Polymerizable Lyotropic Liquid Crystals Containing Transition-Metal and Lanthanide Ions: Architectural Control and Introduction of New Properties into Nanostructured Polymers

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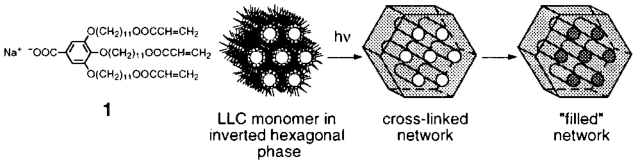
The development of synthetic materials with controlled nanostructures is currently an active area of materials research.[1] Recently, our group devised a new method for synthesizing polymer-based nanocomposites which involves the cross-linking of lyotropic (i.e., amphiphilic) liquid crystals (LLCs)[2] that adopt the inverted hexagonal phase (Scheme 1).[3,4] Inorganic[3] and organic polymer chemistry[4] can be performed inside the hydrophilic domains of these ordered assemblies, and the nanocomposites can be processed into films and fibers prior to photopolymerization.[4] The materials formed inside the periodic microdomains exhibit different properties than corresponding materials formed in bulk or in solution. The constrained environment apparently limits the degree of conversion of these materials, imparting them with different structures than those obtained in bulk.[3,4] Because of this apparent effect of reaction environment size in these systems, we sought to develop methods for varying the small-scale dimensions of these nanocomposites. The geometry of LLC phases depends greatly upon the shape of the amphiphile.[5] Amphiphiles with a small hydrophilic headgroup and a broad, wedge-like hydrophobic tail section would tend to assemble into the inverted hexagonal phase, based on straightforward packing considerations.[6] Because of the ionic nature of our monomers, the use of different metal cations might serve as a viable means of (1) modulating headgroup size and consequently the internal dimensions of the hexagonal assemblies and (2) introducing new properties into these systems.

Herein, we report the synthesis of several transition-metal and lanthanide analogues of monomer **1**[4] and the properties of the resulting cross-linked, inverted hexagonal phases. Transition-metal and lanthanide cations offer a wide range of sizes, charges (valencies), and coordination environments for potential modification of LLC headgroup size. In addition, these metal ions possess a variety of interesting properties ranging from visible absorption and fluorescence to paramagnetism that might be successfully incorporated into the resulting polymers. Thermotropic metallomesogens,[7] and, more recently, their polymerizable analogues,[8] have been well studied. However, only a small amount of research on transition-metal and lanthanide ion containing soaps[9] and LLCs[10] has been performed. To our knowledge, the effect of transition-metal and lanthanide ions on the behavior of *polymerizable amphiphiles* and their ability to form supramolecular architectures has not been investigated.

Scheme 1



To study the effect of transition-metal and lanthanide ions in our polymerizable LLC systems, the Co(II), Ni(II), Cd(II), Eu(III), and Ce(III) analogues[11] of **1** were initially synthesized by ion-exchange.[12] Elemental analysis of the neat salts indicated the presence of coordinated water molecules in all the compounds. This fact was confirmed by the presence of a weak O−H band in the 3300−3500 cm^{-1} region of their FT-IR spectra. The nature of the metal−carboxylate interaction in these compounds was investigated by examining the position and separation ($\Delta\nu$) between the antisymmetric (ν_{asym}) and symmetric (ν_{sym}) stretching bands of the carboxylate group.[13] As can be seen in Table 1, the purely ionic sodium salt **1** exhibits a single ν_{asym} band at 1574 cm^{-1} and a $\Delta\nu$ value of 154 cm^{-1}. In contrast, the divalent transition-metal analogues have two ν_{asym} bands at lower wavenumbers. This leads to smaller $\Delta\nu$ values, as the position of the ν_{sym} band[14] remains essentially unchanged. These smaller $\Delta\nu$ values are consistent with chelation of the carboxylate to the transition-metal centers.[13] The decrease in energy of the ν_{asym} band also implies weakening of the carboxylate C−O bonds and a stronger association between the carboxylate oxygens and the transition-metals. The ν_{asym} bands in the two trivalent lanthanide salts are also split and appear at even lower wavenumbers. The significantly smaller $\Delta\nu$ values are consistent with even stronger chelation/bridging between the carboxylate groups and the lanthanides.[13]

Inverted hexagonal phases of the LLCs were prepared by combining the amphiphiles with distilled water and a xylene solution of 2-hydroxy-2-methylpropiophenone (20 wt %) at a fixed composition of 85/10/5 (w/w/w) LLC/water/photoinitiator

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[1] For recent reviews on nanostructured materials synthesis, see: (a) Calvert, P.; Rieke, P. *Chem. Mater.* **1996**, *8*, 1715. (b) Wen, J.; Wilkes, G. L. *Chem. Mater.* 1667. (c) Frisch, H. L.; Mark, J. E. *Chem. Mater.* 1735. (d) Martin, C. R. *Chem. Mater.* 1739.

[2] For reviews of lyotropic liquid crystals, see: (a) Winsor, P. A. In *Liquid Crystals and Plastic Crystals*; Gray, G. W., Winsor, P. A., Eds.; Volume 1; Ellis Horwood: Chichester, 1974; Chapter 5. (b) Tiddy, G. J. T. *Phys. Rep.* **1980**, *57*, 1.

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[7] For reviews of thermotropic metallomesogens, see: (a) Hudson, S. A.; Maitlis, P. M. *Chem. Rev.* **1993**, *93*, 861. (b) Neve, F. *Adv. Mater.* **1996**, *8*, 277.

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[9] For example, see: (a) Young, S. L.; Matijevic, E. *J. Coll. Interfac. Sci.* **1977**, *61*, 287. (b) Mehrota, K. N.; Shukla, R. K.; Chauhan, M. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1825.

[10] For example, see: Holbrey, J. D.; Tiddy, G. J. T.; Bruce, D. W. *J. Chem. Soc., Dalton Trans.* **1995**, 1769, and references therein.

[11] Metal ions that form strong coordination dimers with carboxylates such as Cu(II) and Rh(II) were avoided since they typically afford thermotropic metallomesogens. See ref 7.

[12] 3,4,5-Tris(11′-acryloyloxyundecyloxy)benzoic acid[4] (1.00 g, 1.16 mmol) was dissolved in a mixture of acetone (100 mL) and methanol (10 mL). The solution was titrated by methanolic NaOH (10 wt %) until pH = 7. After 30 min of stirring, 1.0 equiv of the appropriate metal nitrate or chloride was added slowly to the solution. After stirring for 2 h, the solvent was removed in vacuo, and the solid was washed with distilled water (3 × 20 mL). The residue was then redissolved in acetone (20 mL), filtered, and concentrated. After suspension in additional acetone (20 mL), the solid was dried in vacuo for 12 h to remove residual water (ca. 80% yield). The identities of the metal salts were verified by ^{1}H NMR spectroscopy, FT-IR spectroscopy, and elemental analysis. (The ^{1}H NMR spectra of the paramagnetic salts exhibited poor resolution.)

[13] Deacon, B. G.; Phillips, J. R. *Coord. Chem. Rev.* **1980**, *33*, 227.

[14] The carboxylate ν_{sym} band is a distinct shoulder of an acrylate ester band at 1408 cm^{-1}. The acrylate ester bands do not change with variation in metal cation.

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Table 1. IR Data for the Carboxylate Stretching Bands of Neat Analogues of **1**[a]

metal ion	ν_{asym} (cm^{-1})	ν_{sym} (cm^{-1})	$\Delta\nu$ (cm^{-1})
Na$^+$	1574	1420	154
Co(II)	1577, 1551	1425	152, 126
Ni(II)	1576, 1551	1423	153, 128
Cd(II)	1575, 1552	1424	151, 128
Eu(III)	1558, 1525	1429	129, 96
Ce(III)	1560, 1526	1429	131, 97

[a] Spectra taken on Ge crystals.

Table 2. X-ray Diffraction Data for the Cross-Linked Inverted Hexagonal Phases of Analogues of **1**[a]

metal ion (radius, Å)	d_{100} (Å)	d_{110} (Å)	d_{200} (Å)
Na$^+$ (0.97)	34.5	20.2	17.5
Ni(II) (0.69)	35.8	20.8	18.2
Co(II) (0.72)	35.6	20.3	17.7
Cd(II) (0.97)	35.0	20.6	18.0
Eu(III) (0.98)	30.2	17.6	15.7
Ce(III) (1.07)	30.9	17.8	15.5

(a) The samples all undergo a 4% contaction in the unit cell dimensions upon cross-linking.

solution. X-ray diffraction analysis of the mixtures yielded Bragg spacings with the 1, $1/\sqrt{3}$, $1/\sqrt{4}$, ... ratio (d_{100}, d_{110}, d_{200}, ...) indicative of a hexagonal assembly.[4] The mixtures were cross-linked at ambient temperature with retention of phase microstructure by irradiating the samples overnight with 365 nm light under nitrogen. The extent of polymerization in these systems was determined by monitoring the loss of acrylate bands (1637 and 810 cm^{-1}) using FT-IR spectroscopy. The X-ray diffraction spacings of the cross-linked LLC phases are listed in Table 2 as a function of the size and charge of the associated metal ion. Two general observations can immediately be made from these data: The first is that LLCs containing metal ions of the same charge exhibit inverted hexagonal phases with very similar d_{100} spacings, regardless of metal ion size.[15] The second is that LLC phases of the trivalent lanthanide salts exhibit significantly smaller unit cell dimensions than their divalent transition-metal analogues. This reduction in unit cell size correlates very well with the differences observed by FT-IR spectroscopy in the nature of the metal−carboxylate interaction between these two sets of compounds. It can be rationalized that the stronger lanthanide−carboxylate coordinative interactions decrease the overall size of the amphiphile headgroup, resulting in more efficient packing. It should be noted that monomer **1**, with a monovalent sodium ion, exhibits diffraction spacings very similar to LLCs containing much smaller, divalent transition-metals. This behavior can be attributed to the fact that carboxylate−alkali metal ion interactions are primarily ionic in nature, whereas carboxylates can form stronger coordinative bonds and chelate with d- and f-block ions.[13] These results demonstrate that (1) the dimensions of the inverted hexagonal phase of **1** can be modulated by simply changing the nature of the metal ion[16] and (2) the nature of the metal−carboxylate interaction is more important in determining the overall size of the amphiphile headgroup than the size of the metal counterion.[17]

Incorporation of transition-metal and lanthanide ions also introduces new properties into the nanostructured polymer networks. For example, the polymers possess the absorption characteristics of the incorporated metal ions. The Co(II), Ni(II), and Ce(III) networks are dark green, pale green, and bright yellow, respectively, whereas the Cd(II) and Eu(III) networks are colorless. The Ni(II), Co(II), and Ce(III) networks also are paramagnetic as result of unpaired electrons on the metal centers. The polymerized Ni(II), Co(II), and Ce(III) LLC phases were found to have mass susceptibilities of 3.7×10^{-6}, 5.9×10^{-6}, and 2.1×10^{-6} c.g.s units, respectively.[18] In addition, the Eu(III) network exhibits intense emission bands (593 and 615 nm) in the 400−700 nm region of the visible spectrum when excited with 370 nm light. This phenomenon indicates that the Eu(III) ions in the channels have very few water molecules in their primary coordination sphere since coordinated water quenches Eu(III) fluorescence.[19]

To take advantage of the interesting optical properties of this new material, a poly(*p*-phenylenevinylene) (PPV) nanocomposite[4] was formed using the Eu(III) salt of **1**. A 0.6 wt % aqueous solution of poly(*p*-xylylenetetrahydrothiophenium chloride)[20] was used to form the inverted hexagonal phase with the Eu(III) salt of **1**. This mixture was photopolymerized and then heated at 220 °C in vacuo for 8 h to form PPV in situ. The resulting hexagonal nanocomposite exhibits a new intense emission band centered at ca. 670 nm that is absent in the emission profiles of PPV nanocomposites made with **1**,[4] and Eu(III) LLC networks containing only water in the channels. This new emission band was also not observed in PPV samples formed in the presence of Eu(III) nitrate as a control experiment. The presence of this new band suggests interaction between the Eu(III) cations and PPV chains in the periodic nanochannels and possibly energy transfer between the two components. The behavior of encapsulated PPV chains with other lanthanide and transition-metal LLC analogues is currently under investigation.

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Supporting Information Available: Details on the synthesis and cross-linking of transition-metal and lanthanide analogues of **1**; selected X-ray diffraction and FT-IR spectra; magnetic susceptibility data; and fluorescence spectra of a Eu(III) LLC network and a Eu(III) LLC−PPV composite (8 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[15] LLC mixtures were compared at the same weight composition because the molecular weights of the LLCs are determined primarily by their large organic component, and the self-assembly process depends primarily on the ratio of organic to water.

[16] The dimensions of the inverted hexagonal phase can also be controlled by varying monomer tail length. These results will be reported separately.

[17] The nature and strength of the metal−carboxylate interactions are also expected to affect the overall geometry of the LLC salts, in addition to the size of the headgroups. The precise molecular structures of the complexes have not been ascertained due to difficulties in obtaining single crystals of these compounds.

[18] Cross-linked **1** is diamagnetic, and the cross-linked Cd(II) and Eu(III) salts are weakly paramagnetic. Molar susceptibilities and magnetic moments are not reported because the networks are mixtures, not pure compounds.

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