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Rheological Study of the Mesomorphic State of Dimolybdenum and Dicopper Octanoates

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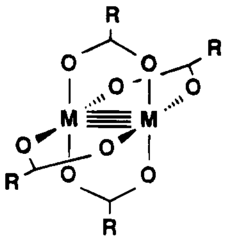
The viscoelastic properties of M_2(octanoate)$_4$ compounds, where M = Mo and Cu, are reported in their mesophase as a function of temperature dependence, strain sweep (1 rad/s), and frequency sweep (2% strain). The viscoelastic properties of the mesophase are comparable to that of polypropylene having M_W exceeding 10^5 kg/kmol. The nonlinear response of G', G'', and η^* with increasing strain and the greater values of these parameters for M = Cu relative to M = Mo are correlated with the dynamics of the microstructure of the mesophase.

Introduction

To date, all applications of liquid crystals involve organic molecules and polymers and these have evolved through synthetic and physical studies of manmade materials. It seems likely that metallomesogens, metal containing liquid crystals, will provide new horizons in liquid crystal technology based on the appropriate selection of metal ion and organic counterpart. For this reason metallomesogens are of current interest.[1−3]

Dimetal tetracarboxylates are known for many transition metal elements, e.g.,[4] M = Cr, Mo, W, Ru, Rh, Cu, and adopt a common lantern or paddle wheel molecular structure, I.



I

The $M_2$4+ center is redox active and may be diamagnetic or paramagnetic depending on the selection of M. For M = Cr, Mo, and W there are M−M quadruple bonds of electronic configuration $\sigma^2\pi^4\delta^2$, while for Ru there is a double bond, $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$, and for Rh a single bond, $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$.[4] For copper the metal ions are merely antiferromagnetically coupled.[5]

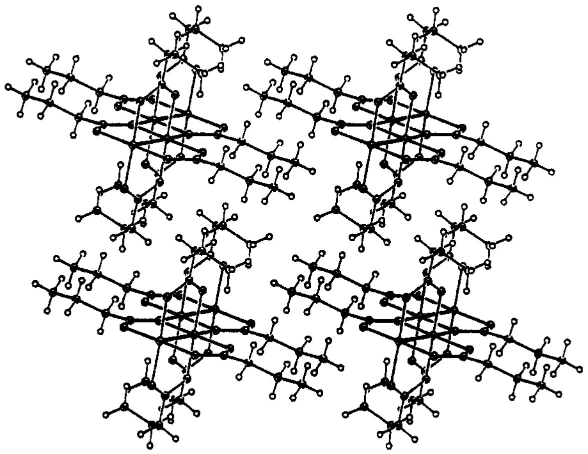


Figure 1. Packing diagram of two unit cells of $W_2(O_2C(CH_2)_2CH_3)_4$.

In the solid state the $M_2(O_2CR)_4$ compounds exist in infinite chains and each chain is parallel to neighboring chains as is shown by the diagram of the unit cells of $W_2(O_2C(CH_2)_2CH_3)_4$ in Figure 1. The organization of the solid state arises from the packing of the *n*-alkyl chains and the intermolecular - - -$[M_2$- - -$O]_\infty$ interactions. Upon heating the long chain *n*-alkanoates of this class show a thermotropic mesophase with the exception of tungsten whose compounds merely melt to give the isotropic liquid phase.[6] For molybdenum it is possible to access the mesophase and the isotropic liquid depending upon the temperature and the selection of a specific alkyl chain. For all other metals (M = Cr, Ru, Rh, and Cu) there is a crystal to mesophase transition, but no clearing is observed prior to decomposition which sets in ca. 250−300 °C. It was previously proposed[6] that the intermolecular - - -$[M_2$- - -$O]_\infty$ interactions are responsible for the mesophase and that these are inversely related to the strength of the M−M interactions which follow the order M = W > Mo > Cr > Ru > Rh > Cu. EXAFs studies have shown that in the mesophase of $M_2(O_2CR)_4$ the - - -$[M_2$- - -$O]_\infty$ bonds are present when M = Cu[7] and Rh.[8]

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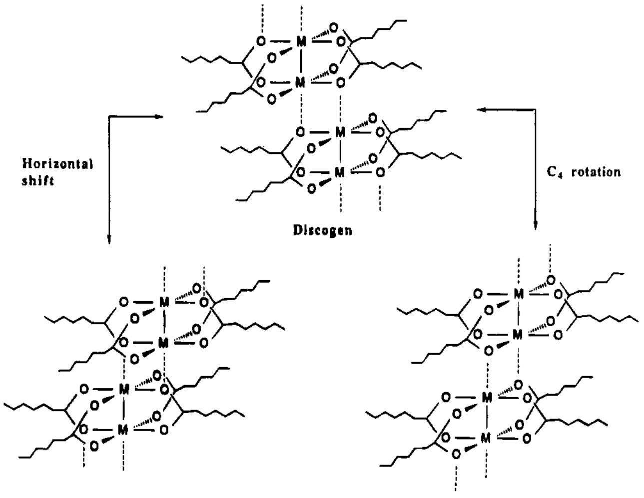

Figure 2. Dynamic behavior within a column in the mesophase of $M_2(O_2CR)_4$ compounds as $M_2\cdots$bonds are rapidly and reversibly broken and formed.

Molecules of type **I** are anisotropic and the Mo$-^4$Mo bond has a relatively large magnetic anisotropy ca. -8000×10^{36} m^3/molecule which may be compared with -340×10^{-36} m^3/molecule for ethyne.[9] The mesophase of $Mo_2(O_2C(CH_2)_6CH_3)_4$ was shown to be D_{hd} with an estimated coherence length along the column of 30–35 Å.[10] The M–M axis aligns perpendicularly to an applied magnetic field and each molecule rotates rapidly on the NMR time scale in the plane of the applied magnetic field. The molecular description of the mesophase is one wherein the weak (M = Mo) intermolecular $\text{- - -}[M_2\text{- - -}O]_\infty$ bonds are kinetically labile, being rapidly and reversibly broken and formed as shown diagrammatically in Figure 2.[10]

We report here a study of the rheological profile of this class of compounds taking as the limiting cases the octanoates of molybdenum and copper which have the weakest and strongest intermolecular $\text{- - -}[M_2\text{- - -}O]_\infty$ interactions, respectively. This study is pertinent for any potential processing of these materials and provides further data for developing a molecular understanding of the mesophase. To our knowledge this is a rare report of the rheology of any metallomesogen.[11]

Experimental Section

Viscoelastic measurements were carried out by using a Rheometrics RDS II mechanical spectrometer configured with an electrically heated oven. This controlled strain dynamic rheometer provides the means for measuring the viscoelastic parameters G' (the oscillatory storage modulus), G'' (the loss modulus), and a complex viscosity, η^*. Because of the air sensitive nature of the sample all operations were carried out under a high purity dinitrogen atmosphere.

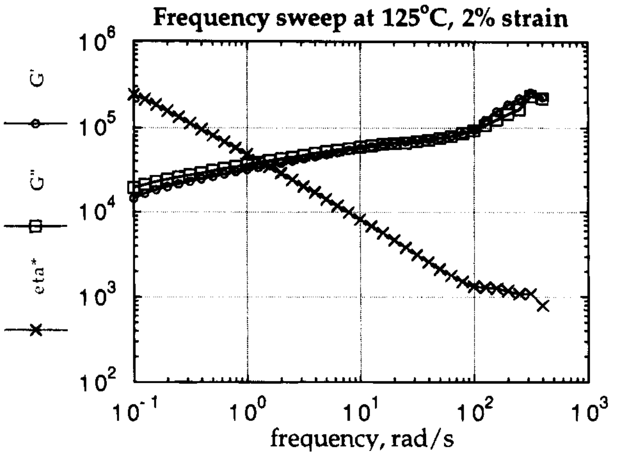

Figure 3. Graph of the frequency sweep data (2% strain) for $Mo_2(O_2CH_2)_6CH_3)_4$ in the mesophase at 125 °C.

The storage and loss moduli represent values that are respectively in-phase and 90° out-of-phase within applied sinusoidal strain deformation.[12] The complex viscosity has the dimensions of viscosity (Pa s) and is related to G' (storage modulus) and G'' (loss modulus) as shown in eq. **1** where ω is the angular frequency at oscillation.

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

$Mo_2(O_2C(CH_2)_6CH_3)_4$ was prepared as previously described.[10]

$Cu_2(O_2C(CH_2)_6CH_3)_4$. $Cu_2(O_2CMe)_4{\cdot}H_2O$[13] (3.0 g, 15 mmol) was mixed with octanoic acid, $CH_3(CH_2)_6COOH$ (4.7 mL, 4.33 g, (4 equiv). Ethanol (100 mL) was added to the mixture, and the resulting solution was refluxed for 72 h, after which time the ethanol was removed under a dynamic vacuum. The product was washed with cold water, hot water, ethanol, and petroleum ether. The final light-blue product was obtained by recrystallization from toluene (10 mL), washed with pentane (10 mL), and dried under a dynamic vacuum (10^{-2} Torr) for 10 h at 50 °C. IR (cm^{-1}, KBr) 1405 (s), 1422 (s), 1446 (m), 1592 (vs), 2843 (s), 2910 (s), 2952 (s).

Results and Discussion

$Mo_2(O_2C(CH_2)_6CH_3)_4$. The variation of η^*, G', and G'' vary with the angular frequency of oscillation at 2% strain in the mesophase, at a temperature of 125 °C, is depicted in Figure 3. The material shows a response very similar to that of a polymer melt or solution.[14] η^* falls as the frequency is increased. At low frequencies G' and G'' are of the same order of magnitude, with G'' being slightly larger than G'. As the frequency is raised, these parameters "cross over" with G' dominating at the higher frequencies.

The high-frequency upturn in values for G' and G'' is not usually seen for conventional polymer melts;[15] however, those parts of the G' and G'' profiles which

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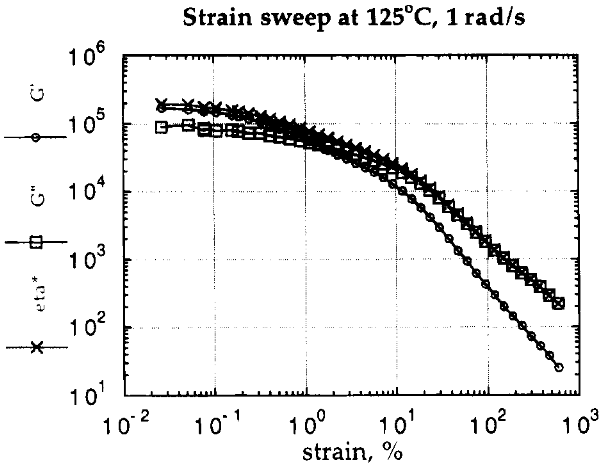

Figure 4. Graph of the strain sweep data (1 rad/s) for $Mo_2(O_2C(CH_2)_6CH_3)_4$ in the mesophase at 125 °C.

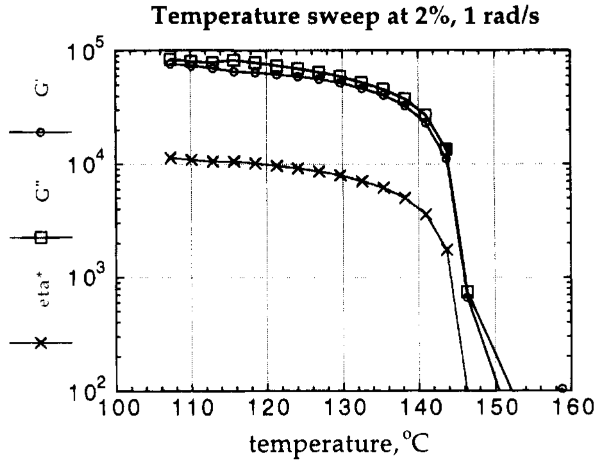

Figure 5. Temperature dependence graph of the viscoelastic behavior of $Mo_2(O_2C(CH_2)_6CH_3)_4$.

are in the range 10^4−10^5 Pa are very similar to the values one might observe for a typical extrusion-grade thermoplastic, and consequently the linear viscoelastic behavior of the material can be compared to that of a thermoplastic melt. Figure 4 shows the strain dependence of G', G'', and η^* for a fixed angular frequency of 1 rad/s at a temperature of 125 °C. These data illustrate a classic polymeric response, in that at low strains the values are essentially strain independent. As the strain value is increased from 1% to 10%, the response becomes nonlinear. Molten polymers typically yield a nonlinear response within the percent range 10^{-2}−10^2, depending on the molecular mass and other factors. The onset of nonlinearity usually occurs at lower strains for high molecular mass materials.

The rheological response of G', G''; and η^* can be used as a means of following structural changes as a function of temperature, and this effect is shown in Figure 5. Here G', G'', and η^* are plotted as a function of temperature for a constant angular frequency of 1 rad/s and strain of 2%. The data reveal that there is an obvious rheological transition in the temperature range between 160 and 140 °C as the material undergoes the isotropic liquid-to-liquid crystal phase change.

Within the mobile liquid crystal region (100−140 °C), there is a small but progressive change in the rheological paramaters, indicating that structural reorganzation is occurring within this temperature window.

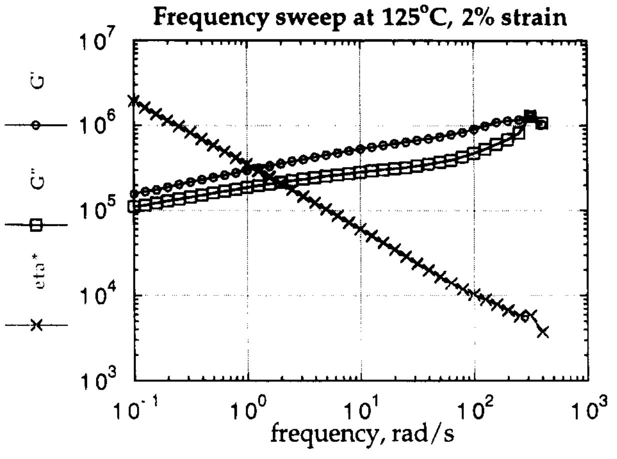

Figure 6. Graph of the frequency sweep data (2% strain) for $Cu_2(O_2C(CH_2)_6CH_3)_4$ in the mesophase at 125 °C.

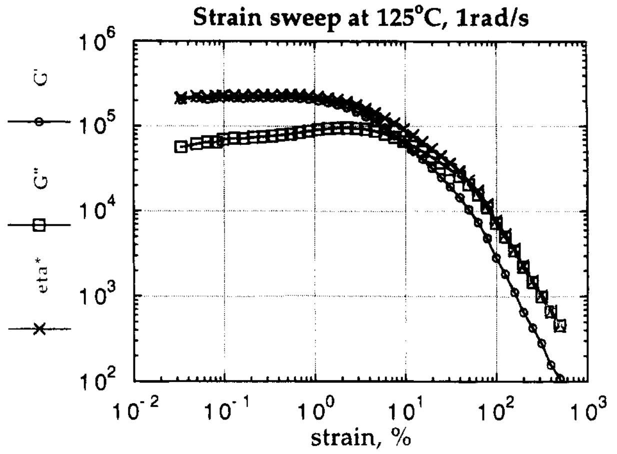

Figure 7. Graph of the strain sweep data (1 rad/s) for $Cu_2(O_2C(CH_2)_6CH_3)_4$ in the mesophase at 125 °C.

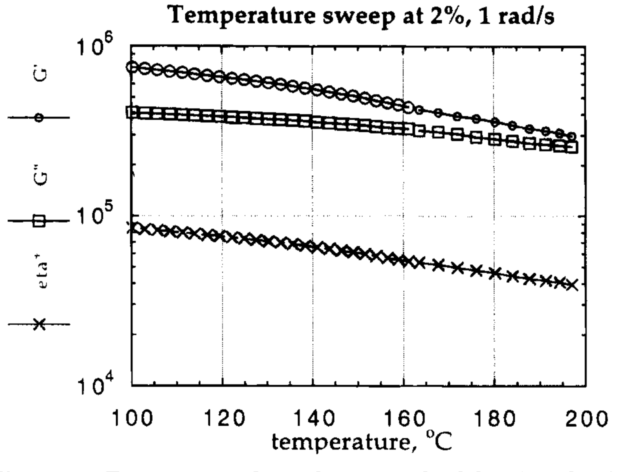

Figure 8. Temperature dependence graph of the viscoelastic behavior of $Cu_2(O_2C(CH_2)_6CH_3)_4$.

$Cu_2(O_2C(CH_2)_6CH_3)_4$. Figures 6−8 present an analogous set of data for dicopper tetraoctanoate. The frequency sweep for the Cu_2 material (shown in Figure 6) again, has similar characteristics to that of a high molecular weight polymer.[14] In this case, G' dominates at all frequencies, and the η^* data have not reached a linear plateau. The values of G' and G'' are greater than those for the molybdenum system, indicating a higher molecular mass and stronger intermolecular interactions within the material.

The strain sweep shown in Figure 8 also has similarities to conventional polymers and to the dimolybdenum system. At low strain, the response is independent of strain, with the material "strain-softening" at larger deformations. This effect occurs in the range of 1–10% strain.

Finally the temperature dependence of the rheological behavior is depicted in Figure 8. The data show progressive stiffening of the material as the temperature is decreased from 200 to 100 °C. However, unlike in the dimolybdenum system, no phase transitions were observed in this temperature window.

The rheological investigations reveal that the $M_2(O_2C(CH_2)_nCH_3)_4$ compounds which contain infinite chains of M_2 units linked by $[M_2 \cdots O]$ bonds in the crystalline state retain these linkages in the mesophase, as has indeed been concluded from other studies. The viscoelastic behavior of the compounds is similar to that of polypropylene[14] having a molecular mass exceeding 10^5 kg/kmol. The polymeric nature of the $M_2(O_2CR)_4$ compounds arises from these extended $[M_2 \cdots O]_n$ interactions within each of the hexagonally packed columns in the mesophase. These intermolecular bonds are kinetically labile and within the column are constantly being broken and reformed.[10] The nonlinear response of G', G'', and η^* with increasing strain can therefore be related, at least in part, to the lability of the polymer backbone.[16] The same is true for the decrease in viscoelastic moduli with increasing temperature.

In comparing the copper and molybdenum systems, the values of G', G'', and η^* are an order of magnitude greater for copper which can be attributed to the stronger intermolecular $[M_2 \cdots O]$ interactions as previously discussed in terms of Δ(M–O) values and the trans effect of the M–M subunit. It is noteworthy that the value of G' (storage modulus) is at all frequencies greater than G'' (loss modulus) for M = Cu, compared to the case of M = Mo where G' and G'' are very similar. G' is, in part, a measure of a restoring energy, and that too may reflect the greater elasticity of the $[Cu_2 \cdots O]_n$ polymer backbone.

The transition from isotropic liquid to mesophase is clearly seen in the temperature profile of the dimolybdenum compound (Figure 5), whereas within the mesophase, the viscosity increases with decreasing temperature relatively slowly for both the dicopper and the dimolybdenum complexes.

Concluding Remarks

This work represents the first complete rheological investigation of a metallomesogen. The fact that both systems exhibited significant linear viscoelasticity in the liquid-crystal state indicates that long range structural ordering must be present. In addition, the similarity to conventional polymer behavior is striking. It supports evidence to suggest that the metallomesogen systems form polymer chains in the liquid crystal state. A large viscosity value is not necessarily a drawback in display technology, as long as a great deal of reorientation is not required for the mesogen to align in response to an applied signal. In addition, comparison of the viscoelastic behavior of the $[M_2(O_2CR)_4]_n$ materials with commercial organic polymers, such as polyethylene and polypropylene, provides a convenient scale of the viscoelasticity of a discotic columnar mesogenic system. It should also be noted that the tetra(pentacosa-10,12-diynato)dicopper compound, $Cu_2(O_2CR)_4$, shows a mesophase from which highly ordered fibers of good optical quality were drawn and polymerized by low intensity UV irradiation with no detectable disruption of the ultrastructure.[17] Thus, by similar processing, access to fibers with a high degree of ordering of the M–M bond should be possible.

From this study it has been shown that the rheology of these metallomesogens in the liquid crystalline state is similar to that of conventional viscoelastic polymers such as polyethylene and polypropylene. The expectation, therefore, is that these metallomesogen materials could be processed in a way similar to that for conventional polymers to form films, fibers, or molded objects.

The viscoelastic relaxation times of these materials will range from about 10^{-3} to 10^2 s, although the internal switching times of the materials could be considerably less due to the internal mobility of the dimetal tetracarboxylates.

The rheological results reported here also bear strong comparison with that observed for certain liquid crystal micelle structures where the wormlike chains are continuously being created and destroyed.[18] The viscoelasticity of this structure has been modelled by Cates et al.,[18] and this modeling could in principle be used for these metallomesogen systems where it is believed that the chains are in a kinetic equilibrium of creation and breakage (Figure 2).

Acknowledgment. We thank the DTI, ICI, Unilever, Schlumberger and Colloid Technology Programme (M.R.M. and R.T.J.M.) and the National Science Foundation (M.H.C. and E.T.P.) for support.

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