Cross-Linked Lyotropic Liquid Crystal−Butyl Rubber Composites: Promising "Breathable" Barrier Materials for Chemical Protection Applications

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Cross-linked butyl rubber (BR) is a low-cost but highly effective protective clothing material that is used in industry[1,2] and in the military[2,3] to protect the wearer against exposure to a variety of hazardous chemical substances. It is produced by cross-linking linear BR (i.e., poly(methylpropene-*co*-2-methyl-1,3-butadiene), which is produced via the cationic polymerization of isobutylene, with 1−3 mol % isoprene to give a material with a controlled amount of residual double bonds.[4,5] The saturated hydrocarbon structure and low chain mobility of the resulting network gives it excellent resistance to most polar chemicals in liquid, aerosol, and gaseous form.[4,5] One of the major drawbacks of BR protective clothing is that it causes severe heat stress in the wearer with prolonged use.[3] Cross-linked BR has low permeability toward air and water vapor, thus preventing moisture vapor from escaping (an important cooling mechanism).[3] What is desired in an advanced protective garment material is the ability to selectively block toxic substances while letting air and water vapor through; and/or the ability to destroy these substances on contact.[2,3] Advanced garments have recently been developed containing functional entities such as selectively permeable membranes, chemical reagents, catalysts, and biocides.[2] However, methods for incorporating similar features into BR, one of the most economical and effective protective materials, have not yet been explored.

Herein, we describe a method for generating nanoporous, "breathable" BR nanocomposites by blending and copolymerizing BR with a cross-linkable lyotropic liquid crystal (LLC) monomer (**1**). Amphiphilic monomer **1** self-organizes into an inverted hexagonal (H$_{II}$) LLC mesophase[6,7] (i.e., a closed-packed ensemble of inverted cylindrical micelles[6,7]) with a monodisperse aqueous pore diameter of ca. 1.2 nm.[8,9] By cross-linking **1** with BR, it was hoped that polymer nanocomposites could be obtained that retain much of the high chemical resistance of BR but allow water vapor transport due to the imbedded nanoporous LLC structure (Figure 1). These pores are too large to selectively transport water molecules over most chemical agents based on size alone.[10] However, they should provide very small, discreet hydrophilic pathways for water transport[11] with only a slight compromise in chemical agent rejection due to the low water solubility of chemical warfare agents at ambient temperature in general.[10] This Communication describes the blending, LLC phase formation, and polymerization behavior of these novel LLC−BR networks. Preliminary permeation studies with water vapor and 1-chloroethyl ethyl sulfide (CEES, a mustard agent simulant), show that the materials still retard the passage of CEES to a large degree (as opposed to completely blocking it) but allow good water vapor permeation with excellent selectivity.

LLC assemblies are miscible with a variety of low-molecular-weight organic additives;[6c] however, only very little is known about how they blend with polymers.[8,12,13] Polymerizable LLCs have been successfully copolymerized with commercial olefin monomers to form anisotropic porous gels,[14−16] but the blending and copolymerization of reactive LLCs with reactive polymers to form nanoporous composites has not been explored. To test this idea, LLC−BR blends were prepared by first forming the H$_{II}$ phase of **1**, and then blending in the BR (Exxon Butyl 165) as a 15.6 wt % solution in hexane to the LLC phase, followed by annealing.[17]

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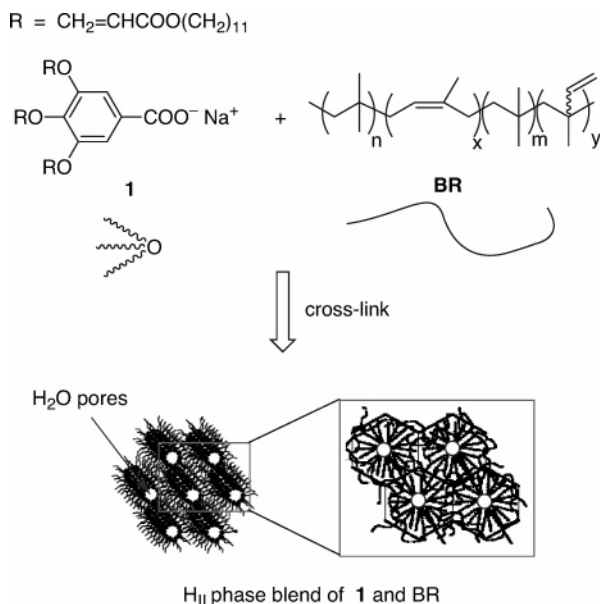
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Figure 1. Blending and copolymerization of LLC monomer **1** and BR into a nanoporous polymer network composite.

The hexane was then allowed to evaporate to form the final mixtures. Using this method, the H_{II} phase region of **1**/BR/H_2O system at ambient temperature (23±1 °C) was plotted in a partial phase diagram (Figure 2).[18] The H_{II} phase boundaries were identified by successively adding water and BR to a preformed H_{II} mixture of **1**, and monitoring the polarized light optical textures of the mixtures until they changed drastically in appearance, signaling a LLC phase change. Mixtures within the bounded region all exhibited X-ray diffraction (XRD) *d* spacings with the characteristic $1:1/\sqrt{3}:1/\sqrt{4}...$ ratio indicative of an H_{II} phase.[6,8,9]

The H_{II} phase of **1** was found to tolerate up to ca. 75 wt % BR with retention of the LLC phase. At first glance, the ability of **1** to accommodate such a large amount of BR seemed quite surprising. To better understand this phenomenon, the microstructure of the LLC−BR mixtures was examined in detail by monitoring their XRD profiles and optical textures as a function of increasing BR. It was found that the primary XRD reflection of the H_{II} blends increases linearly from 35.5 to 39.5 Å with addition of BR up to ca. 25 wt %, at which point the H_{II} unit cell size remains constant with more BR (See Supporting Information). The optical textures of mixtures containing 0−25 wt % BR are fairly uniform, consistent with a well-mixed single LLC phase. Above 25 wt % BR, however, the optical textures show small, colorful domains surrounded by progressively larger dark regions, indicative of phase separation of the LLC domains from the isotropic BR. These data suggest that at low loading levels, the BR resides mainly in the fused hydrophobic tail regions of the H_{II} unit cells. Incorporation of BR within this regime progressively expands the unit cells via a one-phase swelling mechanism, up to a certain size limit.[19] Past that point, the unit cells apparently cannot swell further, and any additional BR becomes excluded from the
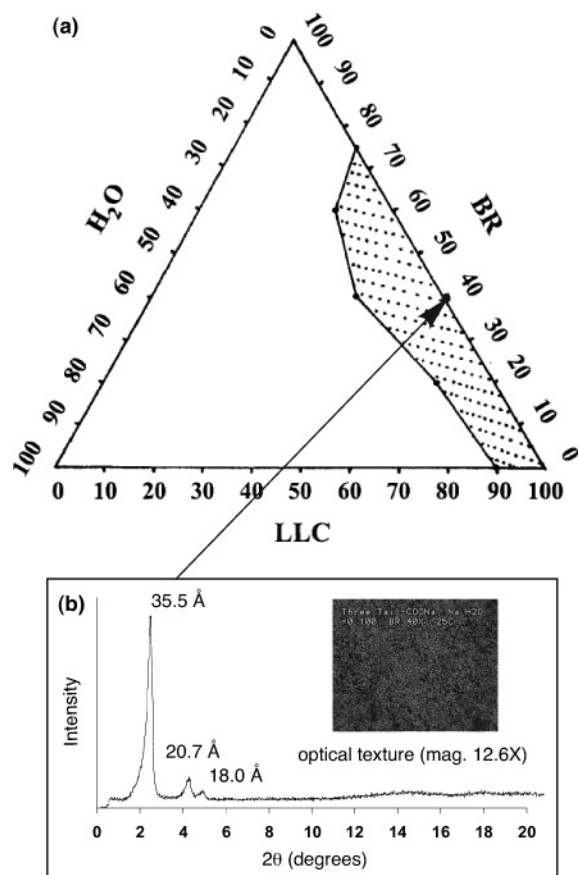

Figure 2. (a) Partial phase diagram of the **1**/BR/H_2O system at ambient temperature (23 ± 1 °C) showing the H_{II} phase regime. (b) A typical XRD profile and optical texture at one point within the H_{II} phase region.

LLC domains, forming a two-phase nanocomposite (See Supporting Information). These results show that **1** and BR are sufficiently compatible to form a nanostructured blend, but two distinct morphologies can be obtained depending on the ratio of the two components.

The nanocomposites were cross-linked by incorporating ≤2 wt % photoinitiator (2-hydroxy-2-methylpropiophenone) into the mixtures, spreading the mixtures as films on glass slides, and irradiating the samples with UV light (365 nm) under light N_2 flush. The initial waxy, off-white LLC−BR mixtures become more brittle solids after irradiation. XRD analysis of the LLC mixtures before and after irradiation indicates that the H_{II} phase is retained upon cross-linking in both the one-phase and two-phase regimes. FT-IR analysis revealed ca. 79% conversion of the acrylate groups upon photopolymerization in almost all cases (see Supporting Information).[20] Very little, if any, extractable components were observed when the cross-linked LLC−BR samples were immersed in organic solvents, indicating good copolymerization of **1** and BR.

(17) If the BR solution is combined with **1** before establishing the initial H_{II} phase, the resulting mixture does not exhibit any LLC behavior.

(18) In the interest of time, the entire phase diagram for the **1**/BR/water system at ambient temperature was not determined at this point in the research. Only the H_{II} region of interest was elucidated.

(19) This one-phase swelling transition to two-phase swelling behavior of the LLC mixtures was also observed when toluene was blended with the H_{II} phase of **1** instead of BR. See the Supporting Information.

(20) The degree of acrylate conversion was determined by monitoring the decrease in intensity of the 810 cm^{-1} band, which is indicative of the =C−H bending motions of the acrylate moieties. It was not possible to quantify the degree of polymerization of the double bonds in the BR by FT-IR because of their low concentration in the polymer (1.2%), and because they exist as a mixture of terminal and internal olefins due to 1,2- and 1,4-polymerization of the isoprene units. See refs 4 and 5.

To test their water and CEES permeabilities, the LLC−BR mixtures were coated onto microporous polymer membrane supports (0.2 μm pore diameter polyacrylonitrile (PAN) or 0.22 μm poly(ether sulfone (PES)) from toluene solution and subsequently photocross-linked.[21,22] Initial vapor transport tests on a photocross-linked film containing 57.6%: 40%:2.4% **1**/BR/water (w/w/w) on the PAN support showed a water vapor flux of 438 g/m^2/day, which is 82% of that of the support alone (534 g/m^2/day). In comparison, pure cross-linked BR has virtually no water vapor permeability. This initial LLC−BR film also exhibited a CEES permeability approximately one-half of that of the noncoated support. Although this CEES penetration level is currently higher than acceptable for true protective garment applications, the large increase in water permeation while still being able to reject CEES to a large degree demonstrates the potential of this approach. Incomplete cross-linking of the BR regions in the blends via photoinitiation alone[23] may be contributing to the observed CEES permeability by allowing CEES to swell the BR regions and more easily diffuse through them. To increase the BR cross-link density, photocross-linked LLC−BR coatings on PES were subjected to a secondary thermally initiated vulcanization step with sulfur-based curatives (73.5%:19.2%:5.0%:1.5%:0.8% **1**/BR/water/photoinitiator/ vulcanizing agents (w/w/w/w/w)). These samples exhibited only about one-third the CEES permeability (61.1 g/m^2/day) compared to the untreated PES support (211.7 g/m^2/day), while exhibiting slightly higher water vapor permeability than uncoated PES (204.8 vs 159.6 g/m^2/day).[21] Photocured and vulcanized pure BR on PES has a CEES permeability of 35.4 g/m^2/day but a negligible water vapor permeability of only 1.3 g/m^2/day.[24] We are currently exploring different methods for increasing the BR cross-link density in the nanocomposites with retention of the LLC order (e.g., electron-beam cross-linking). We are also investigating methods for reducing the effective pore size in the LLC domains to obtain better selectivity of water over certain types of chemical agents via size discrimination.[10,25]

Supporting Information Available: Detailed experimental procedures for the synthesis, blending, polymerization, characterization, and permeation testing of the LLC−BR composites (pdf). This material is available free of charge via the Internet at http:// pubs.acs.org.

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(21) XRD analysis of the cross-linked LLC−BR films on the supports confirmed the presence of nanostructure; however, the background signal from the much thicker polymer support made unequivocal identification of the LLC peaks difficult. See the Supporting Information.

(22) The applied LLC−BR topcoat can be approximately 0.5−2 μm thick, and may be on the surface and/or filling the micropores of the support.

(23) BR contains unactivated olefins, which are less reactive than acrylates. BR typically requires vulcanizing agents to initiate thorough cross-linking. See refs 2 and 3.

(24) Several control experiments were performed to help confirm that the enhanced water vapor permeation observed in the LLC−BR films was due to the porous LLC nanostructure and not due primarily to macroscopic defects or pinhole leaks. See the Supporting Information for details.

(25) The effective molecular diameters of H_2O and CEES were determined to be 3.3 and 5.1 Å, respectively, using molecular modeling (Molecular Modeling Pro, MM2 geometry energy minimization). The effective diameter was taken as the calculated second largest dimension of the molecule in a plane normal to the longest molecular dimension. By this method, mustard gas has an effective diameter of 5.2 Å, and other nonmustard chemical agents are much larger (e.g., sarin, 6.6 Å; soman, 7.3 Å; VX, 9.5 Å). In order for the LLC−BR material to transport water and completely reject CEES, mustard gas, and other chemical agents via size discrimination, the pore diameter must be at most 5 Å. Reducing the pore size to this level may be possible via (1) postsynthesis derivatization of the LLC−BR materials (i.e., grafting additional organic groups onto the channel walls to decrease the inner diameter); or (2) design of new LLC monomers with dimensions that allow them to pack into H_{II} phases with smaller channels.