

Crosslinkable Bicontinuous Cubic Assemblies via Mixtures of Gemini Amphiphiles and Butyl Rubber

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Report Documentation Page

Form Approved
OMB No. 0704-0188

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1. REPORT DATE 2004	2. REPORT TYPE	3. DATES COVERED 00-00-2004 to 00-00-2004	
4. TITLE AND SUBTITLE Crosslinkable Bicontinuous Cubic Assemblies via Mixtures of Gemini Amphiphiles and Butyl Rubber		5a. CONTRACT NUMBER	
		5b. GRANT NUMBER	
		5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)		5d. PROJECT NUMBER	
		5e. TASK NUMBER	
		5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) TDA Research Inc,12345 West 52nd Avenue,Wheat Ridge,CO,80033-1916		8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)	
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited			
13. SUPPLEMENTARY NOTES The original document contains color images.			
14. ABSTRACT			
15. SUBJECT TERMS			
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified	
			18. NUMBER OF PAGES 16
			19a. NAME OF RESPONSIBLE PERSON

Uses of Butyl Rubber (BR) as barrier material fabric

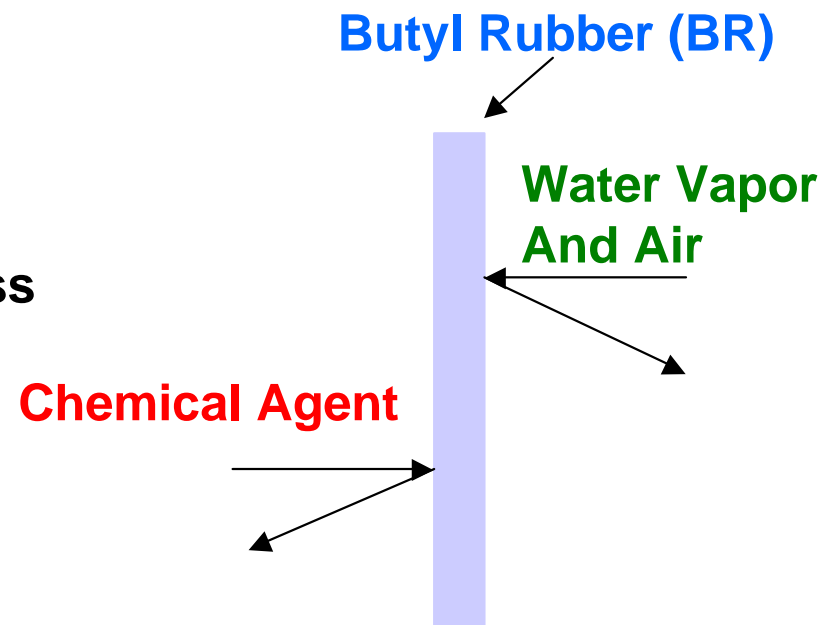
Advantages:

- Low permeability toward organic solvents, and reactive chemicals
- Excellent chemical resistance
- Low cost

Disadvantages:

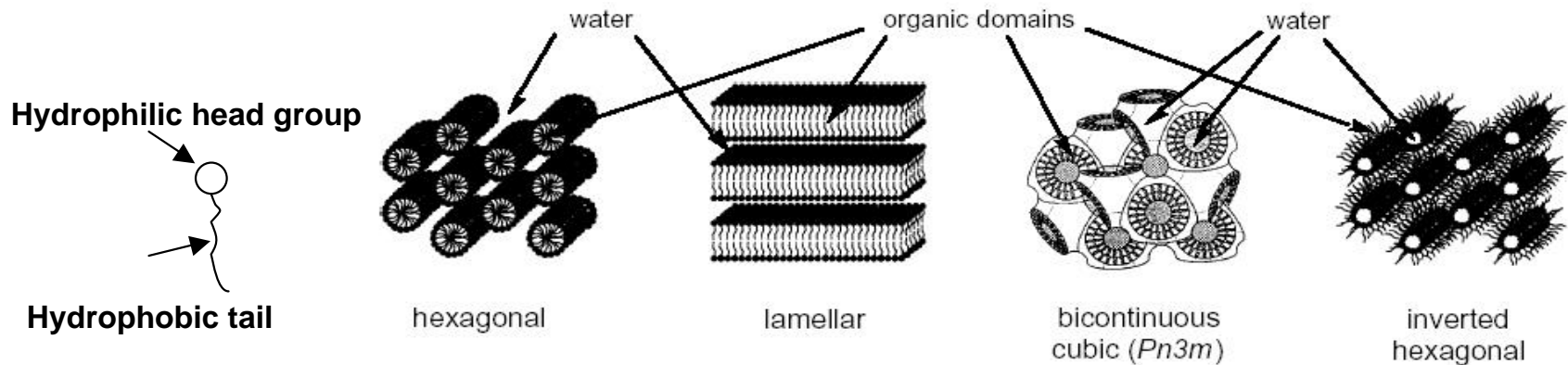
- Lack of permeability of air and water vapor

⇒ Development of fatigue and heat stress in wearer



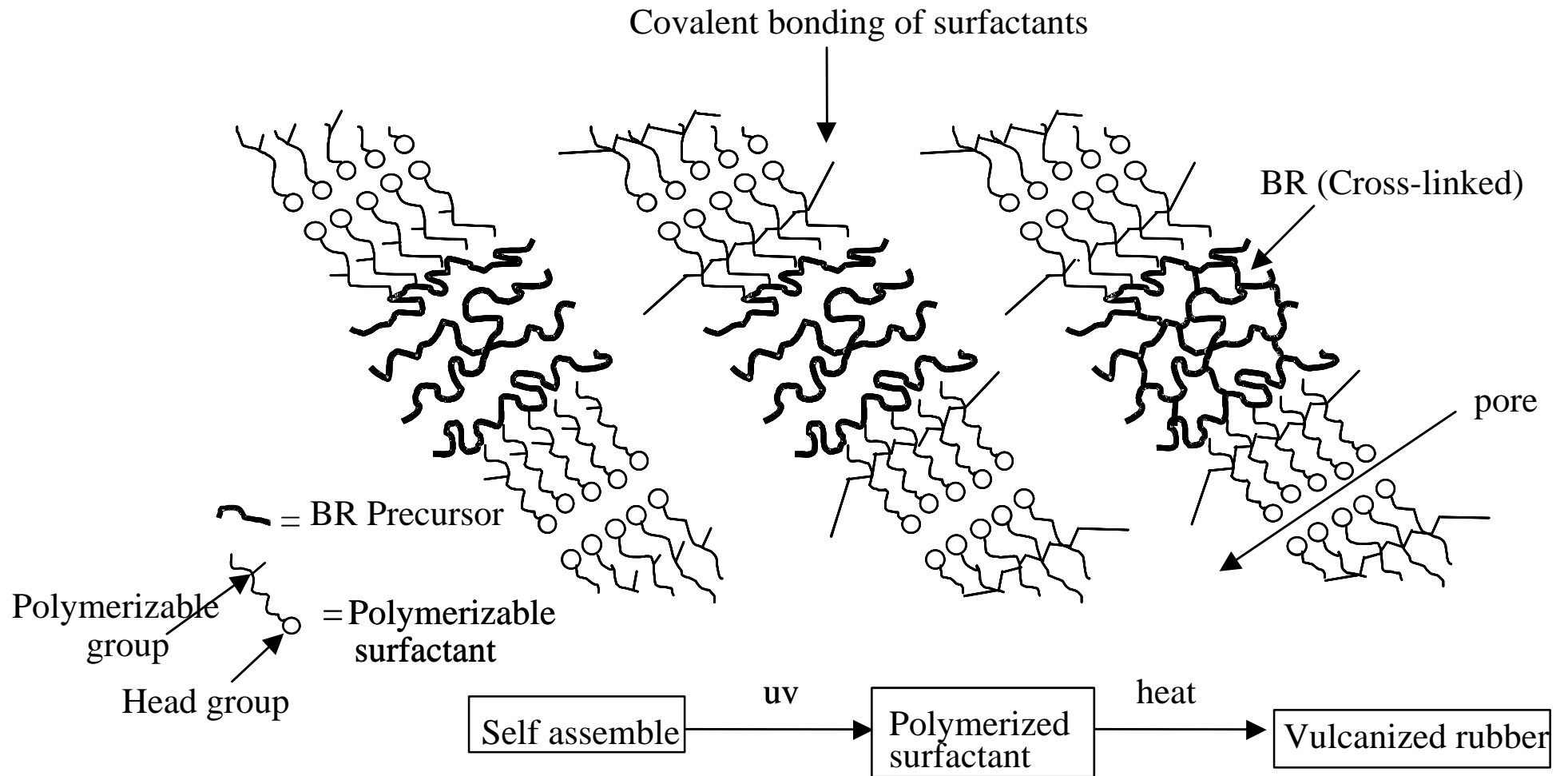
Overview of Lyotropic Liquid Crystals (LLCs)

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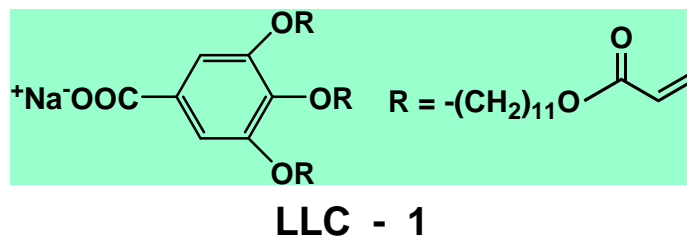
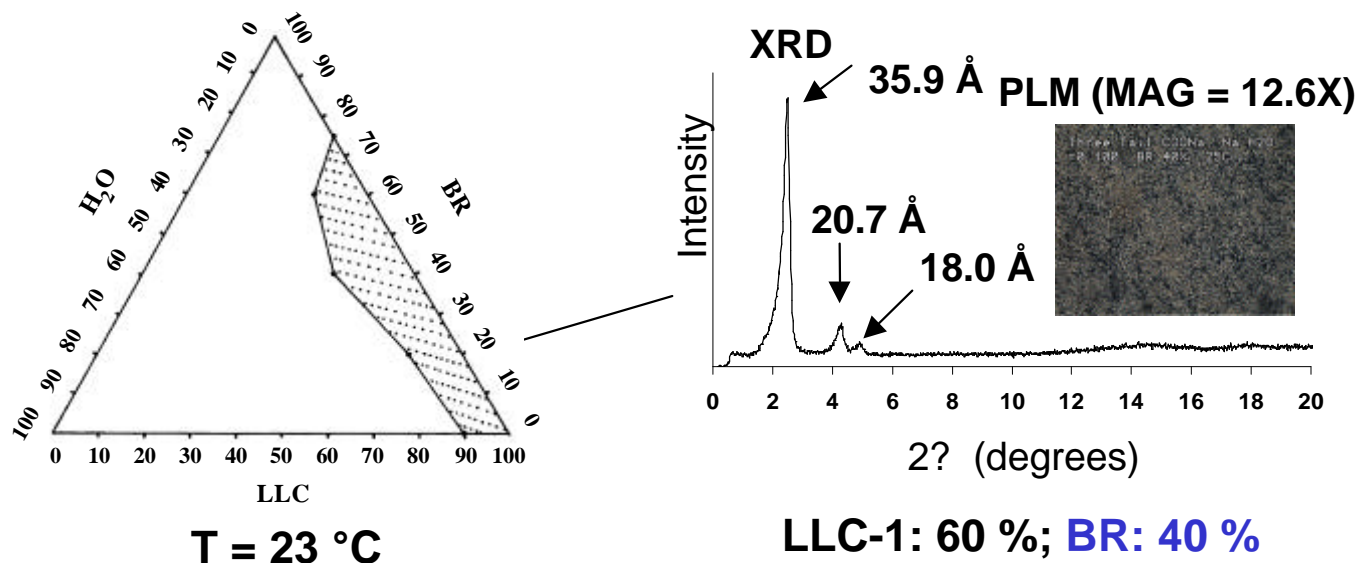
- LLCs are amphiphilic molecules that can self-assemble into nanoporous structures.
- Multiple phases: hexagonal (H_I), lamellar (L), bicontinuous cubic (Q), inverted hexagonal (H_{II}), etc.
- Robust nanoscopic architected material can be obtained upon crosslinking.
- Application: nanoscale reaction, separation, transportation, etc

Approach: LLCs and BR Composites



Prior Work in H_{II} Phase of LLC-1 / BR System

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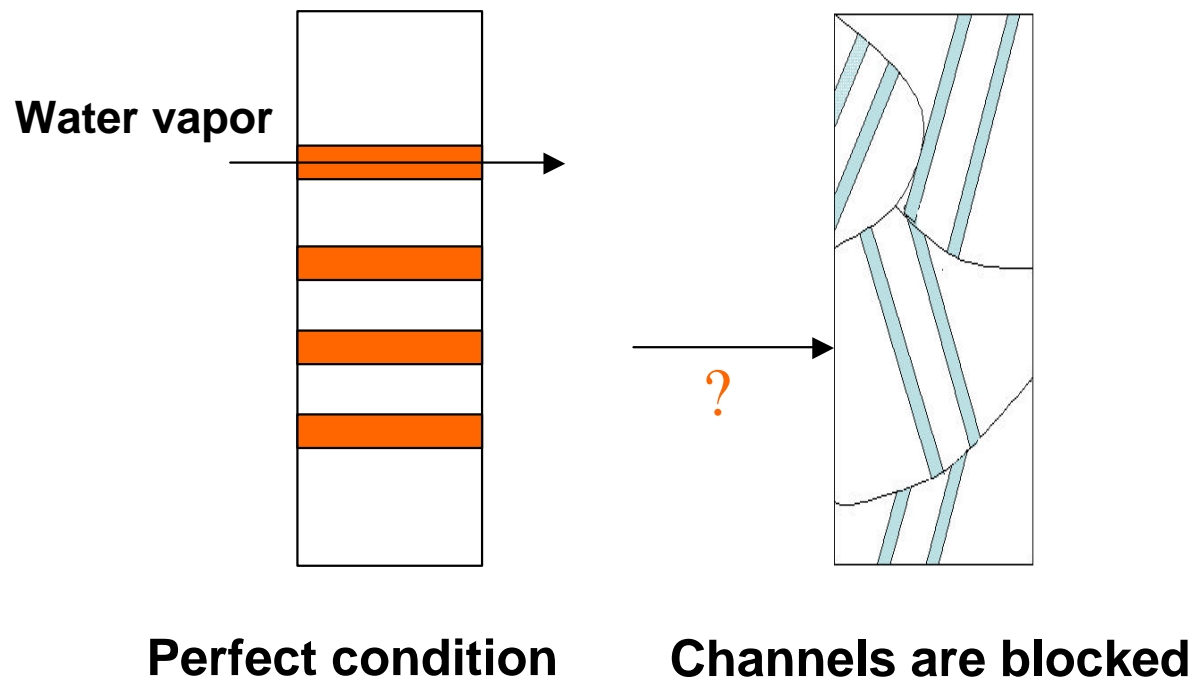


- LLC-1 retains H_{II} phase even with BR content as high as 75 wt %.
- Retention of H_{II} structure upon photo-initiated radical polymerization.
- Water vapor permeable and chemical agent simulant CEES impermeable.

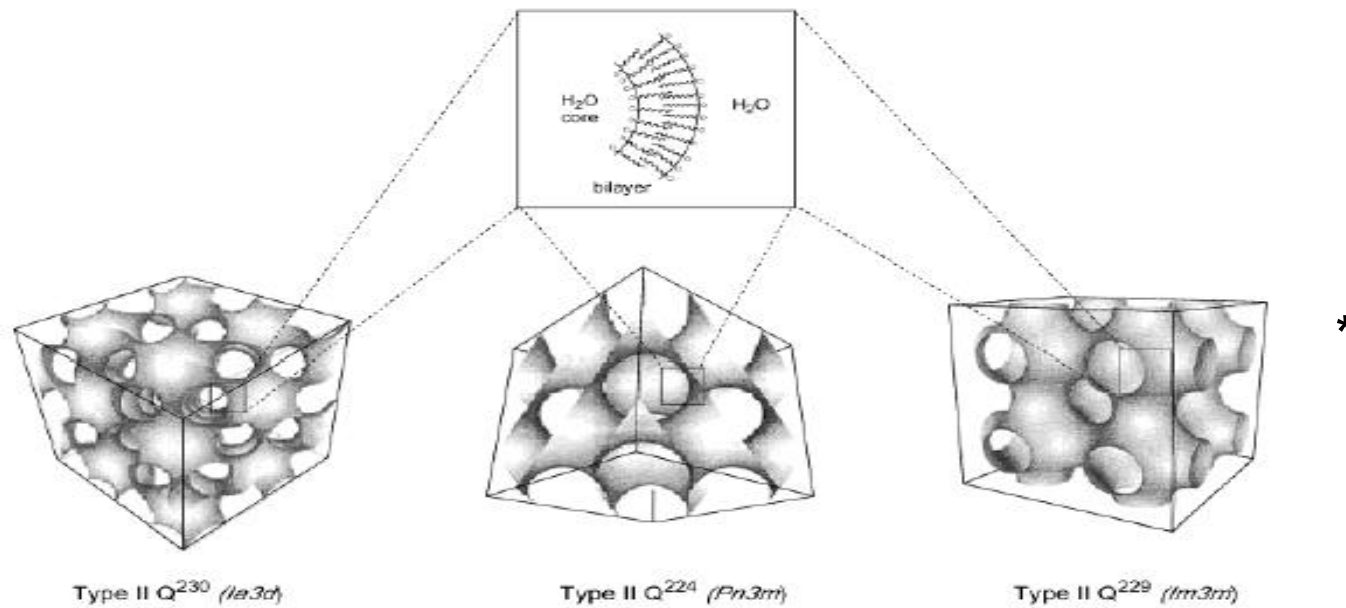
Done by Dr. Jizhu Jin

Problems in LLC-1/BR Composites

- Requires pore alignment and continuity through material for maximum transportation.
- The acrylate ester tail is not hydrolytically stable.



New objective: Bicontinuous Cubic Phases



- Image of polarized light microscopy (PLM): **Black** (Pseudo isotropic)
- X-Ray diffraction(XRD): D-spacing proceeds in the ratio:

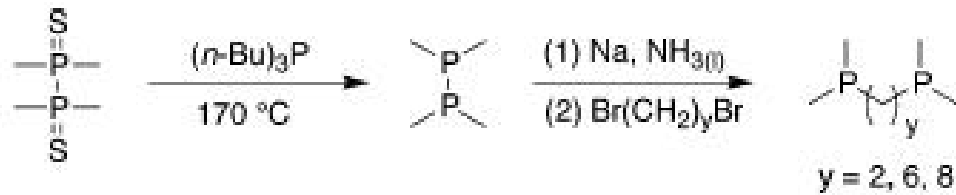
$$1 : 1/2^{1/2} : 1/3^{1/2} : 1/4^{1/2} : 1/5^{1/2} : 1/6^{1/2} : 1/7^{1/2} : 1/8^{1/2} \dots$$

Advantage:

3-dimensional network of pores: eliminate the alignment problem

*Benedicto, A.D.; O'Brien, D.F. *Macromolecules*, **1997**, 30, 3395-3402

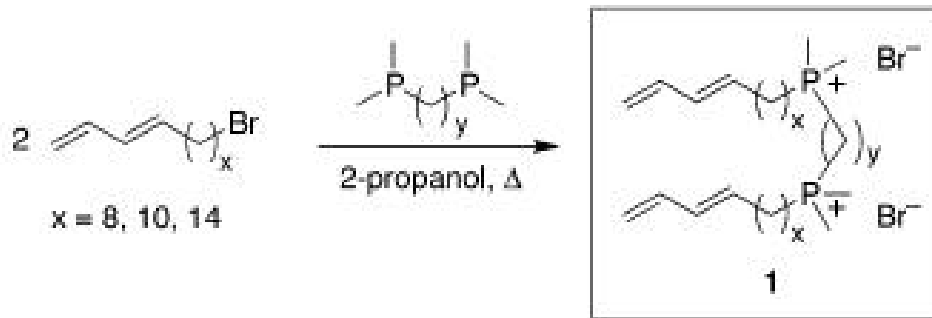
Prior Work on Bicontinuous Cubic Phase LLC Monomers 8



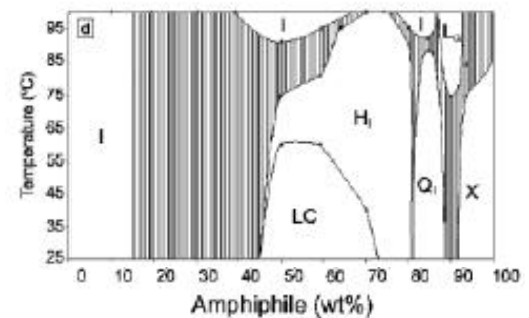
1a: $x = 8; y = 2$
1b: $x = 8; y = 6$
1c: $x = 8; y = 8$

1d: $x = 10; y = 2$
1e: $x = 10; y = 6$
1f: $x = 10; y = 8$

1g: $x = 14; y = 2$
1h: $x = 14; y = 6$
1i: $x = 14; y = 8$



Phase diagram of monomer 1e*



Disadvantage:

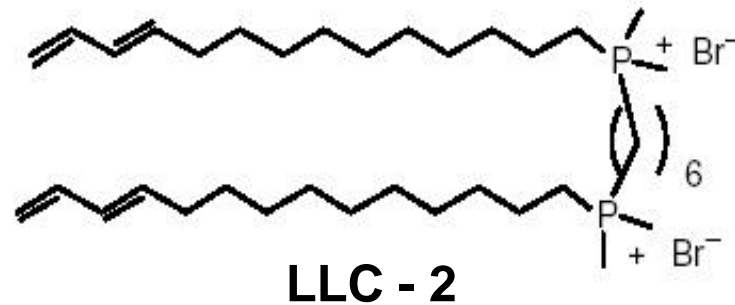
- Brittle after cross-linking in pure form

⇒ Difficult to make barrier material

*Pinzola, B.A.; Jin, J.Z.; Gin, D.L. *J.Am.Chem.Soc.* 2003, 125, 2940-2949

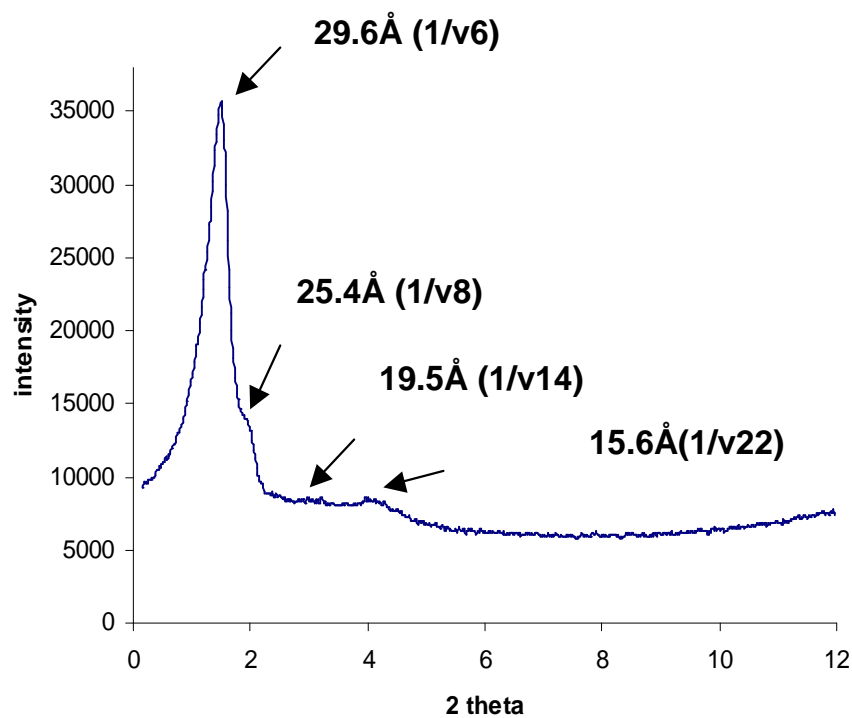
Research Objectives

- **Characterize composition and temperature ranges of LLC BR mixtures and specifically identify the bicontinuous cubic phase region**
- **Produce films of “breathable” cubic phase LLC- BR composites**
- **Characterize and optimize the polymerization of the surfactants and the vulcanization of the BR.**
- **Test the films for permeation of water vapor and rejection of chemical agent stimulants.**

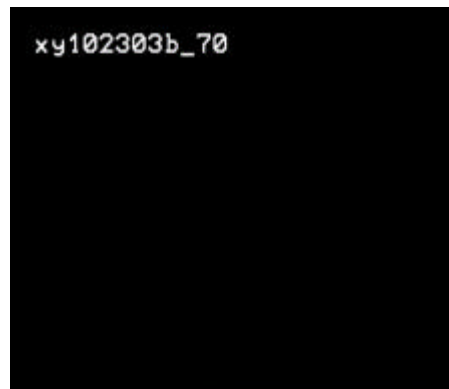


Blending Procedure

- LLCs and H₂O were mixed in a glass vial and centrifuged three times (3800 RPM, 15 min.).
- Add the LLC mixture obtained in the above step with BR precursor solution (10 wt. % in hexane) and then mix/centrifuge three times (3800 RPM, 15 min.).
- Equilibrate above mixture for at least 16 hours at room temperature for testing.



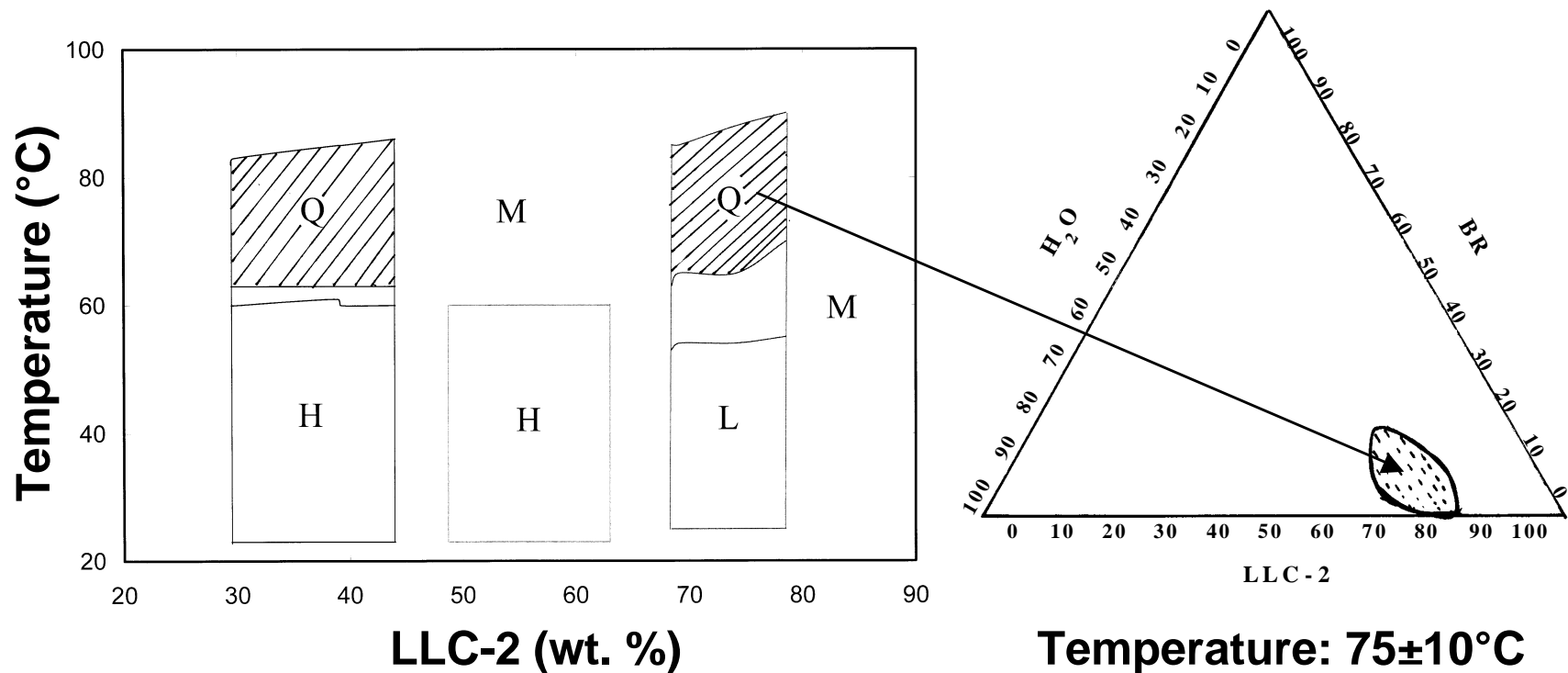
PLM (MAG = 12.6X)



69.1% LLC-2 26.9% H₂O 4.0% BR

- **Proof-of-concept for blending LLC with BR precursor with retention of cubic structure.**

Preliminary Phase Diagram of LLC - BR Composites

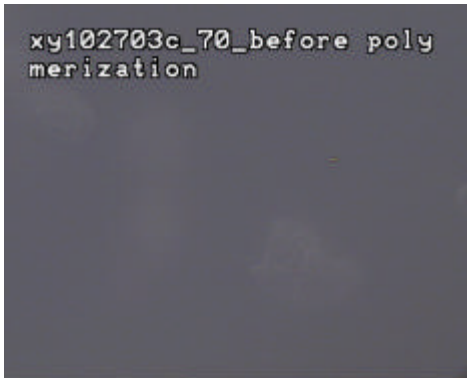


Q: Cubic; H: Hexagonal; L: Lamellar; M: Mixture;
Other regions are unidentified.

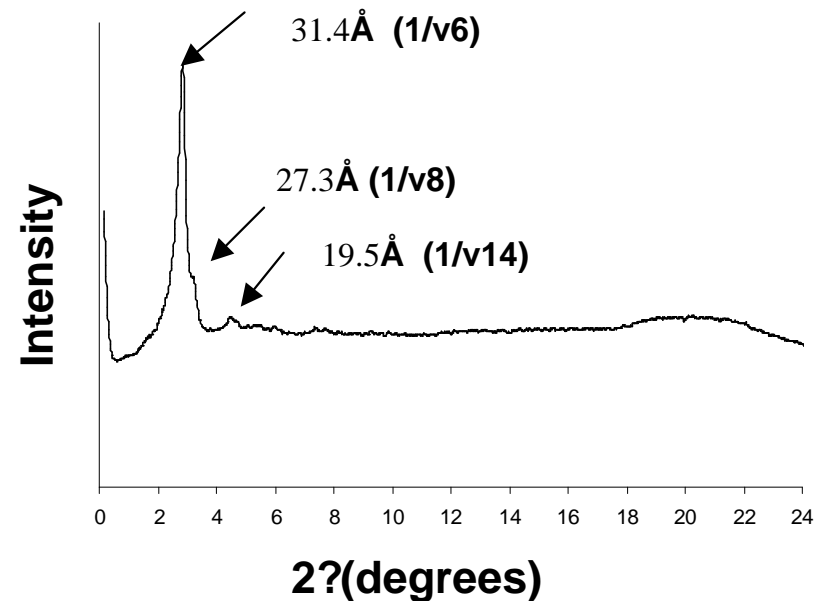
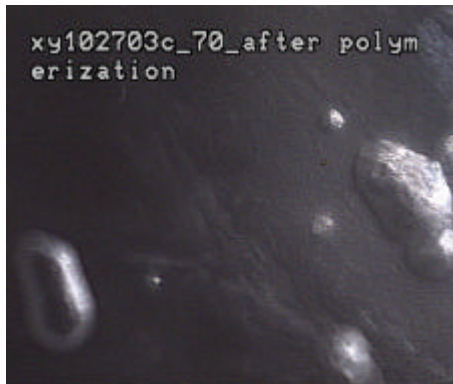
- Cubic phase can be made at high temperature.

PLM (MAG = 12.6X)

Before polymerization



After polymerization



75.3% LLC-2 16.5% H₂O 8.2% BR

- Retention of cubic phase upon radical polymerization
- The polymerized material is flexible.
- Degree of polymerization is to be done by IR.

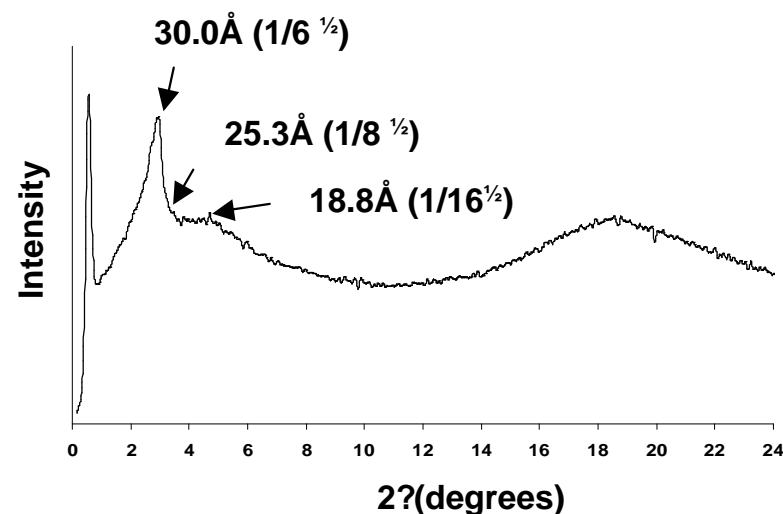
- Solvent casting – no retention of cubic phase after solvent evaporation



- New method: **Pressing**

- The LLC-BR precursor gel is put between two Mylar sheets and pressed by hydraulic press at room temperature
- Heat up to $75 \pm 10^\circ\text{C}$ to form the desired cubic phase
- Cross-link to lock the structure

XRD of above thin film



69.5% LLC-2 27.0% H₂O 3.5% BR

- LLC-BR cubic phase can be formed as supported film for barrier application.

Summary

- **Bicontinuous cubic phase was made by blending and copolymerizing LLC surfactants and commercial BR.**
- **The material can be precessed and applied as thin films for barrier materials.**

Future Work

- **Explore better methods to make supported thin film**
- **Test mechanical properties of breathable cubic LLC-BR composites**
- **Test the permeation of Water vapor and chemical agent simulants with TDA Research**

Acknowledgments

- **Professor Doug Gin**
- **Dr. Jizhu Jin - Gin group**
- **Dr. Brian J. Elliott - TDA Research, Inc.**
- **ARO Funding(grant #:DAAD19-02-C-0018)**