Polar and Luminescent Supramolecular Films

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Received August 8, 1997

We report on two photoluminescent triblock rodcoil molecules that self-organize into thick polar films that may contain up to 10 000 molecular layers. The design of molecules that assemble into polar materials is an important objective for many reasons. One of them is that such materials could open access to films much thicker than molecular dimensions that can adhere to substrates and present a surface of receptors or catalytic sites regardless of substrate roughness. These solids also offer access to properties that require absence of a center of inversion (e.g., second harmonic generation, piezoelectricity, pyroelectricity, ferroelectricity). In centrosymmetric systems, the vanishing of the β tensor (responsible for frequency doubling) eliminates the possibility of generating a second-order nonlinear optical (NLO) signal. Several strategies have been used to externally control the formation of noncentrosymmetric multilayers such as Langmuir−Blodgett (LB) films of molecules and electrical poling.[1−6] For example, Marks et al. reported multilayer films of up to 5 chromophore layers ($\sim$100 nm thick) with remarkable retention of noncentrosymmetry within the films.[7] In addition, an electrically poled smectic A liquid crystal ($\sim$10 μm thick) containing NLO chromophores attached to siloxane rings has shown thermally stable second-order NLO activity.[8] In this general context, self-organizing polar stacks of molecules would be extremely useful indeed.

Our laboratory recently reported on a new class of supramolecular materials composed of miniature triblock copolymer molecules **1** (Figure 1).[9] These molecules form films composed of mushroom shaped supramolecular aggregates, each containing about 100 molecules. Interestingly, these supramolecular nanostructures organize into layers that stack with “caps to stems” polar order. This was confirmed by second-order NLO measurements of solvent cast films. Transmission electron microscopy showed these layers stack over thicknesses on the order of 1 μm.

We report here on the self-organized films formed by triblock molecules **2** and **3** containing conjugated phenylene vinylene segments (Figure 1). Interestingly, we found that polar order of supramolecular units is also observed in these systems suggesting that supramolecular rather than simply molecular effects may be responsible for the formation of these polar solids. This observation demonstrates that additional chemical functionality can be added to the system without disrupting the organizational energetics behind polar ordering. Furthermore, a special feature of the systems described here is their large thickness which varies between 20 and 110 μm. This corresponds to the dimensions of 2 500−13 750 stacked molecular layers. The specific modifications studied here involved the replacement of the terminal biphenyl hydroxyl of **1** with dimers of phenylene vinylene that are either cyano (polar), **2**, or hydrogen (apolar), **3**, terminated.[10] The synthesis and comprehensive characterization of these two triblock molecules will be reported elsewhere.[11] The rodcoil molecules were characterized by ^{1}H NMR and gel permeation chromatography.

Small-angle X-ray scattering (SAXS) scans indicate these molecules pack into layers with a *d*-spacing of roughly 8 nm which is consistent with monolayer as opposed to bilayer formation. The length of an average rodcoil molecule containing a trans phenylene vinylene conformer is 10 nm.[12] The characteristic submolecular spacing observed is consistent with, but does not demonstrate, bulk polar order in the film. To establish if bulk polar order occurred, we investigated second harmonic generation (SHG) in these supramolecular films. Films of **2** and **3** were solution cast from $CHCl_3$ onto glass slides and allowed to dry overnight under nitrogen. SHG measurements were then obtained using a 1064 nm infrared laser beam. Profilometry and SHG scans across the surface of the films are shown in Figure 2 revealing essentially identical fluctuations in the film thickness and intensity of green photons (532 nm).[13] Particular care was taken to prepare films with a wide variation in thickness across the diameter of the film. By varying the film thickness within the sample, direct measurements of thickness and SHG could be obtained from the same film. The thickness of these films range between 20 and 110 μm implying that stacks of up to tens of thousands of molecular layers preserve global polarity. Since the SHG intensity scales with film thickness, we infer polar stacking is a bulk property of the supramolecular films and not the result of loss of centrosymmetry at interfaces.[14,15] Quadrupolar SHG is also unlikely in our films since this effect is much weaker and observed in systems with higher symmetries.[16,17] Furthermore, the solid films exhibit strong photoluminescence when excited

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(10) General procedure: An oven-dried flask was charged with benzene (10 mL) and THF (1 mL), followed by *n*-BuLi (1.0 mmol). Styrene (9.0 mmol) was added via syringe, and the solution was stirred for 30 min after which isoprene (9.0 mmol) was added and stirring continued for an additional 30 min at which time CO_2(g) was bubbled into the flask. The solvent was removed, and the crude material was purified by flash chromatography on silica gel. The purified material (1.0 mmol) was placed into an oven-dried flask along with CH_2Cl_2 (10 mL), 4-(dimethylamino)pyridinium-4-toluenesulfonate (DPTS) (1.0 mmol), diisopropyl carbodiimide (DIPC) (3.0 mmol), and dimethylthexylsilyl-4-(4-hydroxyphenyl)benzoate, and the solution was stirred for 8 h at room temperature. The reaction was then diluted with water and washed with CH_2Cl_2 (25 mL), the solvent was evaporated, and the crude material was purified by flash chromatography on silica gel. The silyl protecting group was removed by dissolving the silylated ester (1.0 mmol) in THF (80 mL) and cooling to −78 °C followed by the addition of TBAF (6 mmol). This reaction was allowed to stir for 3 h at which point additional TBAF was added (3 mmol) and stirring was continued for another 1 h, followed by addition of 10% AcOH/THF also at −78 °C. Generally, this material was sufficiently pure to be carried forward without additional purification. Repeating the DIPC/DPTS coupling and the silyl deprotection reactions afforded material containing two biphenyl units with a carboxylic acid terminus. This product was then placed into an oven-dried flask along with CH_2Cl_2 (10 mL), DPTS (1.0 mmol), DIPC (3.0 mmol), and the phenylene vinylene dimer, and the solution was stirred for 8 h at room temperature. The reaction was then diluted with water and washed with CH_2Cl_2 (25 mL), the solvent was evaporated, and the crude material was purified by flash chromatography on silica gel to yield molecules **2** or **3**.

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(12) Average fully extended lengths calculated in the molecular graphics program SYBYL, version 6.1, Tripos Associates, St. Louis, MO.

S0002-7863(97)02773-X CCC: $15.00

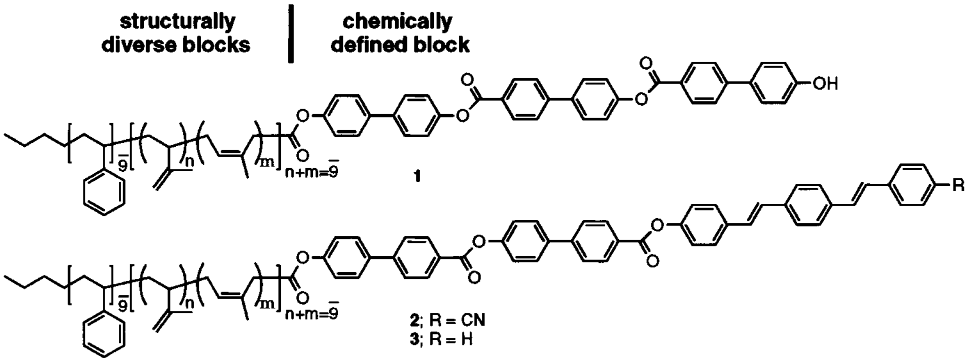

Figure 1. Chemical structure of triblock rodcoil molecules **1**−**3**. These molecules contain average degrees of polymerization of 9 for styrene and isoprene, based on ^{1}H NMR and GPC, covalently grafted to a chemically defined rigid block.

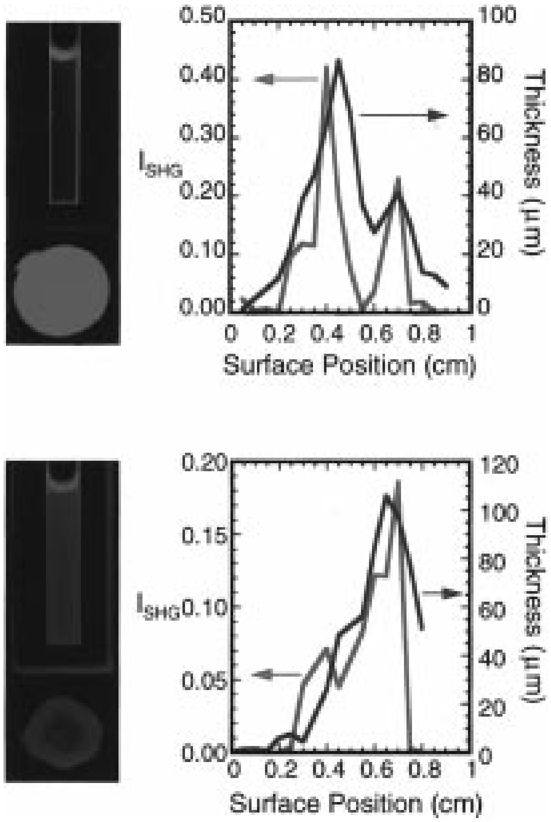

Figure 2. (Top) Profilometry (in blue) and SHG (in red) data obtained at different positions in supramolecular film of rodcoil **2**. The scans show essentially identical fluctuations in both signals. (Bottom) Similar profilometry (in blue) and SHG (in red) data for a supramolecular film of rodcoil **3**. Also shown at the left are the photoluminescent solutions and solid films of both materials irradiated with 365 nm UV light.

by 365 nm UV radiation. As shown in Figure 2, solid-state photoluminescence is particularly strong in films formed by rodcoil material **2**.

We have demonstrated the potential chemical versatility of supramolecular materials formed by triblock rodcoil molecules. We can anticipate that a large variety of chemical structures will exhibit similar self-organizing behavior to that originally reported,[9] including molecules lacking a polar terminus. The nanostructured materials described here contain thousands of molecular layers organized with polar order and give rise to strong photoluminescence. On the basis of these observations, we believe the chemistry of very large supramolecular aggregates can deliver designed materials with extremely valuable and unexpected properties.

Acknowledgment. Supported by grants from the Army Research Office (DAAH04-96-1-0450), the Office of Naval Research (N00014-96-1-0515), and the U.S. Department of Energy (DEFG02-91ER45439 obtained through the Frederick Seitz Materials Research Laboratory). The authors also acknowledge the Beckman Institute for Advanced Science and Technology including the Visualization Laboratory and the Laser Laboratory of the Materials Research Laboratory, both at the University of Illinois at Urbana−Champaign.

JA9727732

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(13) The thickness profiles for the films were measured using a Sloan Dektak3-ST surface profilometer. The locations of the profilometer scanning paths across each film were recorded by applying small dots of ink onto the back of the glass substrates to mark the beginning and ending points of the scanning paths. The nonlinear optical experimental setup is similar to that described by Stupp (Stupp, S. I.; Lin, H. C.; Wake, D. R. *Chem. Mater.* **1992**, *4*, 947−953). Samples for nonlinear optical experiments were mounted onto a rotation/translation stage and either the *p*- or *s*-linearly polarized 1064 nm fundamental was tightly focused onto the sample yielding a peak intensity of about 10 MW/cm^2. The 1064 nm fundamental was produced by a Molectron MY34-20 Q-switched Nd:YAG laser with a 20 ns pulse width operating at a 20 Hz repetition rate. The second harmonic signal at 532 nm was sent through an analyzer and separated from the fundamental via a series of green pass filters and an Instruments SA, Inc. DH-10 double monochromator. The 532 nm light was collected in a Hamamatsu R1477 photomultiplier tube, and the signal was sent out to a Stanford Research Boxcar Averager and then to the digital data acquisition system and an oscilloscope. All data were corrected for transmission of the fundamental and absorption of the second harmonic, and a 3 mm thick single quartz crystal served as a reference.

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