1 / VOL. 3, NO. 4 ISSN 1430-4171
THE CHEMICAL EDUCATOR http://journals.springer-ny.com/chedr

10.1007/s00897980233a

Laboratories and Demonstrations

Preparation and Separation of C_{60} Photopolymers for the Physical Chemistry Instructional Laboratory

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The enormous scientific and popular interest in C_{60}-based materials makes them ideal for incorporation into an instructional laboratory…

We report the development of a new physical chemistry laboratory exercise that uses gel permeation chromatography (GPC) to study pristine and photopolymerized C_{60} materials. GPC is a well-known method for probing molecular weight distributions because of its ability to separate macromolecules based upon size. In this experiment students are interested in the changing molecular weight distribution with irradiation. Students inject both pristine and photoirradiated C_{60} into the system and analyze the retention time data with a differential UV detector set at 300 nm. The observation of higher molecular weight oligomers upon irradiation is consistent with intermolecular bond formation by the proposed [2 + 2] cycloaddition pathway. The implementation of this laboratory in the classroom has been very successful, generating consistently positive feedback from the students.

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (98) 04233-4

Introduction

In the past few years the field of C_{60}-based materials has generated a great of deal of attention due to the facile chemical, structural, and physical tunability of this family of organic molecular solids. C_{60} materials, in particular, are well known to display a wide variety of structural phases [1–10]. These include order/disorder and glassy behavior; doping-induced structure modifications; magnetic phases; and nanophases, such as tubules, onions, and wires. The recent reports of photo-induced and pressure-induced solid-state polymerization of C_{60} are a new twist in this exciting story [11–13].

The polymerization of neutral C_{60} molecules is initiated by a photochemical reaction. A solution or solid film of C_{60} can be irradiated with visible or ultraviolet light to activate a [2 + 2] cycloaddition-reaction pathway [11–19]. Note that while the reaction of neutral C_{60} molecules is thermally forbidden by the well-known Woodward–Hoffman rules, it is photochemically allowed. Although the “pearl-necklace” structure of polymerized buckminsterfullerene has been postulated (Figure 1), it is also possible that polymerization starts in several directions at once, giving rise to two-dimensional or even three-dimensional networks [20, 28]. These branched structures are probably a more realistic view of the actual structure after irradiation.

The enormous scientific and popular interest in C_{60}-based materials makes them ideal for incorporation into an instructional laboratory, and our group’s research work in this field was an additional motivating factor for the development of this laboratory exercise. Students are attracted to modern open-ended problems, and the laboratory situation is a great place to explore such projects. They are also eager to gain hands-on experience with modern techniques, such as gel permeation chromatography (GPC), which serves as training for future employment. There is no doubt that separation techniques (such as GPC) are the backbone of modern analysis laboratories in academia and industry, and they occupy an important place in the instrumental laboratory [21–27]. While chromatography has been used extensively for the purification of fullerene compounds, less has been done to exploit this technique for the study of photopolymers.

In order to bring the topic of C_{60} photopolymerization into the classroom, we developed a new experiment in which students study the separation of C_{60} photopolymers via GPC. Our overall goal was to create an up-to-date experiment both

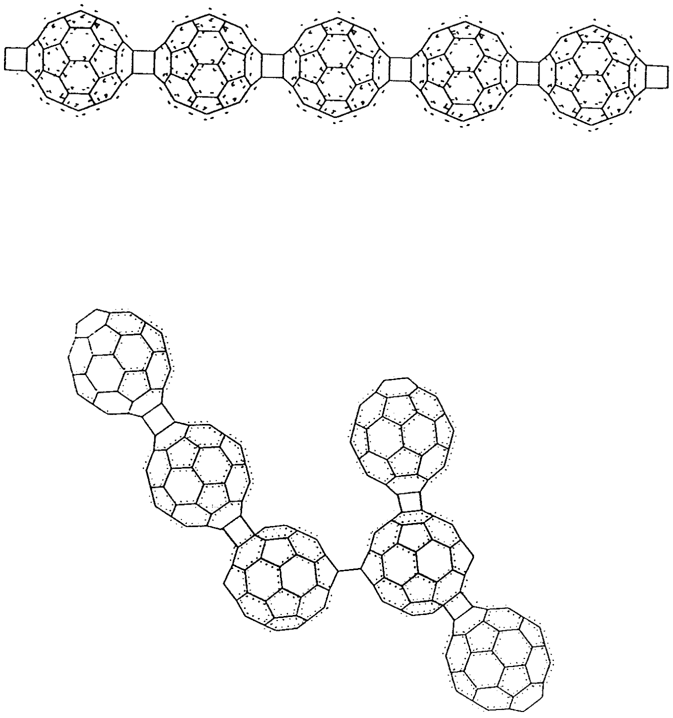

FIGURE 1. UPPER PANEL: IDEALIZED “PEARL-NECKLACE” STRUCTURE OF THE C_{60} PHOTOPOLYMER. LOWER PANEL: A HYPOTHETICAL BRANCHED STRUCTURE OF THE PHOTOPOLYMER.

in terms of scientific content and instrumentation for use in the instructional physical chemistry laboratory.

Method

Sample Preparation

Before the beginning of the semester, samples of pristine and photopolymerized C_{60} were prepared for the students using a technique called the “fast method” in an oxygen-free environment inside a glove box [28–30]. The “fast method” technique adds the acetonitrile solution component very quickly to a solution of toluene containing dissolved C_{60} [28]. Solutions of fullerene were made with a concentration of 1×10^{-4} M in a 60:40 mixture solution of toluene and acetonitrile. The acetonitrile/toluene emulsion is important for stabilizing the fullerene in solution [28–30]. Subsequent dilutions were made in toluene with the acetonitrile component added quickly on the last dilution (40% of total volume). Solution ratios of toluene and acetonitrile are dependent on the concentration of C_{60} [28]. After mixing, a rubber septum was placed

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http://journals.springer-ny.com/chedr
S 1430-4171 (98) 04233-4

on top of the 25-ml volumetric flask. Use of the septum avoids exposing the solution to the air while allowing a syringe to penetrate into the flask for sampling.

An identical C_{60} solution in acetonitrile/toluene emulsion formed the basis for the photopolymerized sample. Again, all steps were carried out inside a glove box. The solution was poured into an open beaker containing a magnetic stir bar, and a blacklight was positioned to shine directly over the beaker onto the solution. The blacklight served as a source of ultraviolet (UV) radiation, and the open beaker allowed for direct exposure. Other sources such as a high-powered xenon lamp or UV laser may be used, but obviously a blacklight is a very economical alternative. The sample was irradiated for 100 hours under the lamp with constant stirring. It is important to note that the photoexposure must be carried out in an oxygen-free environment, as oxygen contamination is well known to reduce the efficiency of the reaction [28]. During the 100-hour photoirradiation process, we flushed out the glove box several times each day and replenished the solutions. Because acetonitrile evaporates more quickly than toluene under the UV lamp, it has to be replaced gradually. Thus, at the end of the run, the 60:40 solvent ratio was only an estimate.

GPC Setup

Gel Permeation Chromatography separates molecules based on their physical size; thus, it is also known as size exclusion chromatography [31–36]. The physical mechanism of separation is well-understood: smaller molecules are trapped in the column's microporous material; therefore, it takes longer for them to elute from the column. In contrast, the larger molecules cannot penetrate into the pores of the stationary phase, so they elute much more quickly. Here, GPC is used to analyze the molecular weight distribution of pristine and photoexposed C_{60} samples.

The GPC setup in our instructional laboratory represents a good compromise between cost, versatility, and value. The setup contains a Waters 510 HPLC pump, three Waters Styragel high-temperature columns (HT6, HT4 and HT2), a 486 Waters tunable UV–vis absorbance detector, and a Waters 410 refractometer. The cost of our GPC setup was approximately $23,700. The elimination of the refractive index detector can further reduce the cost by approximately $5000. The absorbance detector was set at 300 nm because the C_{60} absorbs radiation at this wavelength, whereas the toluene mobile phase is transparent at this energy. We employed a flow rate of 1 ml min^{-1}. For detecting the fullerenes as they eluted from the column, the Waters 486 tunable absorbance detector was used as the primary detector. The 486 functions like an unsophisticated UV–vis spectrometer; it is optically tunable but monitors only one wavelength. Thus, when C_{60} passes through the detector, it measures signal intensity as a function of retention time (in minutes) as compared with the mobile-phase reference. On the chromatogram, any change with respect to the mobile-phase baseline will be represented as an absorption peak with respect to time. The Waters 410 refractometer was also part of the setup, but this type of detector proved to be less useful due to sample solution/mobile phase interference. With a toluene mobile phase and a sample suspended in an acetonitrile/toluene emulsion, the RI detector was highly sensitive to the acetonitrile component in the sample due to the large difference in refractive index.

After the students make an injection, the monomer signature elutes in about 36 min. (Typically, we suggest they set up a 45-min run time.) Once the students are satisfied with the quality of the chromatogram, they inject the irradiated sample for the same run time. Because higher molecular weight samples elute from the column faster, the students should see a collection of smaller structures preceding the response of the pristine C_{60}. A copy of the GPC/C_{60} laboratory experiment is available at our Website, http://chemiris.chem.binghamton.edu:8080/MUSFELDT/DSC.htm.

Cleaning the GPC Injector

The difficulty in cleaning C_{60} from chromatography instrumentation is well known [37]. In order to assure a clean set of injections for each laboratory period, we developed a rigorous cleaning procedure, described below.

After the flow rate has been reduced at the conclusion of the experiment, we ask each group of students to flush out the injector with toluene. They fill a 20-cm^3 syringe with toluene and place the white needle port cleaner at the end of the syringe. With the injector handle in the INJECT position, they flush through the toluene mixture, which elutes into a waste beaker before the guard column. After repeating this two more times, the tubing is reconnected to the guard column. For more effective cleaning at the end of the semester, one can carefully disassemble the injector and sonicate the parts in *o*-dichlorobenzene [37]. We also found it helpful to use separate injection syringes for the pristine and photoexposed samples.

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Safety

The handling of C_{60} compounds presents no known dangers, but as in the handling of any highly conjugated material, it should be carried out with care. Safety glasses should be worn at all times during the experiment, and latex gloves should be worn when handling the C_{60} or the solvents. To prevent eye damage, one should also avoid looking directly at the blacklight.

Results and Discussion

GPC Data

Figure 2 displays the chromatographic data of three C_{60} samples. The top panel shows the data for pristine C_{60} in pure toluene. We have assigned the larger feature (near 37 min) to the elution of C_{60} and the smaller structure (near 34.7 min) to small amounts of C_{70}. The middle panel displays the pristine C_{60} sample in an acetonitrile/toluene emulsion. This chromatogram contains three peaks, two of which are identical to the aforementioned injection of pristine C_{60} in toluene. The additional feature (at 35.7 min) is attributed to the elution of acetonitrile based upon a comparison of the top and middle panel in Figure 2, as well as an acetonitrile blank run. The acetonitrile signature is absent in the chromatogram of the pristine C_{60} solution in toluene only.

The bottom panel of Figure 2 displays the chromatogram of the photoexposed C_{60} sample. The aforementioned C_{60}, C_{70}, and acetonitrile peaks are still present, and a series of small peaks are detected in front of the larger peaks in the range of 28–34 min. Figure 3 shows an enlargement of this area for both the pristine and photoexposed samples. Several clear structures are now observed in the response of the photoirradiated material. We believe these signatures correspond to higher molecular weight fractions of C_{60}. We have assigned them as C_{60} dimers ($n = 2$), trimers ($n = 3$), tetramers ($n = 4$), and pentamers ($n = 5$), based upon their relative position with respect to the pristine C_{60} signature. As mentioned previously, larger molecules have shorter elution times, so the earliest peak to elute corresponds to the oligomer with the highest degree of polymerization. Observation of these higher molecular weight species is consistent with intermolecular bond formation.

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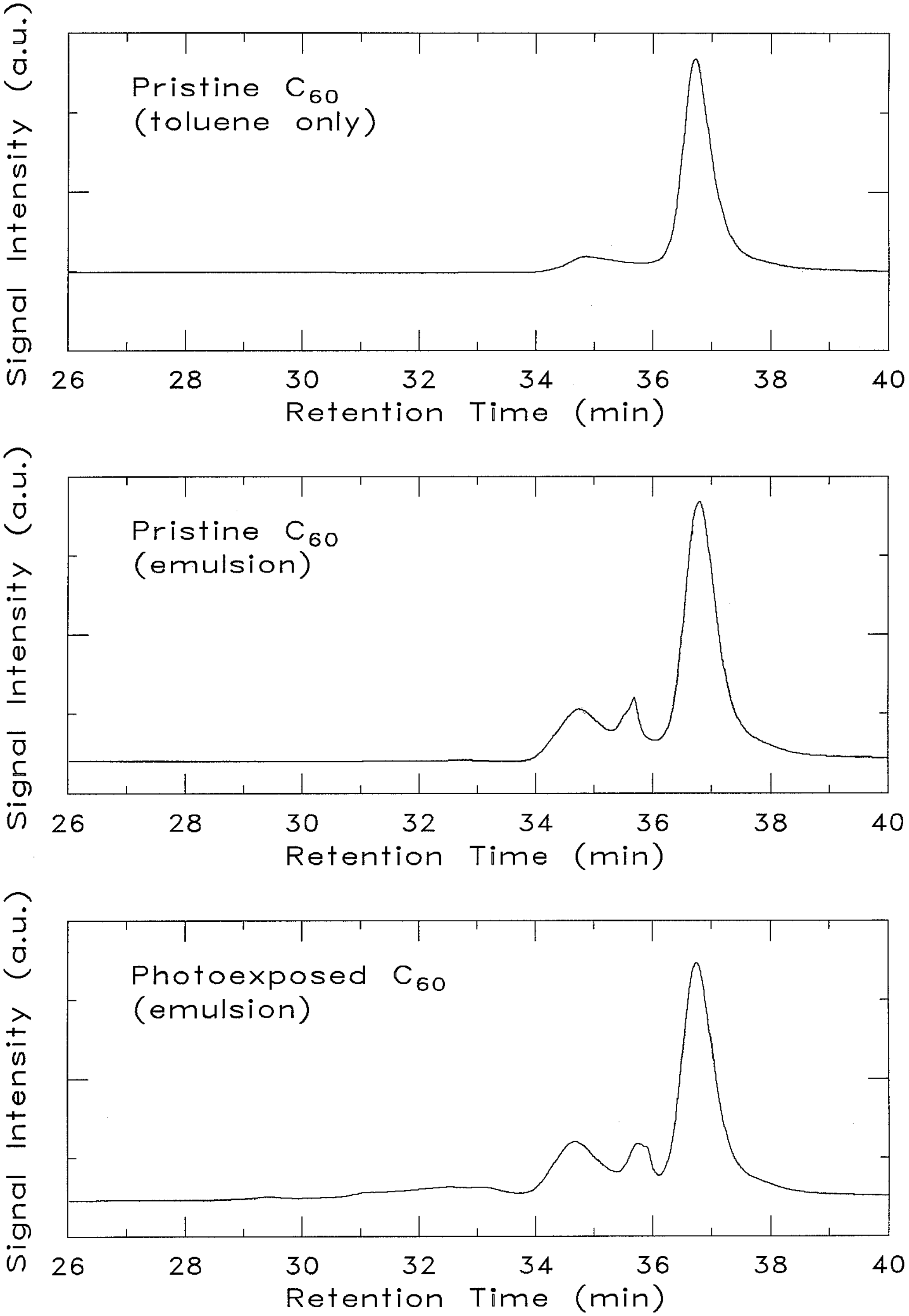

FIGURE 2. UPPER PANEL: CHROMATOGRAM OF PRISTINE C_{60} IN TOLUENE ONLY; MIDDLE PANEL: PRISTINE C_{60} IN ACETONITRILE/TOLUENE EMULSION; LOWER PANEL: PHOTOEXPOSED C_{60} IN ACETONITRILE/TOLUENE EMULSION. THE ABSORBANCE DETECTOR (SET AT 300 nm) WAS USED IN EACH OF THESE RUNS.

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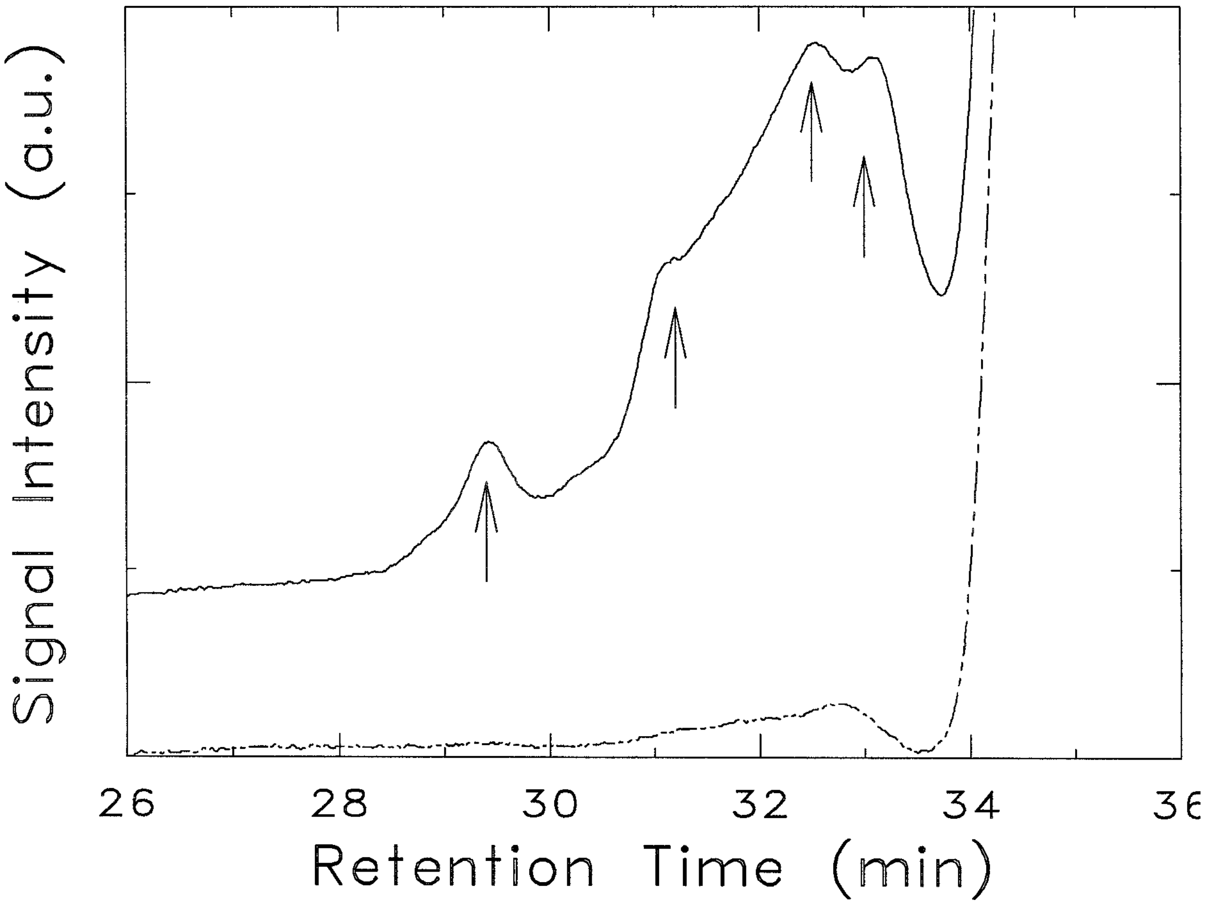

FIGURE 3. ENLARGEMENT OF THE PRISTINE C_{60} (DASHED LINE) AND PHOTOEXPOSED C_{60} (SOLID LINE) CHROMATOGRAMS. ARROWS MARK THE POSITION OF THE *N*-MERS.

While it is clear that higher molecular weight fractions form upon photoirradiation, students are often curious about the low overall signal level of the oligomers with respect to the pristine sample. We believe the low conversion is a result of two factors. First, the polymerization reaction was carried out using a low-intensity energy source (i.e., a black-light bulb), which may explain the low concentration (and thus the small signal intensities) of the higher molecular weight fractions. Second, the mediocre quality of our glove box environment may contribute to the low degree of polymerization, as small amounts of oxygen can inhibit the photopolymerization process. The polymerization of C_{60} may be enhanced with the use of a more powerful energy source such as a xenon lamp. Nevertheless, it is clear that higher molecular weight species did form upon irradiation.

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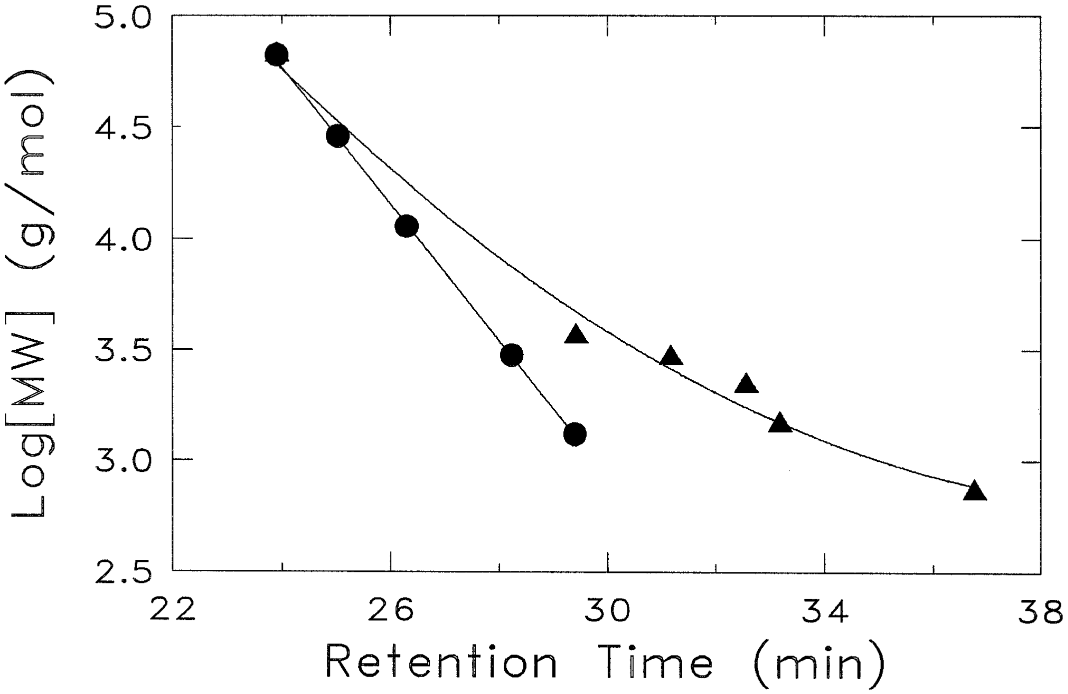

FIGURE 4. LOG[MW] VERSUS RETENTION-TIME CALIBRATION CURVE FOR A SERIES OF LINEAR HIGH-MOLECULAR-WEIGHT POLYSTYRENE STANDARDS (●) AND C_{60} OLIGOMERS (▲).

Finally, it is interesting to note that the response of the C_{60} compounds was not amenable to analysis using the standard GPC calibration with polystyrene. This comparison can be seen in Figure 4 where we show the retention time of the fullerene, the fullerene-based oligomers, and a series of linear high molecular weight polystyrene standards. Normally, the linear log[MW] versus retention-time response of the polystyrene samples is the appropriate calibration curve for high molecular weight macromolecules. The C_{60} oligomers, however, seem to fall on a different curve, which we attribute to the difference between a rigid and a highly coiled molecule, conjugation, and solvent interaction properties of the C_{60} compared with the polystyrene standards.

To investigate this discrepancy further, the retention time of each C_{60} oligomer (degree of polymerization = 2 to 5) was obtained via Lorenzian fitting of the chromatogram structure (Figure 3). Using these data points and the highest molecular weight of the polystyrene standard (66,000 g mol^{-1}) as the infinite-chain extrapolation, our C_{60} retention time data were well-fit by a 2nd-order polynomial ($y = 14.912 - 0.60149\,x + 0.0074631\,x^2$). It should be noted that we do not consider

ISSN 1430-4171
http://journals.springer-ny.com/chedr
S 1430-4171 (98) 04233-4

this “makeshift” calibration curve to be rigorous, and we do not share it with our students. Nevertheless, we include it here for completeness, as the reader might wonder whether polystyrene is an appropriate standard for GPC calibration with fullerenes.

Classroom Response

This experiment has been used for a full semester in the instructional physical chemistry laboratory at the State University of New York at Binghamton. The laboratory ran effectively, and students had no problems getting reliable data. The experiment usually took about three hours to complete. The main weakness of this experiment was the time spent waiting for sample elution. To overcome this weakness, we typically spent this time discussing the components and general operation of the GPC as well as the interesting aspects of the chromatograms and data interpretation.

Central themes in the students’ responses to our in-class survey relate to the modern scientific, open-ended, and instrument-based nature of the experiment. The open-ended nature of the experiment is inherent in that the C_{60} polymerization problem is still an active area of research, and it has not been conclusively proven that intermolecular bonding is occurs upon photoirradiation. Therefore, students, must critically assess both their data and the recent literature to put the problem in context. In addition, one student remarked in the survey that “it was exciting that the background reading for the experiment referred to recent journal articles (1995–1997).” Most students commented that they liked studying an experimental problem that is of interest in the real world. The modern scientific focus of the experiment clearly had an impact. Other students were more interested in learning about up-to-date instrumental techniques. This is a very natural response, because separation techniques, such as GPC, are very important in a variety of industries.

Laboratory Report Discussion

Our physical chemistry laboratory is a “scientific writing emphasis” course. Therefore, the reports contained all aspects of a well-written scientific paper: abstract, introduction, experimental, results, discussion, conclusion, and reference sections. It is especially important to note that students are asked to supplement background information from the laboratory manual with literature references and current scientific hypothesis. In addition to the aforementioned sections, several key questions were expected to be addressed in the write-up. These included:

- What is the difference between a thermally and photochemically allowed reaction?
- How should polymerization in solution differ from that on a solid substrate?
- What is the physical basis for the separating abilities of GPC? How do the detectors that are used in the experiment work?
- What might be the source of trouble with the refractive index detector? Why is this detector less useful in this experiment than the absorption detector?
- Why is absorption detector set at 300 nm?
- What might be the effect of running an acetonitrile/toluene blank?
- Discuss and rationalize your peak assignments in the chromatograms.
- Does this experiment prove that intermolecular bonds are forming between C_{60} units? If not, what are you proving through this experiment?
- Is any more research necessary on this system? If so, what other techniques or methods can be employed to reach more conclusive results and address the important outstanding problems?

Curriculum Placement

It is worth mentioning that this experiment could be implemented in several different advanced laboratory courses including experimental physical chemistry, instrumental analysis, and materials chemistry. Although the focus may be different in each case, the experiment is very multidimensional and can fit the needs of each course. For instance, in using this experiment in the physical chemistry laboratory we concentrated on the scientific results (using GPC as a tool); whereas, an instrumental class may prefer to focus on specific aspects of the GPC instrument (using C_{60} simply as a sample to analyze).

Conclusion

We report the development of a new physical chemistry laboratory exercise that uses GPC to study pristine and photoirradiated C_{60} materials. In the laboratory, students inject both pristine and irradiated C_{60} samples and analyze the retention time data. It is clear that photoirradiation results in the formation of higher molecular weight species, suggesting that intermolecular bonding takes place, as expected. The implementation of this laboratory in the classroom has been very successful and has received a great

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http://journals.springer-ny.com/chedr
S 1430-4171 (98) 04233-4

deal of positive feedback from students. In surveys, students commented on how much they appreciate the organized layout of the experiment, and that they enjoyed an experiment which utilized modern equipment to investigate a modern problem.

ACKNOWLEDGMENT

Financial support from the Instrumentation and Laboratory Improvement Program (DUE-9650197), the Career Development Program (DMR-9623221) provided through the Division of Materials Research, and the Division of International Programs (INT-9722488) at the National Science Foundation is gratefully acknowledged. J.M.P. wishes to thank the Dean's Office at SUNY–Binghamton for financial assistance though the Undergraduate Research Awards Program. This work benefited from conversations and correspondence with D. C. Doetschman, K. Kamarás, V. C. Long, M. S. Meier, S. Pekker, and D.M. Sarno. Also, we would like to thank S. Pekker for his assistance with the chemical structure drawings in this document.

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