Self-Assembled Structures Through Triblock Terpolymers Forming Gyroid Structures

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Abstract:

Gyroid, which is one of the three-dimensional continuous network structures, is a promising structure. Gyroid structures were achieved by the use of block copolymers that show micro-phase separated structures through a self-assembly process. We fabricated a template of gyroid structures by blending triblock terpolymers and homopolymers. After self-assembled structures were prepared, homopolymers were removed by solvents, so that porous structures were obtained. Structures were evaluated by transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

Introduction:

The colors of morpho butterfly's wings are derived from their wing's structure, the so called 'structural color' [1]. It has been ascertained that one of the structures is gyroid, which is a 3D continuous network structure. This structure has been and is expected to be used in many fields, for example fuel cells, solar cells, metamaterials, etc., so it is important to be able to fabricate gyroid structures easily.

Gyroid structures were achieved by the use of block copolymers. Block copolymers consist of chemically distinct components that show immiscibility due to their different chemical affinities. Since they are covalently bonded to each other, they show various micro-phase separated structures through a self-assembly process. Gyroid is one of the micro-phase separated structures, but gyroid areas on a phase diagram of diblock copolymers are generally small. We used triblock terpolymers to extend the gyroid areas because gyroid areas on a phase diagram of triblock terpolymer become larger.

Our plan to fabricate gyroid structures was to use triblock terpolymers as a template [2]. After one component of triblock terpolymer was removed by selective etching, porous structures for templates could be obtained. Our strategy for the selective etching was to blend triblock terpolymers and oligomers, which are supposed to be miscible with one component of triblock terpolymers. Because oligomers are easily removed by solvents, selective etching could be achieved. We used poly(isoprene-*block*-styrene-*block*-glycidyl methacrylate) (PI-PS-PGMA; ISG) and 1,2-polybutadiene (B), which was supposed to be miscible with polyisoprene block. And poly(glycidyl methacrylate) (PGMA) was also blended to tune the volume fractions of samples. PGMA components would keep their structure after crosslinked by acid.
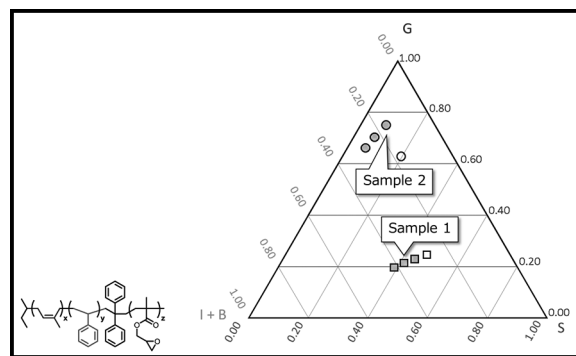

Figure 1: Chemical structure of ISG and volume fractions of each samples on phase diagram. Open square indicates ISG [1] and black squares indicate ISG [1] + B in different compositions. Open circle indicates ISG [2] and black circles indicate ISG [2] + B in different compositions.

Experimental Procedure:

ISGs (ISG [1]: M_n(I) = 10.5 kg/mol, M_n(S) = 21.3 kg/mol, M_n(G) = 40.7 kg/mol, ISG [2]: M_n(I) = 4.9 kg/mol, M_n(S) = 6.2 kg/mol, M_n(G) = 13.9 kg/mol), homopolymers B (M_n = 3.0 kg/mol) and/or poly(glycidyl methacrylate) (PGMA) were dissolved into tetrahydrofuran (THF) in different compositions (10 wt%) (Figure 1). Then photoacid generator (Irgacure PAG 290) was added to the solutions (1 wt% of total solute). After they were poured in aluminum dishes, they were kept overnight at 50°C during which time THF evaporated from the solutions. After light irradiation for 15 minutes to cross link the PGMA component, samples were observed by transmission electron microscopy (TEM). In preparation for TEM, specimens were
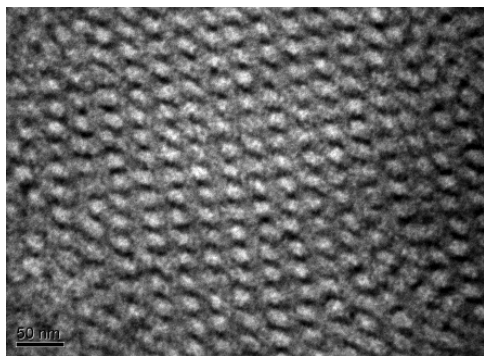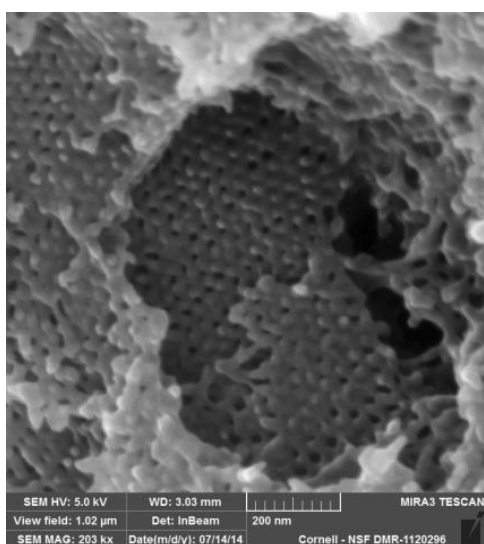
Figure 2: TEM image of Sample 1.

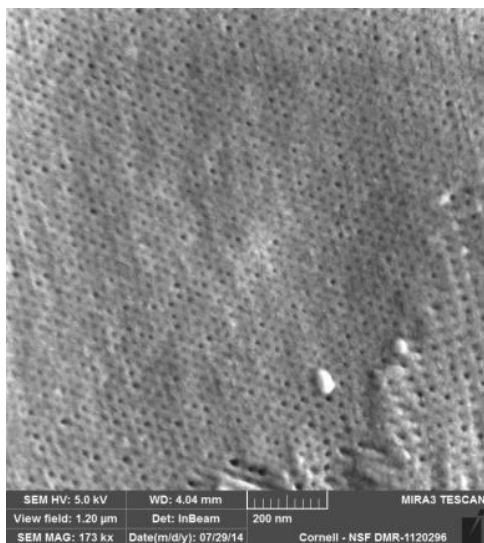*Figure 3: SEM image of Sample 1 after immersed in hexane to remove B.*

Figure 4: SEM image of Sample 2 after immersed in hexane to remove B.

cut with a cryomicrotome at -60°C, then exposed to osmium tetraoxide vapor to stain I component. After samples were immersed in hexane to remove B, they were observed by SEM.

Results and Conclusions:

ISG [1] + B (square). Micro-phase separated structures were found in each sample by TEM measurement, and especially the sample shown as the middle one of black squares in the phase diagram (Figure 1) showed the most ordered self-assembled structure (Sample 1, Figure 2). This structure might be gyroid or cylinder, but it was difficult to determine its structure because the intensity of small angle x-ray scattering (SAXS) — which could identify their structures — was too weak. After it was immersed in hexane to remove B, Sample 1 was observed by SEM (Figure 3). Porous structure was found and its diameter was 15-20 nm.

ISG [2] + B + G (circle). ISG [2], B and homopolymer G were blended to fabricate samples with high G ratio. Micro-phase separated structures were found in each samples by TEM measurement, and especially the sample that is shown as the top one of the black circles in the phase diagram (Sample 2) (Figure 1) showed the most ordered self-assembled structure, which was hexagonal-packed cylinder. And then Sample 2 was immersed in hexane to remove B, followed by SEM measurements of the structure (Figure 4). Porous structure was found and its diameter was below 10 nm.

In conclusion, we could achieved the selective etching of B component from self-assembled structures. We fabricated two porous samples in different compositions and pore diameters were also different, which indicates that we could control the pore size by control the ratios of homopolmer B.

Future Work:

Future research is needed to optimize the etching conditions; temperatures, solvents, immersing time, etc. After that, porous structures will be used as a template to be replicated with functional materials by deposition of other materials.

Acknowledgments:

References:

[1]   R. O. Prum, et al., PNAS 2010, 107, 11676.

[2]   K. Hur, et al., Angew. Chem. Int. Ed. 2011, 50, 11985.

Developing Methodology for Living Polymerization of Functionalized Conjugated Monomers using Nickel Catalysts with Electron-Rich Phosphine Ligands

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Abstract:

The potential applications of polymers in the semiconductor industry have spawned further research into developing their synthetic routes. Organic semiconductors are poised to revolutionize the electronics industry because the devices made using organic semiconductors are inexpensive to fabricate when compared to their traditional silicon counterparts. One difficulty associated with polymer synthesis is molecular weight control. Living polymerization, a form of chain growth polymerization that allows for precise control of molecular weight and dispersities, has been shown to potentially solve this issue. Methods such as the Kumada Ni-Catalyzed Transfer Polymerization allow such control through the adjustment of monomer to catalyst ratios. Also problematic of polymer synthesis is the use of toxic organometallic monomers. This may be solved by involving C-H functionalization, eliminating the need for organometallic monomers, and reducing overall environmental impact. Recent reports [1] of C-H/C-O biaryl coupling of benzoxazoles via Ni(0) with electron-rich phosphine ligands have inspired our approach towards a living polymerization methodology with functionalized conjugated benzoxazole monomers. In this report, the syntheses of monomer precursors are reported.

Introduction:

Semiconductors have revolutionized human technological advancement. Used in electronics and solar energy industries, semiconductor devices made from silicon (Si) are by far the most prevalent. Despite its popularity, Si fabrication is rather expensive. Electronics-grade Si must be extremely high in purity, refined in a process that is expensive and energy intensive, both in man hours and energy used. Si production also utilizes many toxic materials, creating environmental issues that must be dealt with.

Organic semiconductors, such as conjugated polymers, have presented themselves as a viable alternative to silicon. Devices made using organic semiconductors are typically less expensive than their Si counterparts. They also utilize lower production temperatures and may have attractive properties such as transparency and flexibility that expand their range of possible uses.

Current polymer synthesis techniques pose two challenges for organic semiconductor production: molecular weight control and the use of toxic organometallic monomers. The two can be solved by utilizing living polymerization (a form of chain growth polymerization where the growing polymer chain cannot self-terminate) to solve molecular weight issues and C-H functionalization (replacing organometallic aryl
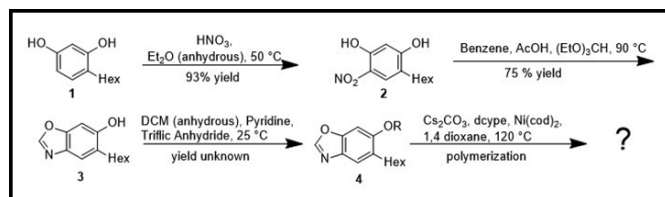

Figure 1: Reaction schemes, reactions progress in order from top to bottom.

nucleophiles/electrophiles in traditional cross-coupling with hydrogen/oxygen) to eliminate the need for organometallic reagents.

The goal of this project is to develop a methodology for the living polymerization of functionalized conjugated benzoxazole monomers using C-H functionalization. Specifically, benzoxazole monomers and monomer precursors were synthesized, and polymerizations were attempted and analyzed.

Methodology:

The synthetic steps used are shown in Figure 1.

Monomer precursors were synthesized from the starting material 4-hexylresorcinol, which was first nitrated to form
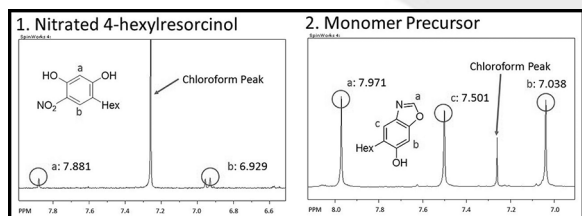
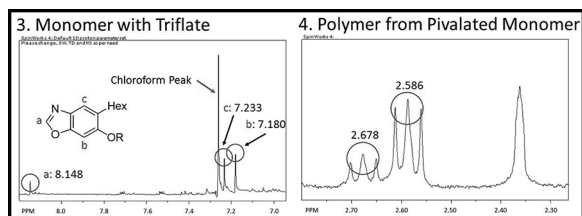Figure 2: ¹H NMR of molecules **2** and **3**.

Figure 3: ¹H NMR of molecule **4** and polymerization mixture.

6-nitro-4-hexyresorcinol. A ring-closing reaction was then performed to produce 5-hydroxyl-6-hexylbenzoxazole. This monomer precursor was functionalized with either a pivalate or trifluoromenthanesulfonate (triflate) to produce the benzoxazole monomer [1]. Living polymerization trials were then performed with benzoxazole monomers with either group [1, 2].

Results and Discussion:

Analysis of ¹H NMR data as well as mass spectrometry data show that the benzoxazole monomer **3** as well as precursor **2** were successfully synthesized (Figure 2). The labeled peaks strongly suggest the presence of the desired products.

In Figure 3, molecule **4** (monomer functionalized with triflate) shows a shift in peaks in comparison to the monomer precursor **3**. Note that multiple peaks have shifted both downfield and upfield. This may indicate that triflation has indeed occurred as the electronegative triflate group deshields the proton furthest away from it while shielding the two closest to it. Yields of the triflate functionalized monomer have yet to be determined. Figure 3 also shows a polymerization attempt of the benzoxazole monomer functionalized with the pivalated monomer. The presence of the two triplets in the hexyl region indicate that a dimer may have formed. This is a promising sign that biaryl coupling may have occurred, indicating that the monomer is reactive, but is not a good indication that living polymerization is successful with this monomer.

Refer to Table 1 for polymerization conditions and results.

Conclusions:

The development of a methodology for the living polymerization of functionalized conjugated benzoxazole monomers using C-H functionalization was attempted. Synthesis of benzoxazole monomers and their precursors proved successful, but successful living polymerizations were not achieved. Benzoxazole monomers functionalized with pivalate groups show promising reactivity, as shown by dimer formation during living polymerization attempts, but further work must be done to achieve living polymerization of benzoxazole monomers. Monomers functionalized with triflate groups did not display reactivity, and further work must be performed to achieve successful polymerizations.

Future Work:

Currently, the only step of the methodology that has failed is the polymerization itself. This may be due to poor monomer quality or an unreactive C-O group. Therefore, refinement of the C-O group is required, as well as refinement of the monomer synthesis reaction. Further living polymerization attempts of the triflate monomer are also to be attempted. If proven successful, adjustments of monomer to catalyst ratios may be attempted to see if polymer chains of varying lengths may be achieved while maintaining low dispersities.

Acknowledgements:

References:

[1]   Muto, K.; Yamaguchi, J.; Itami, K. Nickel-Catalyzed C-H/C-O Coupling of Azoles with Phenol Derivatives. Journal of the American Chemical Society. 2012, 134, 169-172.

[2]   Housekeeper, J. Laboratory Notebook Book II; University of Washington: Seattle, 2013. p 195.

Polymerization Conditions	Result
Pivalated monomer (1 equiv), CsCO$_3$ (1.5 equiv), dcype (0.2 equiv), Ni(cod)$_2$ (0.1 equiv), 1,4 dioxane (4 mL)	Indication of dimer
Pivalated monomer (1 equiv), CsCO$_3$ (1.5 equiv), dcype (0.2 equiv), Ni(cod)$_2$ (0.1 equiv), 1,4 dioxane (4 mL)	No indication of polymerization
Triflated monomer (1 equiv), CsCO$_3$ (1.5 equiv), dcype (0.2 equiv), Ni(cod)$_2$ (0.05 equiv), 1,4 dioxane (2 mL)	No indication of polymerization
cod = 1,5-cyclooctadiene, dcype = 1,2-bis(dicylohexylphosphino)ethane	

Table 1: Polymerization conditions and results.

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