Ordered Poly(*p*-phenylenevinylene) Matrix Nanocomposites via Lyotropic Liquid-Crystalline Monomers

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The construction of synthetic nanocomposites[1,2,3] and materials with nanometer-scale domains[4,5] has received considerable attention over the past decade. The impetus for much of this work has been to synthesize analogs to biological materials, which possess unique properties as a result of their sophisticated nanoarchitectures.[6] One of the principal questions being addressed in this area of research is whether materials with unique or superior properties could be manufactured if nanometer-scale architectural control could be achieved with modern engineering components. Conventional processing techniques are unable to achieve this level of control in the fabrication of bulk, man-made materials.[6a] Herein, we report a novel strategy for constructing highly ordered, polymer-based nanocomposites with well-defined architectures using self-organizing monomers based on lyotropic (i.e., amphiphilic) liquid crystals (LCs)[7] (Scheme 1). Polymerizable lyotropic LCs are used to form spontaneously an ordered inverse hexagonal LC matrix around aqueous solutions containing reactive agents. Subsequent photopolymerization to lock-in the matrix architecture,[8] followed by the initiation of chemistry within the resulting hydrophilic domains, yields the final material. In order to demonstrate that this approach can be used to synthesize well-defined polymer−polymer nanocomposites, a highly ordered poly(*p*-phenylenevinylene) (PPV) composite was constructed. PPV was chosen as the "filler" in this demonstration because (1) it is formed from a water-soluble precursor[9] and (2) PPV and its derivatives have recently been used to make polymer-based light-emitting diodes[10] and lasing materials.[11] Consequently, PPV is an

Scheme 1
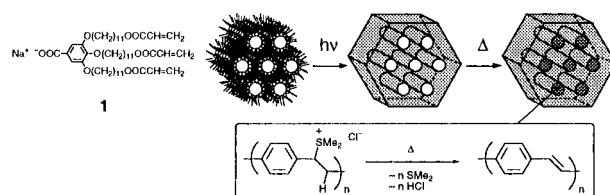
excellent platform for investigating the effects of nanometer-scale engineering on the optical properties of a material.

The hexagonally ordered PPV nanocomposite was formed by initially mixing an aqueous solution of the PPV precursor, poly(*p*-xylylenedimethylsulfonium chloride),[9,12] with **1** and an organic solution of a radical photoinitiator (2-hydroxy-2-methylpropiophenone) to establish the desired LC phase. Monomer **1** is a polymerizable, amphiphilic, acrylate analog of a class of tapered thermotropic LCs originally developed by Percec and co-workers that exhibit columnar discotic LC phases in the *absence* of water.[13] Monomer **1** is synthesized by coupling methyl gallate with 3 equiv of 11-bromoundecan-1-ol to form the basic platform of the amphiphile.[13] Saponification of the ester, followed by acrylation[14] of the terminal hydroxy groups, generates the acid form of **1**. Neutralization with NaOH affords **1** in 59% overall yield.

In order to generate the PPV nanocomposite, a 0.4 wt % aqueous solution[15] of poly(*p*-xylylenedimethylsulfonium chloride) was used as the hydrophilic component in the formation of the phase. The radical photoinitiator was introduced into the phase as a 20 wt % solution in *p*-xylene. Typically, a mixture consisting of 8:1:1 (w/w/w) pure **1**/aqueous PPV precursor solution/2-hydroxy-2-methylpropiophenone solution affords a well-defined, stable, inverse hexagonal phase at ambient temperature (19 °C). When the sample is prepared by simply mixing the components at ambient temperature, it displays an optical texture under crossed polarizers similar to that of Aerosol OT (a commercial surfactant) in the inverse hexagonal phase.[7b,16] Low-angle X-ray diffraction yielded *d* spacings with the 1, $1/\sqrt{3}$, $1/\sqrt{4}$... ratio (d_{100}, d_{110}, d_{200} ...) characteristic of a hexagonal phase (Figure 1a).[7b] The aforementioned aqueous PPV precursor solution can be accommodated up to 20% by total weight in the LC monomer mixture with retention of the inverse hexagonal architecture.

Polymerization with retention of phase architecture was performed by irradiating the viscous LC monomer mixture at ambient temperature with 365 nm light (1800 μW/cm^2) under nitrogen. Typically, thin films ($\leq$100 μm thick) require 1 h of irradiation time to obtain a high degree of polymerization. During irradiation, the initially soluble LC monomer mixture becomes a tough, pale yellow, translucent polymer that is insoluble in common solvents. The polymerized material exhibits an optical texture under crossed polarizers and an X-ray diffraction profile (Figure 1b) virtually identical to that of the original LC monomer mixture. The unit cell dimensions in the photopolymerized material are slightly smaller, consistent with slight volume contraction upon network formation. The loss of acrylate bands (1637 and 811 cm^{-1}) in the FT-IR spectrum of the photolyzed material indicates that a high degree of

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(10) For example, see: Burn, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W. *Nature* **1992,** *356,* 47.
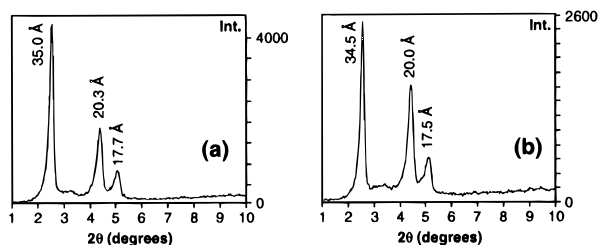
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(14) Broer, D. J.; Boven, J.; Mol. G. N.; Challa, G. *Makromol. Chem.* **1989,** *190,* 2255.

(15) Aqueous PPV precursor solutions 0.4−1 wt % or above were too viscous to homogeneously form the desired LC phase with **1**.

(16) The low water content in the mixture is also consistent with an inverse phase.

Figure 1.

polymerization occurs under these photolysis conditions. Extraction of the polymer with deuterated solvents and subsequent ^{1}H NMR analysis of the extracts did not reveal any residual free monomer. Preliminary transmission electron microscopy (TEM) images have also been obtained of the as-polymerized composite.[17] It can be assumed that the PPV precursor resides solely in the aqueous channels of the LC monomer phase and the resulting polymerized network[18] because the precursor is a highly charged polyelectrolyte that is completely insoluble in nonpolar media.

Conversion of the PPV precursor in the nanocomposite proceeds partially during photolysis but the reaction can be accelerated by subsequent thermal treatment. The concentration of PPV (<0.04 wt %)[19] in the composite is well below the detection limit of many characterization techniques such as UV−vis, solid state ^{13}C NMR, FT-IR, and Raman spectroscopy; however, the degree of PPV conversion can be monitored qualitatively by fluorescence spectroscopy. A typical PPV nanocomposite film photopolymerized for 1 h at ambient temperature exhibits fluorescence at 504 and 534 nm when excited with 370 nm light, even though the electronic absorptions of the PPV segments in the composite are too weak to be observed by UV−vis spectroscopy. In comparison, pure PPV typically prepared by heating the precursor at 220 °C in vacuo for 20 h exhibits fluorescence at 517 and 547 nm.[12] When the nanocomposite is subjected to the same thermal treatment to drive the PPV conversion, its fluorescence intensity at first increases dramatically as a function of heating time, consistent with an increase in the number of emitting PPV segments as a higher degree of conversion is achieved.[20] After 4 h at 220 °C, the fluorescence of the nanocomposite reaches a maximum value and then remains relatively constant over the next 24 h of heating, even though the order in the material begins to exhibit signs of very gradual degradation after approximately 4 h of heating. At the 4 h point, the nanocomposite, which contains less than 0.04 wt % PPV (and still hexagonally ordered), emits approximately 3.7 times more light *per unit volume* than pure PPV over the 410−650 nm range.[21] This ratio translates into a very large photoluminescence enhancement based on the amount of PPV in the two samples. The emission wavelengths remain essentially unchanged during the heating process.

Fluorescence enhancement in conjugated polymers has been reported for polymers that can be dissolved in solution or interchain-separated in amorphous composites and copolymers to minimize self-quenching mechanisms.[22] Dilution/isolation of the PPV segments or chains[22b] and the unique environment inside the ordered channels are undoubtedly partly responsible for the enhanced fluorescence in our nanocomposite. The NaCl formed during PPV conversion in the composite apparently does not play a role.[23] The exact nature of the factors responsible for the differences in fluorescence behavior between our nanocomposite and pure PPV is the subject of ongoing investigations. However, these differences do indicate that the ordered, ionic channels of the matrix represent a substantially different local environment for PPV.

The nanocomposite can be fabricated into highly aligned free-standing thin films and fibers. Thin films several square centimeters in area with the aqueous channels almost uniformly aligned perpendicular to the film surfaces were produced by heating the monomer mixture in a 90 °C oven into a fluid, isotropic state between glass slides, pressing the fluid into a film, and then allowing the mixture to slowly cool between the plates before photopolymerization.[24] Fibers can be obtained by extruding the viscous monomer mixture through a syringe needle at ambient temperature and photopolymerizing the resulting fiber.

In summary, a route to new nanocomposites with a well-defined hexagonal architecture has been developed that is amenable to conventional fabrication techniques. We have demonstrated that PPV can be incorporated into these nanocomposites and that significant enhancement of photoluminescence is one phenomenon that appears to be a result of separation and architectural control on this size regime. We are currently working with collaborators to perform detailed photophysical studies on the nanocomposite and to determine whether it can be made to electroluminesce. Solutions containing precursors to other organic and inorganic materials have also been found to form the inverse hexagonal phase with **1**. Thus, this method appears to be quite general for forming ordered nanocomposites of variable composition.

Supporting Information Available: Experimental details and analytical data for **1** and its synthetic intermediates; optical textures, spectroscopic characterization, a TGA profile, and preliminary TEM images of the nanocomposite; representative spectra of PPV for comparison (20 pages). See any current masthead page for ordering and Internet access instructions.

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(17) See the Supporting Information for the preliminary TEM images, sample preparation, and imaging parameters. Images were difficult to obtain due to decomposition of the polymer matrix under the electron beam. TEM conditions are currently being optimized.

(18) Isolated single chains of conducting polymers have been grown in mesoporous sieves: Wu, C.-G.; Bein, T. *Stud. Surf. Sci. Catal.* **1994**, *84*, 2269. The number of PPV chains in the channels of our nanocomposite has not yet been ascertained.

(19) The PPV precursor undergoes 63% weight loss upon conversion. However, the degree of conversion in the matrix could not be quantified because of the low loading level of the PPV precursor. Higher loading levels were not possible because of the viscosity and the total amount of precursor solution tolerated by the LC phase.

(20) The PPV in the nanocomposite may consist of partially converted chains consisting of conjugated segments separated by unconverted segments or fully converted chains in a twisted conformation that limits conjugation length. For PPV in silica composites, see: Wung, C. J.; Pang, Y.; Prasad, P. N. Karasz, F. E. *Polymer* **1991**, *32* (4), 605.

(21) Comparative fluorescence spectra were collected under the same conditions and corrected for instrument response and sample size. See the Supporting Information. The polymer matrix itself is nonfluorescent.

(22) (a) Smilowitz, L.; Hays, A.; Heeger, A. J.; Wang, G.; Bowers, J. E. *J. Chem. Phys.* **1993**, *98*, 6504. (b) Jenekhe, S. A.; Osaheni, J. A. *Chem. Mater.* **1994**, *6*, 1906 and references therein.

(23) No attempts were made to extract the NaCl formed in the nanocomposite during the PPV conversion. Control experiments with added NaCl (5 equiv relative to PPV repeat units) in the preparation of PPV yielded samples with the same emission wavelengths and intensities per unit volume as PPV samples without added NaCl. Similarly, nanocomposite samples with the same amount of added NaCl did not show any difference in emission behavior compared to normally prepared nanocomposite samples.

(24) The films appear uniformly dark under crossed polarizers but bright around areas of applied stress. When ground-up, they exhibit the X-ray diffraction pattern for a hexagonal phase, consistent with overall homeotropic alignment. See ref 7a.