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Acquisition of Preparative Gel Permeation Chromatography for Research and Education in Energy Conversion and Nanocomposites

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14. ABSTRACT
The acquired Preparative Gel Permeation Chromatography (pGPC) and DMF GPC not only enhance the PI's ongoing DOD project on nanocomposites and energy pertinent to national defense, but also strategically stimulate and reinforce the research collaborations at the Georgia Institute of Technology between DOD- and NSF-funded projects in the areas of nanoscience listed in the proposal. The pGPC system possesses several advantages: the system allows extremely useful and monodisperse polymeric materials to be obtained from inexpensive, intractable, and sustainable sources; the system allows quantitative separation (gram quantities) and collection of several different sizes allowing for a systematic study of the properties of resulting synthesized nanostructures; and the system will greatly reduce the time necessary to develop novel, large quantities of many useful inorganic nanostructures (rod, tube, core/shell, hollow, etc.) by eliminating conventional, time consuming purification techniques. The acquired pGPC and DMF GPC systems are anticipated to enable new integration of research with education at all levels across a broad range of materials, and create important opportunities to expose and train undergraduates, women, and students from underrepresented communities as well as graduates and postdocs, on these characterization instruments.

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Acquisition of Preparative Gel Permeation Chromatography for Research and Education in Energy Conversion and Nanocomposites

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Final Report on the DURIP project: FA9550-16-1-0115 (01/15/2016-01/14/2017)

We acquired the following equipment over the past year with the DURIP support for research and education in nanocomposites, energy, and biotechnology.

Preparative Gel Permeation Chromatography from Shimadzu and Shodex

An essential tool in the systematic investigation of nanoscale materials employing complex polymer architectures is preparative gel permeation chromatography (Preparative GPC; pGPC). This technique can be used to separate polymers by their size in quantitative yields which can then be characterized, undergo further reaction into many inorganic nanostructures, or be incorporated directly into devices as is. This single instrument alone can have a truly transformative effect on the pace and applicability of nanoscale materials research and design because it can eliminate nanoscale size variability in complex macromolecular systems. This leads to reproducibility and reliability in material properties and therefore understanding; two important benchmarks for justifying the scale-up, commercialization and ultimate incorporation of novel technologies into our lives.

The acquired preparative gel Permeation chromatography (pGPC) from Shimadzu and Shodex features a high throughput design which allows gram quantity separation and collection of highly monodisperse polymer templates (cellulose, chitosan, lignin, and starch) from messy and often intractable raw sources with minimal waste of materials. It *not only* enhances the PI's ongoing DOD project on nanocomposites and energy pertinent to national defense, but also strategically stimulate and reinforce the research collaborations at the Georgia Institute of Technology between DOD- and NSF-funded projects in the areas of nanoscience and materials for energy.

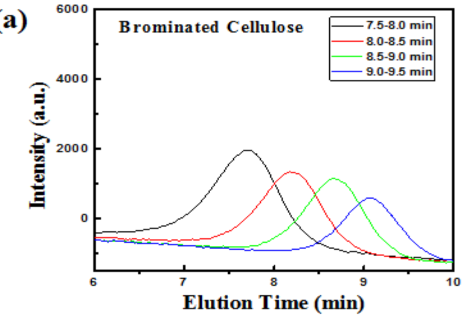
Figure 1. Preparative Gel permeation chromatography (pGPC) system from Shimadzu.

The pGPC acquired from SHIMADZU SCIENTIFIC INSTRUMENTS is equipped with one LC-20AR HPLC Pump (MAX flow rate 20ml/min), one SIL-20A Prominence HPLC Autosampler (high-speed accurate injection of samples), one CBM-20A HPLC System Controller, one CTO-20A Prominence HPLC Column Ovens (large capacity, temperature up to 85^{o}C), one RID-20A Refractive Index Detector, two Shodex HPLC Preparatory Scale Column (KF-2004), one LabSolutions Workstation Single-LC Software, and one LabSolutions Workstation GPC Software (**Figure 1**), and one FRC-10A

Fraction Collector (**Figure 2**). In addition, a Shodex HPLC Analytical Scale Column (KF-804, identical but downscale version of KF-2004) was ordered prior to ordering KF-2004 (preparatory scale) to ensure that the column type is adequate for fractionating cellulose-based polymers. THF is used as mobile phase and the columns are calibrated with polystyrene standards.

Figure 2. FRC-10A Fraction Collector from *Shimadzu Corporation*, featuring a proprietary band function that enables obtaining accurate fractions even with varying peak elution times (*Shimadzu Corporation*)

(a)



(b)

Elution Time (min)	Avg. *Mn* (g/mole)	PDI
7.5-8.0	36.3k	1.14
8.0-8.5	20.4k	1.14
8.5-9.0	11.3k	1.14
9.0-9.5	6.4k	1.16

Figure 3. GPC of fractionated brominated cellulose using the newly acquired pGPC system.

We have used the new pGPC to fractionate and characterize cellulose-based nonlinear polymers. The pGPC shows low PDI brominated cellulose that has been fractionated using this new system (**Figure 3**). Moreover, the brominated celluloses with different molecular weights are well resolved and separated, suggesting a good resolution of the acquired pGPC system. We plan to further narrow down the polydispersity (PDI) of brominated cellulose by controlling the elution time in future experiments.

DMF Gel Permeation Chromatography from Shimadzu and Phenomenex

Gel permeation chromatography (GPC) is a technique that is widely used for separating and analyzing polymers. It is one type of size exclusion chromatography (SEC) which separates analytes based on their different hydrodynamic volume or radius of gyration. This is different from other separation techniques which separate analytes on the basis of physical or chemical interaction. Separation is achieved via porous beads packed in the HPLC column. Analytes with smaller sizes can enter pores with smaller pore size, and therefore spend more time in more pores. The retention time of smaller analytes is longer in the column, which corresponds to lower molecular weight. By contrast, larger analytes eluted quickly from the column as they can only enter fewer pores due to their large size. All GPC columns have a range of molecular weight that can be measured. Molecular weight and molecular weight distribution (PDI) are two very important parameters for polymer, which can be readily obtained by the GPC measurement.

The GPC that uses dimethylformamide (DMF) as a solvent (hereafter referred to as DMF GPC) acquired from SHIMADZU SCIENTIFIC INSTRUMENTS is equipped with one LC-20AD HPLC Pump, one CTO-20A Column oven, one RID-20A,120V, Refractive index detector, one CBM-20A Communications bus module, and the LabSolutions Single-LC software (**Figure 4**). The column oven can maintain stable temperature (±0.1℃) within column for consistent separation of molecules. RID-20A can effectively detect the change in reflective index coming from concentration variation. Additionally, a Phenogel 5u 10E4A New Column 300 x 7.8 mm (in DMF) from *Phenomenex, Inc.* was purchased. The column is in DMF mobile phase and is designed to only measure molecules dissolvable in DMF with a molecular weight between 5K and 500K. The columns are calibrated with polystyrene standards. Due to the absorption of polymer and polar impurities onto the column which may affect the column performance after a certain period of usage (usually several years), an additional column of same type was also purchased for replacement when the original one fails.

Figure 4. Gel permeation chromatography (GPC) that runs DMF as mobile phase from Shimadzu.

We have been using DMF GPC to characterize nonlinear homopolymers and block copolymers with polar segments (**Figure 5**). The left panel shows a GPC trace of a star-like homopolymer, (i.e., star-like poly(4-vinyl pyridine; P4VP), possessing a molecular weight of 48, 000 g/mole and a narrow molecular weight distribution (PDI =1.12). The right panel display a GPC trace from star-like poly(4-vinyl pyridine)-block-poly(*tert*-butyl acrylate)-block-poly(ethylene oxide) (i.e., P4VP-*b*-P*t*BA-*b*-PEO), possessing a molecular weight of 59, 000 g/mole and a narrow molecular weight distribution (PDI =1.08). The peaks from two non-linear polymer samples are well resolved with narrow molecular weight distribution, signifying a good resolution of the acquired DMF GPC system.

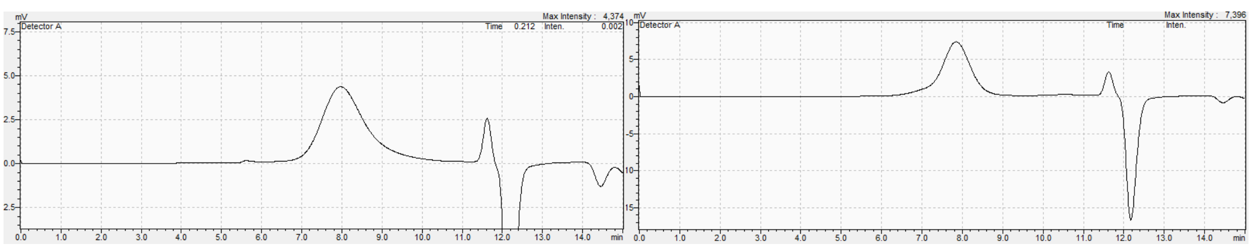


Figure 5. DMF GPC traces of star-like P4VP homopolymer (*left*), and star-like P4VP-*b*-P*t*BA-*b*-PEO triblock copolymer (*right*).

Dryfast 2042B Diaphragm Pumps from Gardner Denver Welch

High vacuum pumps are an essential technology required to prepare samples that are suitable for characterization by GPC as well as other techniques. In the case of our brominated cellulose, brominated beta-cyclodextrin and associated block copolymers, this is especially true. The synthesis processes of these materials necessitate high polarity and high boiling point solvents. These solvents need to be completely removed prior to material characterization because these residual solvents can damage chromatography columns and interfere with their analysis. In addition, residual solvents can affect the quality of subsequent nanocrystal templating.

The acquired pumps from Welch (a Gardner Denver company) are Dryfast© model 2042B-01 (**Figure 6**). These pumps have superior vacuum-drawing properties without the need to change out messy oil. Consequently they have long continuous run times for enabling complete removal of solvent residues. The pumps are also fitted with a variable vacuum strength knob to precisely dial in on the necessary ultimate vacuum strength. High purity samples have been prepared using these pumps which has led to high quality nanocrystal synthesis results.

Research-Related Education

The acquired pGPC and DMF GPC will also serve as an educational wellspring for undergraduates, graduates and researchers who are most likely new and unfamiliar with this important technique. With an emphasis on characterization and practical knowledge education, Georgia Tech's materials science, chemical engineering, mechanical engineering and other curricula will benefit greatly from this resource.

Figure 6. Welch Dryfast 2042B high vacuum oil-free diaphragm pump.

Instrument Training for Students and Postdocs. One educational objective of this DURIP project is that the students using the instrument would gain a better understanding of the working principle of pGPC and DMF GPC and their capability of producing large scale pure polymeric fractions and molecular weights of polar polymers analytically, respectively. Students, postdocs and faculty alike will be able to receive training on the aforementioned pGPC and DMF GPC for use in their own research projects as well and serve as practical support for fundamentals taught in undergraduate classes in polymer science and engineering, characterization and separation across all engineering and scientific fields. Additional students and researchers from the School of Materials Science and Engineering, as well as from other schools throughout Georgia Tech, will also be using the acquired GPCs.

Teaching and outreach. Coincident with instrument training, the acquisition of the pGPC and DMF GPC will directly impact our planning efforts in the "*Nanostructured Materials*" course for a broad audience to enhance the class interactivity through incorporation of live demonstrations and video modules. Furthermore, as part of the School of Materials Science and Engineering's ongoing efforts in educational outreach through the GHOST program (Georgia High School Outreach for Science and Technology), visiting high school students will also receive demonstrations on this equipment as part of interactive STEM-focused (Science, Technology, Engineering and Mathematics) tours and presentations to underscore the importance of scientists and engineers and convince them to consider careers in STEM fields. The goal of outreach activities is to increase the numbers of young people, especially minorities and women, who pursue advanced degrees in science and engineering.