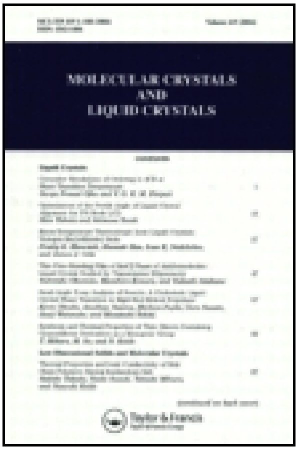


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis of Functional, Nanostructured Composites and Catalysts using Polymerizable Lyotropic Liquid Crystals

Douglas L. Gin [a], Hai Deng [a], Walter M. Fischer [a], David H. Gray [a], Elizabeth Juang [a], Esther Kim [a] & Ryan C. Smith [a]

[a] Dept. of Chemistry, University of Califrnia, Berkeley, CA, 94720, USA

Version of record first published: 24 Sep 2006

To cite this article: Douglas L. Gin, Hai Deng, Walter M. Fischer, David H. Gray, Elizabeth Juang, Esther Kim & Ryan C. Smith (1999): Synthesis of Functional, Nanostructured Composites and Catalysts using Polymerizable Lyotropic Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 332:1, 423-429

To link to this article: http://dx.doi.org/10.1080/10587259908023787

Mol. Cryst. Liq. Cryst., 1999, Vol. 332, pp. 423-429
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Synthesis of Functional, Nanostructured Composites and Catalysts using Polymerizable Lyotropic Liquid Crystals

DOUGLAS L. GIN, HAI DENG, WALTER M. FISCHER,
DAVID H. GRAY, ELIZABETH JUANG, ESTHER KIM and
RYAN C. SMITH

Dept. of Chemistry, University of California, Berkeley, CA 94720, USA

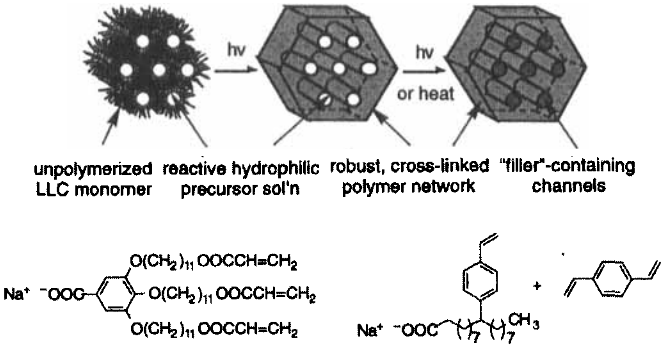
We have developed a general scheme for synthesizing nanostructured, polymer-based materials with hexagonal symmetry. This strategy involves the cross-linking of lyotropic liquid crystal monomers that form the inverted hexagonal mesophase in the presence of pure water or reactive solutions. Depending on the nature of the hydrophilic solution, inorganic or organic solid-state fillers can be formed inside the channels of these ordered templates to afford a variety of functional nanocomposites. In addition, the nanostructured polymer networks can also act as heterogeneous catalysts for organic reactions (i.e., organic "analogs" to molecular sieves). The design, synthesis, and control of these materials will be described. The effect of the nano-architecture on their properties and reactivity will also be discussed.

Keywords: lyotropic liquid crystals; cross-linked; nanocomposite; catalyst

INTRODUCTION

The development of synthetic materials with controlled nanostructures is currently an active area of scientific research encompassing many disciplines ranging from chemistry to engineering[1]. Recently, we developed a novel strategy for synthesizing a new class of nanostructured, polymer-based materials with hexagonal symmetry by taking advantage of the self-assembly properties of *polymerizable*, lyotropic liquid crystals[2] (LLCs) (i.e., amphiphiles)[3,4]. This strategy involves the following steps: (1) Design and synthesis of cross-linkable LLCs that self-assemble into the inverted hexagonal phase in the presence of pure water or hydrophilic reagents. (2) Photopolymerization of the matrix monomers into a heavily cross-linked network to lock-in the microstructure. (3) In situ conversion of the precursors inside the nanochannels into solid-state "filler" materials (Scheme 1).

SCHEME 1 Synthesis of hexagonal nanocomposites.



1 **2**

Using LLCs **1** and **2**, this synthesis approach yields robust, organic networks possessing hexagonally-packed hydrophilic channels that are approximately 2 nm in diameter with an interchannel spacing of 4.1 nm, according to X-ray diffraction and TEM studies. Silica particles have successfully grown inside the nanostructured matrices[3]. Additionally, the intrinsically conducting polymer, poly(*p*-phenylenevinylene) (PPV), has been grown inside the cross-linked inverted hexagonal phase[4]. The materials formed inside the periodic microdomains exhibit different properties than corresponding materials formed in bulk or in solution. The dimensionally constrained environment apparently limits the degree of conversion of these materials, thereby imparting them with different structures, and consequently different properties, than that obtained in bulk[3,4].

Herein, we present the extension of this LLC polymer technology to two new areas of application. The first area is the synthesis of nanostructured polymer composites with novel magnetic and optical properties using transition-metal and lanthanide analogs of the monomers. The second area is the use of the cross-linked inverted hexagonal phase as nanoporous, heterogeneous catalysts for organic reactions (i.e., "organic analogs to molecular sieves").

EXPERIMENTAL SECTION

Materials and Instrumentation

Monomers **1** and **2** were synthesized and cross-linked in the inverted hexagonal phase according to literature procedures[3,4]. Transition-metal and lanthanide salts of **1** and **2** were synthesized by ion exchange with the appropriate metal nitrate or chloride as described previously.[5,6] Na-zeolite

Y was obtained from Zeolyst International, Inc. Na-MCM-41 was obtained from Dr. Jacek Klinowski (Cambridge University). FT-IR spectra were recorded using a Perkin–Elmer 1616 spectrometer on films cast on Ge crystals. Low-angle X-ray diffraction studies were performed using an Inel CPS 120 powder diffraction system employing Cu K_α radiation. Magnetic susceptibility measurements were performed using a Johnson–Matthey balance. Fluorescence measurements were performed on a Spex Fluoromax 2. Gas chromatography was performed using a Hewlett–Packard 5890 GC.

Typical Heterogeneous Catalysis Experiment

Ethyl cyanoacetate (0.254 mL, 2.50 mmol), benzaldehyde (0.266 mL, 2.50 mmol), and *n*-dodecane (0.142 mL, 0.625 mmol) were added to THF (5 mL) under N_2. The reaction mixture was placed in an oil bath at 67 °C and then 5 mol % of cross-linked **2** in the inverted hexagonal phase (based on the number of sodium carboxylates) was added as a fine powder. Aliquots taken at regular time intervals were centrifuged at 2500 rpm and filtered through glass fiber. This solution was diluted in THF and analyzed quantitatively by gas chromatography using dodecane as an internal standard.

RESULTS AND DISCUSSION

Novel Nanocomposites via Transition-Metal and Lanthanide Ion Containing LLC Monomers

The geometry of LLC phases depends greatly upon the shape of the amphiphile[5]. 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. In order to study the effect of transition-metal and lanthanide ions in our polymerizable LLC systems, several transition-metal and lanthanide analogs of **1** and **2** were prepared by ion-exchange[6,7].

The X-ray diffraction spacings of the cross-linked LLC phases of different analogs of **1** and are listed in Tables I and II respectively, as a function of the size and charge of the metal ion. As can been seen from Tables I and II, increasing metal ion radius does not afford larger unit cell dimensions as expected. Detailed FT-IR studies indicate that the strength of the metal–carboxylate interaction for analogs of **1** is more important in determining the overall size of the hydrophilic headgroup and the dimensions of the inverted hexagonal phase, than the size of the metal counterion[6]. For analogs of **2**, the nature of the metal ion also has a pronounced effect on the type of LC phase preferred at room temperature.

Table I X-ray diffraction data for the cross-linked inverted hexagonal phases of analogs of **1** (85/5/10 (w/w/w) LLC/H_2O/initiator solution).

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

Table II X-ray diffraction data for the cross-linked LLC phases of analogs of **2** (87/7/5/1 (w/w/w/w) LLC/divinylbenzene/H_2O/initiator.

Metal ion (radius, Å)	Phase	d_{100}(Å)	d_{110}(Å)	d_{200}(Å)	d_{210}(Å)
Na^+ (0.97)	Inv. hex.	36.2	20.9	18.3	13.6
K^+ (1.33)	Lamellar	37.2	19.6	13.2	9.91
Ca(II) (0.99)	Inv. hex.	31.9	18.4	16.2	12.0
Co(II) (0.72)	Inv. hex.	29.6	17.3	15.0	11.4
Mn(II) (0.80)	Inv. hex.	29.0	17.0	14.7	11.1
Cd(II) (0.97)	Inv. hex.	30.0	17.1	15.0	11.3
Cu(II) (0.72)	Col. hex.	22.6	13.2	11.5	

The 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 Ni(II), Co(II), and Ce(III) networks also are paramagnetic as result of unpaired electrons on the metal centers. For example, the polymerized inverted hexagonal phases of the Ni(II), Co(II), and Ce(III) salts of **1** 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[6]. In addition, the Eu(III) network of **1** exhibits intense, sharp emission bands (593 and 615 nm) characteristic of Eu(III) ions when excited with 370 nm light. When a 0.6 wt % aqueous solution of PPV precursor was used to form the inverted hexagonal phase with the Eu(III) salt of **1**, the resulting hexagonal nanocomposite exhibited a new intense emission band centered at ca. 670 nm. This 670 nm band is absent in the emission profiles of pure PPV, PPV nanocomposites made with the sodium salt **1**[4], and LLC networks of the Eu(III) salt of **1** containing only water in the channels. This new 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 and possibly exciplex formation between the Eu(III) cations and PPV chains in the periodic nanochannels[6].

In order to demonstrate that the cross-linked metallomesogens could also function as templates for forming new filler materials, the cross-linked

Cd(II) salt of **2** was exposed to H_2S gas to generate CdS nanoparticles within the hydrophilic channels[7]. After 1 h of H_2S exposure, UV-visible characterization of the sample revealed the presence of a new intense absorption band centered at 380 nm with an absorption threshold at 465 nm. Based on correlations of CdS particle size with UV-visible absorption features[8], CdS particles with diameters of 40 Å or less were formed.

Heterogeneous Catalysis with the Cross-linked Inverted Hexagonal Phase

Molecular sieves such as zeolites are able to act as efficient, highly selective heterogeneous catalysts for a variety of organic reactions by localizing reactant molecules in their 3–10 Å diameter pores and providing a high local concentration of active sites (typically acidic or basic)[9]. In addition, the strong electric fields in the nanochannels, together with electronic confinement of the guest molecules, contribute to pre-activation of the reactants[9]. Unfortunately, pore size tunability and processability in zeolites are extremely difficult. In 1992, Mobil developed a new family of synthetic molecular sieves, named MCM-41, with a one-dimensional hexagonal channel structure and tunable pore sizes in the 20–100 Å range[10]. Unlike zeolites which are crystalline materials, these "mesoporous" sieves are amorphous, silicate-based networks formed by sol gel condensation around a sacrificial organic surfactant template. A variety of active sites can be incorporated into these materials through chemical modification, but mesoporous sieves are generally not as reactive as zeolites[9,11]. The channel walls of MCM-41 are amorphous in nature, and it is difficult to exclusively concentrate active sites into their interiors. Based on the structural and dimensional similarities of our cross-linked inverted hexagonal phases to inorganic zeolites and mesoporous sieves, we rationalized that our LLC networks might be able to act as heterogeneous catalysts as well. In addition, these organic networks may offer unique advantages, such as processability prior to photo-cross-linking[3,4], and the potential for enhanced reactivity due to the fact that the ionic functional groups of the system are exclusively concentrated in the walls of the channels.

Since the ionic functionality within the channels of our LLC networks are slightly basic sodium carboxylate groups, they were initially tested as heterogeneous base catalysts for organic reactions. Previous studies with the basic forms of zeolite Y and MCM-41 used the base-catalyzed Knoevenagel condensation of ethyl cyanoacetate and benzaldehyde as a platform to gauge activity. Corma et al. found that sodium-exchanged zeolite Y (Na-zeolite Y) afforded 19% conversion to the condensation product after 2 h when an equimolar solution of the two reagents was heated at 140 °C[12]. Kloetstra et al. found that sodium exchanged MCM-41 (Na-MCM-41) yielded ~94% conversion after 3 h in H_2O at 100 °C[13]. More recently, Macquarrie et al. found that amine-derivatized MCM-41 (NH_2-MCM-41) afforded 94% conversion of the Knoevenagel reaction after 36 h in cyclohexane[14]. Using the conditions specified by Kloetstra, the cross-linked hexagonal phase of **2** afforded 94% conversion after just 15 min in refluxing water.

In order to slow down the reaction rate and compare several of the heterogeneous catalysts under the same conditions, more detailed comparisons were performed in THF. With refluxing THF as the solvent, Na-zeolite Y and Na-MCM-41 exhibited negligible activity. In contrast, the cross-linked inverted hexagonal phase of **2** afforded 87% condensation of ethyl cyanoacetate and benzaldehyde after 7 h under the same conditions (Figure 1).

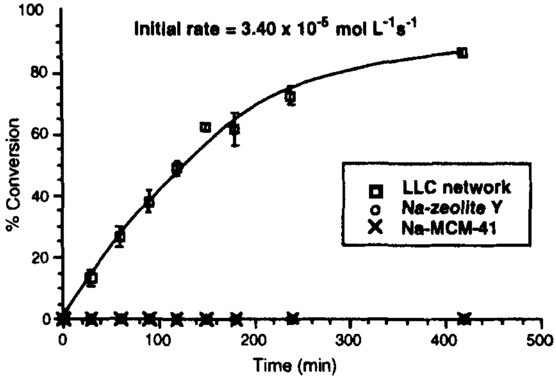


FIGURE 1 Kinetics of heterogeneous base catalysts in THF at 67 °C.

This enhanced activity of our LLC network was confirmed by a number of control experiments. Initial experiments revealed that differences in catalyst particle size and stirring rate were not responsible for the observed differences in activity between the LLC network and Na-zeolite Y and Na-MCM-41. Control experiments were performed to confirm that residual H_2O was not playing a role in the observed activity of our catalyst. The addition of H_2O to a solution of the two substrates in dry THF at 67 °C did not result in any conversion to the desired product. Experiments were also performed to confirm that the observed catalytic activity of cross-linked **2** was not simply due to the presence of surface carboxylates but rather to the high local concentration of carboxylate groups in the nanochannels. A control reaction with 5 mol % powdered sodium acetate gave some conversion, as expected, but at 1/3 the initial rate as that observed with cross-linked **2**. Although recyclability experiments with washed LLC network showed a 30% decrease in initial rate, the recycled cross-linked **2** is able to catalyze the Knoevenagel condensation with almost *twice* the initial rate of an equimolar amount of sodium acetate under identical conditions. Extraction studies suggest that leaching of residual soluble, unpolymerized monomer may account for the slightly lower activity of the washed LLC network. These results confirm that the enhanced base catalysis observed with the cross-linked LLC phase of **2** is not an artifact arising from external factors or experimental design.

SUMMARY

The cross-linking of LLCs in the inverted hexagonal phase generates ordered polymer networks that exhibit novel properties ranging from optical emission, paramagnetism, and catalytic activity, as a result of their chemical composition and engineered nano-architecture.

Acknowledgments

Financial support for this work was provided by the National Science Foundation (DMR-9625433), the Office of Naval Research (N00014-97-1-0207), the U.S. Dept. of Energy (DE-AC03-76SF00098), and the Exxon Education Fund. D.L.G. thanks 3M for an Untenured Faculty Award and Raychem for a research gift. R.C.S. thanks Chevron for a predoctoral fellowship. The authors also thank Zeolyst International, Inc. for samples of Na-zeolite Y, and Dr. Jacek Klinowski for samples of Na-MCM-41.

References

[1] A. H. Heuer, D. J. Fink, V. J. Laraia, J. L. Arias, P. D. Calvert, K. Kendall, G. L. Messing, J. Blackwell, P. C. Rieke, D. H. Thompson, A. P. Wheeler, A. Veis, and A. I. Caplan, *Science,* **255,** 1098 (1992).
[2] P. A. Winsor, in *Liquid Crystals and Plastic Crystals;* edited by G. W. Gray and P. A. Winsor (Ellis Horwood, Chichester, 1974), Volume 1, Chap. 5.
[3] D. H. Gray, S. Hu, E. Juang, and D. L. Gin, *Adv. Mater.,* **9,** 731 (1997).
[4] R. C. Smith, W. M. Fischer, and D. L. Gin, *J. Am. Chem. Soc.,* **119,** 4092 (1997).
[5] H. Deng, D. L. Gin, and R. C. Smith, *J. Am. Chem. Soc.,* **120,** 3522 (1998).
[6] D. H. Gray and D. L. Gin, *Chem. Mater.,* in press.
[7] J. N. Israelachvili, *Intermolecular and Surface Forces with Applications to Colloidal and Biological Systems* (Academic Press, London, 1985), pp. 255–258.
[8] M. Moffit, L. McMahon, V. Pessel, and A. Eisenberg, *Chem. Mater.,* **7,** 1185 (1995).
[9] A. Corma, *Chem. Rev.,* **97,** 2373 (1997).
[10] C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck., *Nature,* **359,** 710 (1992).
[11] A. Sayari, *Chem. Mater.,* **8,** 1840 (1996).
[12] A. Corma, V. Fornés, R. M. Martin-Aranda, H. García, and J. Primo, *Appl. Catal.,* **59,** 237 (1990).
[13] K. R. Kloetstra and H. van Bekkum, *J. Chem. Soc., Chem. Commun.,*1005 (1995).
[14] D. J. Macquarrie and D. B. Jackson, *Chem. Commun.,* 1781 (1997).