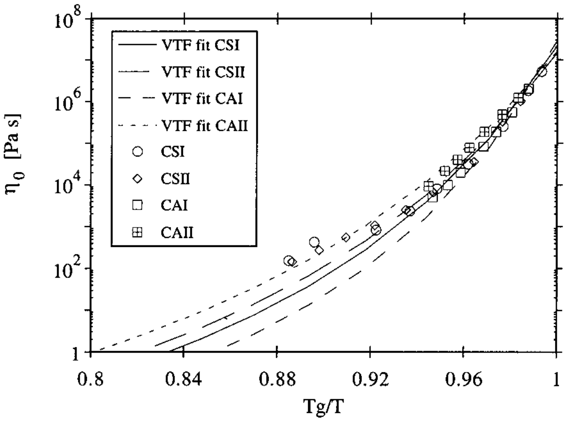

Figure 8. Fit of the Vogel–Tammann–Fulcher equation to all cyclic LC compounds.

Table 2. VTF Parameters

sample	D	T_0 (°C)	T_g (°C)
CS I	4.5	16.6	62
CS II	5.1	6.0	57
CA I	4.2	−14.7	30
CA II	5.9	3.2	51

information about the types of molecular interactions that exist as well as the stucture of the glass network. This has been done in previous studies[9–11] by using the Vogel–Tammann–Fulcher equation

$$\eta = A \exp\left[\frac{DT_0}{T - T_0}\right] \tag{1}$$

where A, D, and T_0 are experimentally determined constants. Here we are primarily interested in the value of the parameter D, which relates to the type of bonding between molecules in a glass-forming liquid.[9,10] High values of D were found for compounds with strong intermolecular attractions such as in SiO_2 or GeO_2 where relaxation behavior is of the exponential Arrhenius type between T_g and very high temperatures. Such compounds are classified as "strong" liquids. Materials with low D values (i.e., $D < 10$) were characterized by weak intermolecular attractions such as hydrogen bonding or even weaker van der Waals forces and are characterized as "fragile" glass-forming liquids.

In our analysis, we fit eq 1 to our data by nonlinear regression. The value of A was fixed at 10^{-5} Pa s so that we could compare our results to those reported by Kim and Karis[11] for hydrogen-bonding and non-hydrogen-bonding glass formers. The values of D and T_0 are given in Table 2 and the fits are plotted in Figure 8. The D values of the cyclic compounds in our study range from 4.2 to 5.9, which are close to the values of 4.1 and 4.7 found for a branched oxazole and imidazole examined by Kim and Karis.[11] The structure of their two compounds contains a heterocyclic core with three pendant side chains. In their analysis, they propose that the fragile network structure of the branched compounds is held together by weak van der Waals forces between mechanically interlocked side chains. They compare these results to four sugar compounds (sucrose, α–D-glucose, D-galactose, and D-fructose) which were able to undergo hydrogen bonding due to their chemical structure. The D values of the sugars were found to be in the range of 6.8–7.4, which suggests that they exhibit a stronger network than the interlocking compounds which do not have hydrogen bonding.

Since the cyclic LCs have such a strong temperature dependence of the viscosity near T_g which can be characterized by low values of D, two conclusions can be made. First, due to their similar general branched structure and low values of D as the oxazole and imidazole, it is plausible that the glass network of the cyclic LCs is most likely formed through mechanical interlocking of side chains as proposed by Kim and Karis.[11] Second, these compounds can be classified as fragile glass-forming liquids. This finding is consistent with the results of Etienne et al.,[23] who also classified cyclic siloxane-based LCs as fragile liquids.

Though the cyclic LCs are fragile liquids with a weak network structure, one may expect them to be weak-forming glasses with poor long-term stability. However, these compounds are good glass formers with excellent long-term stability. In fact, the siloxane compounds do not crystallize at all while cyclohexane compound CA I will eventually crystallize given the proper processing conditions.[24] The same long-term stability has been observed for the branched oxazole and imidazole. Kim and Karis[11] explain this long-term suppression of crystallization in terms of hindered rotational isomerism of pendant branches that are adjacent to one another. Because of steric interference, rotational isomerism of adjacent branches becomes more difficult as the temperature decreases toward T_g. The result is that a mixture of diasteromers becomes frozen in and suppresses nucleation. This observation is consistent with the results of the cyclic siloxane compounds in that the large bulky cholesterol group can certainly cause hindered rotational isomerism with an adjacent cholesterol or a biphenyl group. Cyclic siloxane compounds with 100% biphenyl groups have been reported to crystallize while 100% cholesterol samples do not.[18] The effect of hindered isomerism in the 100% biphenyl cyclosiloxane LC would be drastically reduced due to the fact that the biphenyl units are so much smaller than the cholesterol units. The result is a decrease in the potential for steric hindrance and an increase in the potential for nucleation of crystals.

Dynamic Mechanical Data and Molecular Interactions. In the previous section, we propose the type of network structure that likely exists in the cyclic LCs by analysis of viscosity–temperature relationships and comparing the results to those found for molecules of similar shape. In this section, we analyze dynamic mechanical spectra to determine the presence of intermolecular forces in the cyclic and linear LCP compounds.

Information regarding whether intermolecular associative forces are present such as hydrogen bonding, physical entanglements, etc. can be inferred from dynamic data. It has been reported that nonassociating liquids exhibit dynamic relaxation patterns that can be described by a single relaxation time while liquids that show association exhibit a spectrum of relaxation times.[27] Some earlier studies of the mechanical relaxation of glasses near T_g have compared dynamic mechanical data to that prescribed by a single Maxwell element which is described by a single relaxation time.[2,3] The storage and loss moduli of a Maxwell element are given by

$$G' = G_\infty \frac{(\omega\lambda)^2}{1 + (\omega\lambda)^2} \tag{2}$$

$$G'' = G_\infty \frac{\omega\lambda}{1 + (\omega\lambda)^2} \tag{3}$$

where G_∞ is the limiting maximum value of G' at high frequencies and λ is the characteristic relaxation time. Deviations from the Maxwell model provide evidence as to whether the relaxation behavior of these compounds must be described by a spectrum of more than one relaxation time. The result described by the Maxwell element does not infer any type of specific molecular relaxation process, only that a single time is sufficient to characterize the spectrum.

This type of analysis has been reported by Benbow et al.[2,3] for two low molar mass glass-forming organic compounds. In Benbow's study, he compared the normalized dynamic shear loss modulus of two compounds, 2′-hydroxy-2, 4,4,5′,6-pentamethylflavan (HPF) and glycerol sextol phthalate (GSP), to that prescribed by a single Maxwell element. It was observed that GSP, which has the ability to undergo intermolecular hydrogen bonding, displayed a broader loss modulus peak than HPF, which does not undergo intermolecular hydrogen bonding. For GSP there was excellent agreement with the Maxwell model in the terminal zone but significant deviation from the model at higher frequencies. The broadness of the loss modulus peak was attributed to intermolecular associations due to hydrogen bonding, which causes the molecular size to increase. This increases the number of relaxational processes that can take place to dissipate stress under shear flow, thus causing a boadening of the relaxation time spectrum.

Figures 9 and 10 show the comparison of a single Maxwell mode to the normalized dynamic moduli of the siloxane- and aliphatic-based backbone compounds, respectively. All cyclic compounds show very good agreement between the data and the phenomenological model. This data supports the result we found in the last section in which we proposed only weak van der Waals forces exist between interlocking branches. If stronger intermolecular forces such as hydrogen bonding were present, we would have expected to see a broader loss modulus peak.

There is some discrepancy at the low-frequency region in G', where the data deviate from the typical slope of 2 given by the Maxwell model. This could be due to two possible reasons. First, at the lowest frequencies of the master curve, it is common for G' data to scatter due to the fact that the limit of transducer torque sensitivity is being approached.

Another possible explanation for the low-frequency discrepancy may be due to the liquid crystalline structure of the material. Evidence of this low-frequency shear thinning region was reported by Ahuja et al.[22] for cholesteric cyclosiloxane LCs of similar structure to the ones examined in our study. As already mentioned, they attributed this behavior to distortion and eventual rotation of the helical axis during flow alignment, which causes the decrease in $|\eta^*|$ with increasing frequencies. Similar behavior of G' at the lowest frequencies has been reported by Yamaguchi et al.,[28] who examined a cholesteric side-chain linear siloxane LCP. They attributed these observations to changes in the domain structure. Scatter of the values of G'' at high frequencies is most likely due to the lack of sensitivity of G'' in this region where the material behaves more like a solid.

A major conclusion of this work is that the relaxation patterns for all the cyclic compounds near T_g are similar even though they differ significantly in chemical structure and exhibit different mesophases. We conclude that the important molecular feature responsible for the observed viscoelastic behavior is therefore not chemical composition or phase behavior but the general shape of these molecules. The important common molecular characteristic that these low molar mass LC compounds share is their cyclic bulky structure which frustrates the crystallization process and allows glass formation to take place as the temperature is decreased. As already mentioned, similar viscoelastic behavior near T_g has been observed for other low molar mass organic molecules which also have bulky structures.

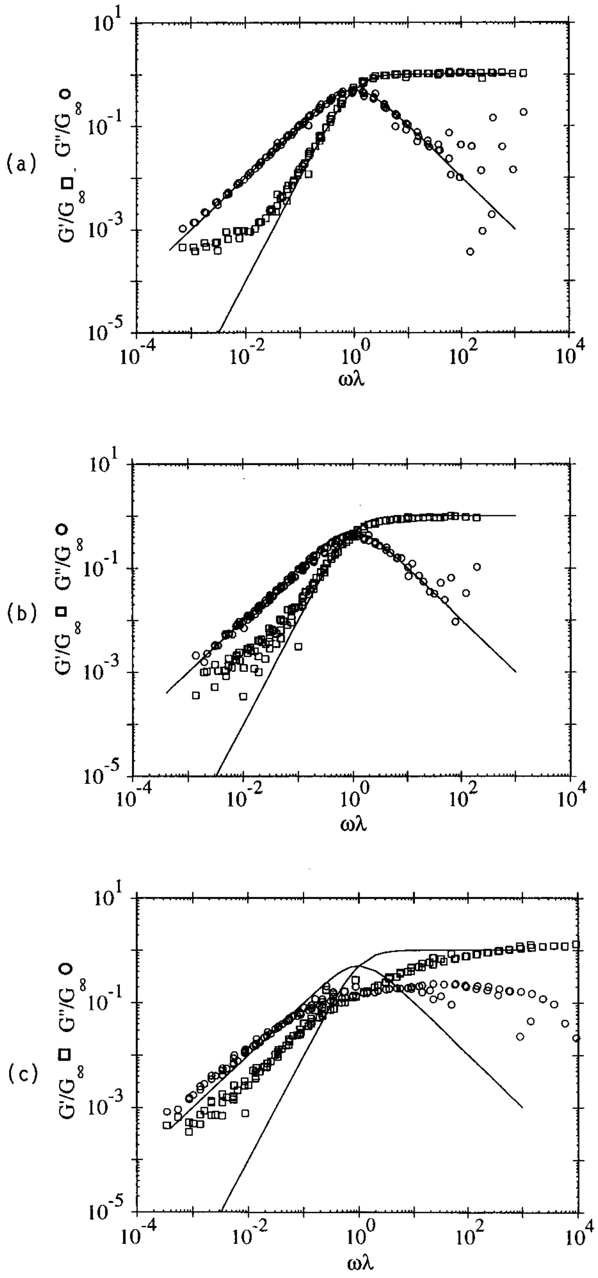

Figure 9. Normalized storage (G'/G_∞) and loss (G''/G_∞) moduli of (a) CS I, (b) CS II, and (c) LS. The solid line indicates the pattern given by a single Maxwell mode.

The dynamic data of the linear compounds show significantly different patterns than their cyclic analogues. The linear siloxane displays the greatest deviation from the spectrum of the Maxwell model while the aliphatic compound displays only a slight deviation of G'' with a greater deviation of G' in the terminal zone. Since the backbones of the linear compounds are polymeric and much larger than the cyclics, we would expect to see a broader spectrum as the relaxation

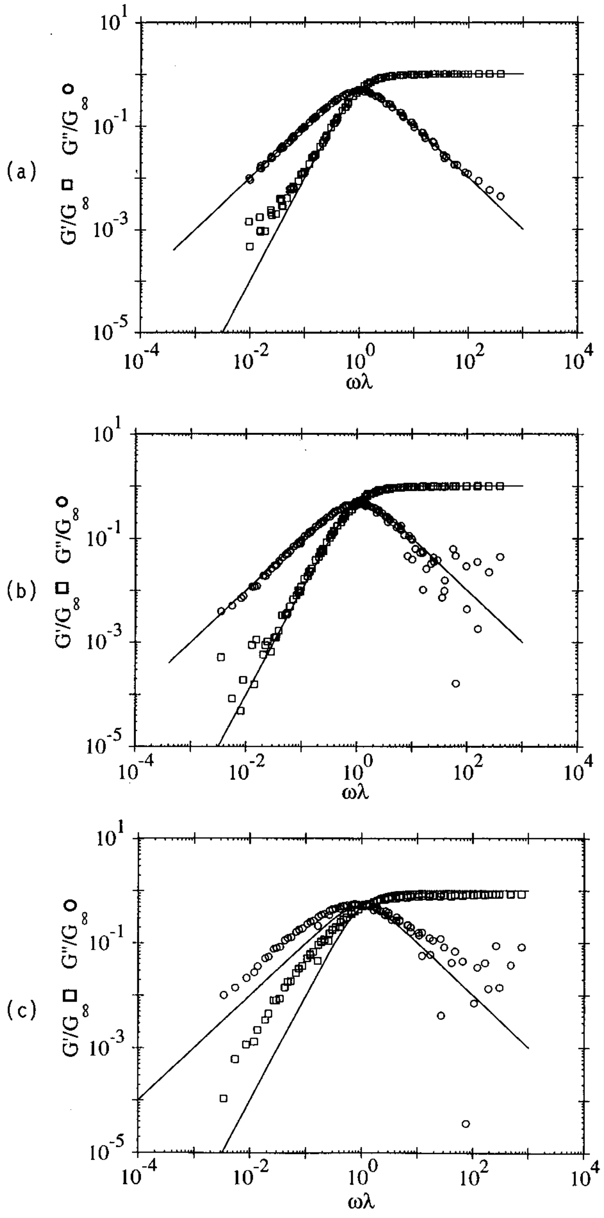

Figure 10. Normalized storage (G'/G_∞) and loss (G''/G_∞) moduli of (a) CA I, (b) CA II, and (c) LA. The solid line indicates the pattern given by a single Maxwell mode.

dynamics become more complex with the large polymer chains. In the case of the linear siloxane LCP, the spectrum is significantly broader than both the cyclic siloxane compounds and the linear aliphatic LCP. Physical entanglements cannot be an explanation for why the linear siloxane spectrum is so broad since the length of the backbone of the siloxane LCP is below that of the entanglement molecular weight of poly(dimethylsiloxane).

A possible explanation for why the linear siloxane behaves so differently from the linear aliphatic LCP may be due to the relative size of the mesogens attached to the backbone and how their motions are coupled to the backbone.[23,29,30] In the case of the siloxane, the cholesterol mesogen is much larger (i.e., bulkier) than the cyanotolan which is attached to the aliphatic chain. In addition, the spacer group that attaches the cholesterol unit to the siloxane backbone is shorter than the spacer group of the cyanotolan. The longer spacer group which attaches the smaller cyanotolan unit would help to decouple the motions of the mesogen from the motions of the backbone to a greater extent than for the siloxane LCP. Weakly coupled mesogen motions could possibly cause the aliphatic LCP to have a narrower spectrum and lower viscosity than the siloxane LCP.

Conclusions

In this study, we examined the viscoelastic behavior of a new class of glass-forming material based on cyclic backbones with pendant liquid crystalline mesogens and compared them to their linear analogues. These compounds exhibit shear relaxation behavior that has previously been observed for other low molecular weight organic glass-forming liquids. The bulky shape of these compounds appears to be the predominant factor which dictates their viscoelastic behavior near T_g, not chemical composition. Analysis of the data through the Vogel–Tammann–Fulcher (VTF) equation provides evidence that cyclic siloxane- and cyclohexane-based liquid crystalline compounds can be classified as fragile glass-forming liquids that form weak network structures through van der Waals interactions between mechanically interlocked mesogens. Dynamic mechanical spectra show that all cyclic compounds can be represented by a Maxwell element which is characterized by a single relaxation time. This finding is also consistent with results that have been recently reported in the literature for molecules having a similar branched structure as the compounds examined in our study.

In the case of the linear compounds, we have found two things. First, due to their large size, the rate of mechanical relaxation above T_g of the linear compounds is much slower than that of their cyclic analogues. This makes cyclic liquid crystalline compounds an attractive candidate for materials to be used as bulk films for optical applications since their lower viscosity makes it easier to process mesogens into the desired orientation. Second, dynamic mechanical data of the linear samples show that the spectra are much broader than those observed for the cyclics. This broadened spectrum suggests that the large size of the backbone along with possible complex side-chain motion coupled to the backbone most likely plays a major role in influencing the relaxation spectrum by increasing the number of relaxation modes that are necessary to adequately describe their flow behavior.

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