2310 *J. Org. Chem.* **1997,** *62,* 2310−2311

Preparative Benchtop Enrichment of C_{60}, C_{70}, and the Higher Fullerene Allotropes Using a Brominated Polystyrene Stationary Phase

Walter A. Scrivens, Adam M. Rawlett, and James M. Tour*

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208

Received January 21, 1997

Since the discovery of fullerenes in 1985,[1] much effort has been devoted to their purification.[2−5] Fullerenes are easily synthesized by the carbon arc method,[6] and we have reported simple charcoal-based benchtop protocols for obtaining multigram quantities of both C_{60} and C_{70}.[7,8] However, isolation of macroscopic quantities of the higher fullerenes ($>C_{70}$) required use of specialty high-pressure liquid chromatography (HPLC) techniques.[3,9−11] The minute quantities of higher fullerenes available through conventional HPLC has limited research in this field. Preparative HPLC columns for fullerene separations are expensive, and they require multiple passes, often >30, to obtain even submilligram quantities of the enriched higher fullerenes. Additionally, in order to maintain adequate separation profiles on most HPLC-based stationary phases, potent fullerene solvents cannot be used, thereby inhibiting the dissolution of the higher fullerenes. Outlined here is a simple method for the benchtop enrichment of preparative amounts of C_{60}, C_{70}, and the higher fullerenes ($<C_{100}$) from a crude fullerene mixture by a single elution through a column of poly(dibromostyrene)/divinylbenzene (PDBS/DVB) using chlorobenzene as the mobile phase.

Size-exclusion chromatography (SEC) generally follows the trend of larger compounds (greater hydrodynamic volume) eluting from the column first. Previous experiments on fullerene separations using the common polystyrene/DVB-based SEC columns indicated that an atypical elution trend was followed; the smaller fullerenes eluted first while the larger fullerenes eluted last.[9−13] This unusual trend was intriguing with a possible $\pi-\pi$ or charge-transfer interaction between the fullerenes and the styrenes dictating the affinity mechanism. We therefore investigated use of functionalized polystyrene stationary phases for the purification of fullerenes using various styrene monomers that were similar in structure to potent fullerene solvents.[14] The suspension polymerized resins prepared and screened for their efficacy in fullerene separations included polystyrene/DVB, poly(4-chlorostyrene)/DVB, poly(4-naphthylstyrene)/DVB, and PDBS/DVB. The PDBS/DVB stationary phase permitted a superior separation. This new stationary phase (1) was inexpensive since the monomer is produced in bulk (the polymer is used as a flame-retarding additive for commodity plastics), (2) was easily produced in large quantities by a suspension polymerization, (3) permitted the use of potent fullerene solvents, and (4) could be easily reused. Numerous potent fullerene solvents[14] including chlorobenzene, 1,2-dichlorobenzene, carbon disulfide, and toluene were investigated as mobile phases; chlorobenzene gave the optimal separation for fullerenes in $<C_{100}$ range.[15]

The preparation of the PDBS/DVB stationary phase involved a simple bead suspension polymerization. Inhibitor-free dibromostyrene[16] (90 g, 50 mL, 344 mmol) and divinylbenzene[17] (2.7 g, 3.0 mL, 21 mmol) were mixed with AIBN[18] (400 mg, 2.44 mmol) and added to a solution of methyl cellulose[19] (2.0 mg) in 400 mL of deionized water. These components were stirred in an industrial blender set at low for 8 min.[20] The resulting suspension was then heated at 75 °C for 2 days. The polymer beads were then poured into a 43 mm × 123 mm Soxhlet thimble and extracted with acetone for 12 h.[21] The beads were dried in a vacuum oven at 45 °C (2.0 mmHg) overnight. The beads that had aggregated into clumps were gently ground with a mortar and pestle and size fractionated using stainless steel full-height laboratory sieves. The 200−400 mesh (37−74 μm) particle size range was chosen for gravity column chromatography. The polymerization afforded 73 g (79% yield, mass to mass) of the resin, and 41 g (44% overall) of the particles obtained had the desired 200−400 mesh particle size.

A typical fullerene purification was performed as follows. The PDBS/DVB stationary phase (140 g) in chlorobenzene (250 mL) was permitted to stand for 1 h to permit swelling of the resin before pouring into a 4.5 × 60 cm glass column that had a cotton plug at the bottom and a 500 mL solvent reservoir at the top. The slurry was allowed to settle and the solvent drained until

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(15) Preliminary results have indicated that 1,2,4-trichlorobenzene is a particularly good mobile phase for preparing fullerene mixtures highly enriched in $C_{100}-C_{200}$ using our stationary phase described here. This observation was noted by Dr. L. D. Lamb at the University of Arizona.

(16) Dibromostyrene was obtained from Great Lakes Chemicals and purified by passage through neutral alumina. The dibromostyrene was reported by the manufacturer to be a mixture of the following isomers: 3,4-dibromostyrene (43%), 2,4-dibromostyrene (27%), 4-bromostyrene (15%), 2,5-dibromostyrene (10%), 2,4,5-tribromostyrene (5%).

(17) Divinylbenzene, technical grade, a mixture of isomers, was purchased from Aldrich and purified by passage through neutral alumina. This is used as the resins' cross-linking component.

(18) AIBN was purchased from Pfaltz and Bauer and used without purification.

(19) Methyl cellulose was purchased from Fisher, had a viscosity of 1500 centipoise, and was used without purification.

(20) A Waring two-speed commercial blender, Model 5011, with a standard offset four blade stirrer was used for bead suspension. The low setting afforded optimal results.

(21) Soxhlet extraction with *o*-dichlorobenzene and chlorobenzene did not give better separation in comparison with the acetone-washed resin.

S0022-3263(97)00098-4 CCC: $14.00

Table 1. Fractions Collected from the PDBS/DVB Column

band no.[a]	band color	constituent(s) (% purity)[b]	isolated wt (mg)
1	purple	C_{60} (99.3)	51.2
2	dark brown	C_{70} (98.8)	19.3
3	golden	C_{76} (30.0) C_{78} (61.1)	0.7
4	golden gray	C_{78} (98.7)	2.0
5	olive	C_{84} (84.3) C_{86} (10.0)	10.9
6	light gray	C_{90}, C_{92} (mix, 100)[c]	1.0
7	dark gray	C_{90}, C_{92} (mix, 10.9)[c] C_{94}, C_{96} (mix, 89.1)[c]	10.0

[a] The lower the band number, the faster the elution rate. [b] The purity was determined by HPLC on a C-18 column using a 55:45 MeOH/toluene mixture at a flow rate of 1 mL/min and UV detection at 340 nm. The peak identities were determined relative to authentic samples.[23] [c] The broadened peak did not have adequate resolution to permit quantitation of each of the two components in the mixture.

the solvent was ca. 1 mm above the stationary phase. The stationary phase should not be allowed to become solvent free. A homogeneous saturated chlorobenzene (20 mL) solution of crude fullerenes (100.4 mg) extracted from carbon arc soot[22] was slowly poured onto the top of the PDBS/DVB stationary phase. The mixture was then eluted, under gravity pressure, at a flow rate of 1 mL/min using chlorobenzene as the mobile phase. Application of a head pressure (5−20 psi) caused compression of the stationary phase, thereby retarding flow through the column. Seven distinct colored bands were visually distinguished as they moved through the column, and they were each collected and tested by HPLC to determine their purity (Table 1).[23] Note that 95% of the original material weight applied to the column was recovered; therefore, unlike alumina or charcoal stationary phases for C_{60} and C_{70} purifications,[5,7,8] there was little irreversible adsorption during the chromatographic process. The total volume of chlorobenzene needed for the recovery of all seven bands was 3 L, though nearly all of the solvent (>95%) was easily recovered and reused throughout the purification process by rotary evaporation using an ice water-cooled condenser. To our knowledge, there are no preparative separation methods that permit this level of separation from a single column elution of mixed fullerenes. Moreover, the column was reusable simply by washing with chlorobenzene; there was no noticeable decomposition of the column material after multiple runs. In fact, the efficiency of the column improved slightly after the first use.

In summary, we developed a method for the simple benchtop enrichment of C_{60}, C_{70}, and the higher fullerenes ($<C_{100}$) using a PDBS/DVB stationary phase with chlorobenzene, a potent fullerene solvent, as the eluent. Obtaining higher fullerenes by simple methods is a necessary step in exploring the chemistry of these large carbon structures.

Acknowledgment. Support came from the Office of Naval Research and the National Science Foundation (EHR-91-08772, DMR-9158315). We are grateful to Dr. L. P. Felipe Chibante of BuckyUSA Inc. for conducting the HPLC analyses of all of the enriched fullerene fractions.

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(22) The soot was obtained by the carbon arc method and extracted with toluene and sonication as described previously.[7b] Therefore, most of the fullerenes $>C_{100}$ were not present in the sample since their solubility in toluene is minimal.[15]

(23) The HPLC chromatographic analyses and assignments were obtained by BuckyUSA Inc., Bellaire, TX.