

# Gel Permeation Chromatography of Fullerene-Centered Macromolecules

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## Abstract

Gel permeation chromatography (GPC) behavior of fullerene-centered macromolecules is investigated. Because of the globular shape of the macromolecules, their GPC results are different from those of linear polystyrene standards. These macromolecules may serve as alternative molecular weight standards for polymers or dendrimers of similar globular structures. The results also show that the GPC analysis is capable of discerning relatively minor structural differences in the fullerene-centered macromolecules.

## Introduction

Fullerene  $C_{60}$  is a spherical molecule that can be symmetrically functionalized in three dimensions (1,2). It is considered an ideal core block for globular dendrimers or dendrimer-like macromolecules (3–6). For example, dendritic macromolecules of branches including benzyl ethers, photoresponsive azobenzenes, water-soluble moieties, and liquid crystalline cyanobiphenyl units have been reported (7–14). We have synthesized a series of  $C_{60}$ -centered lipophilic macromolecules Ii ( $i = 1 - 6$ ) and IIj ( $j = 1 - 5$ ) (15). Results from the gel permeation chromatography (GPC) investigation of these macromolecules are reported.

## Experimental

GPC experiments were performed on a system equipped with a Shimadzu LC-10AS pump (Kyoto, Japan), a Rainin Instrument UV-1 UV-vis detector (Mettler Toledo, Columbus, OH), and a set of three serially connected PerkinElmer PL-gel columns (Wellesley, MA). The mobile phase was tetrahydrofuran (THF), which was pre-treated by being passed through 5- $\mu\text{m}$  poly(tetrafluoroethylene) (PTFE) membrane filters, with a flow rate of 1 mL/min. The sample solutions for GPC measurements were filtered through 0.2- $\mu\text{m}$  PTFE membrane filters before injections. Polystyrene

standards were measured as references at the beginning and end of each experiment to verify the consistency.

## Results and Discussion

Shown in Figure 1 are GPC results of the  $C_{60}$ -centered macromolecules in comparison with those of polystyrene standards. The observed polydispersity index (PDI) values are all close to

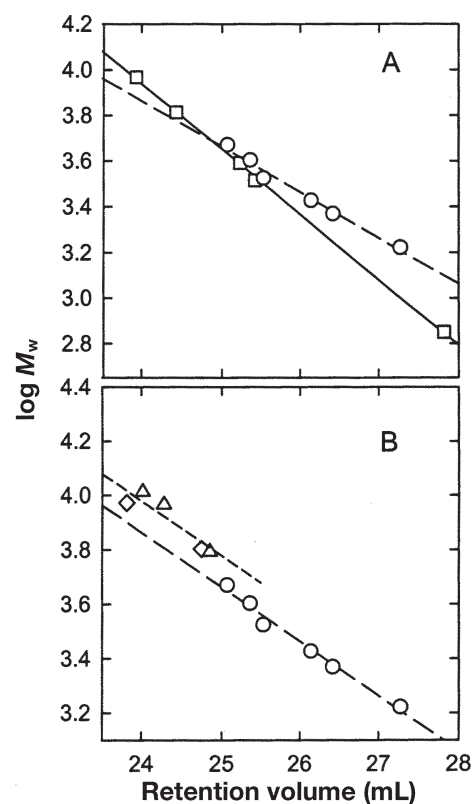


Figure 1. The GPC results of the series I macromolecules (O) are compared with those of (A) the linear polystyrene standards ( $\square$ ) and with those of (B) II<sub>1-2</sub> ( $\diamond$ ) and II<sub>3-5</sub> ( $\triangle$ ).

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unity for the macromolecules (Table I), consistent with the fact that these are monomolecular species. However, the GPC behavior of the macromolecules is obviously different from that of the linear polystyrene standards. The series I macromolecules all have smaller hydrodynamic volumes than the linear polystyrenes of the same molecular weights (Figure 1A), consistent with their more compact molecular structures. Thus, these C<sub>60</sub>-centered macromolecules could be used as alternative molecular weight standards for polymers or dendrimers of similar globular structures in GPC analyses.

The GPC results of the series II macromolecules deviate significantly from the linear relationship of the series I macromolecules (Figure 1B). The hydrodynamic volumes of the macromolecules, as reflected in their retention volumes, are smaller than what are expected in terms of their known molecular weights. This is consistent with the fact that the macromolecules in the series II are likely more dense than those in the series I. In order to compare the densities of macromolecules in

the two series, the commercial software Hyperchem (Hypercube, Gainesville, FL) (MM+ force field) (16) was used to estimate the relative molecular volumes in vacuum at 300 K. The molecular densities thus calculated vary with the molecular weights in each series, but the variations in I and II are different. The difference apparently compensates the deviation of the series II results from the relationship for the series I in Figure 1B. Shown in Figure 2 is a semilogarithmic plot of the calculated volumes of the macromolecules against their experimental GPC retention volumes. Both series of macromolecules can be correlated using a single linear relationship, despite the crude nature of the Hyperchem calculation.

All of these macromolecules share the same structural components, including a fullerene core and hydrophobic tails. The difference of series II from series I is that macromolecules in these series contain spacers between the core and tails. The molecular weight increases associated with the spacers may not result in proportional increases in the hydrodynamic volume, which is probably responsible for the different GPC results of the two series. Moreover, for macromolecules in the series II itself, the GPC results are not represented well by a simple linear relationship. This is interesting because it shows that the GPC analysis is responsive to the relatively subtle structural variations in the spacers, hydrophilic hexane-diol versus ethylene glycol chains. In particular, the macromolecule II<sub>5</sub> is known to contain hydrophilic cavities (3–6). The unimolecular reverse micelle-like properties of the macromolecules containing ethylene glycol spacers may have contributed to the sensitivity of the GPC results to relatively minor changes in macromolecular structures. There may also be minor contribution from a trace amount of water in the mobile phase THF, despite the rigorous drying of the solvent before use.

Again, these fullerene-centered macromolecules may be used as GPC standards, especially for globular molecules and in the low molecular weight region.

	Molecular formula	MW*	PDI†	Retention volume (mL)‡	Normalized density§
I <sub>1</sub>	C <sub>102</sub> H <sub>60</sub> O <sub>24</sub>	1670	1.01	27.28	1
I <sub>2</sub>	C <sub>150</sub> H <sub>156</sub> O <sub>24</sub>	2343	1.01	26.42	0.84
I <sub>3</sub>	C <sub>174</sub> H <sub>204</sub> O <sub>24</sub>	2679	1.01	26.14	0.78
I <sub>4</sub>	C <sub>222</sub> H <sub>300</sub> O <sub>24</sub>	3353	1.02	25.53	0.76
I <sub>5</sub>	C <sub>270</sub> H <sub>396</sub> O <sub>24</sub>	4026	1.02	25.36	0.73
I <sub>6</sub>	C <sub>318</sub> H <sub>492</sub> O <sub>24</sub>	4699	1.01	25.07	0.68
II <sub>1</sub>	C <sub>402</sub> H <sub>528</sub> O <sub>60</sub>	6320	1.05	24.75	0.78
II <sub>2</sub>	C <sub>618</sub> H <sub>960</sub> O <sub>60</sub>	9350	1.08	23.81	0.72
II <sub>3</sub>	C <sub>378</sub> H <sub>480</sub> O <sub>72</sub>	6176	1.04	24.85	0.84
II <sub>4</sub>	C <sub>594</sub> H <sub>912</sub> O <sub>72</sub>	9206	1.05	24.28	0.76
II <sub>5</sub>	C <sub>642</sub> H <sub>1008</sub> O <sub>96</sub>	10263	1.05	24.02	0.72

\* Molecular weight from the chemical formula.  
 † Polydispersity index from GPC experiment.  
 ‡ Retention volume from GPC experiment.  
 § Normalized density obtained from the Hyperchem (MM+ force field) calculation.

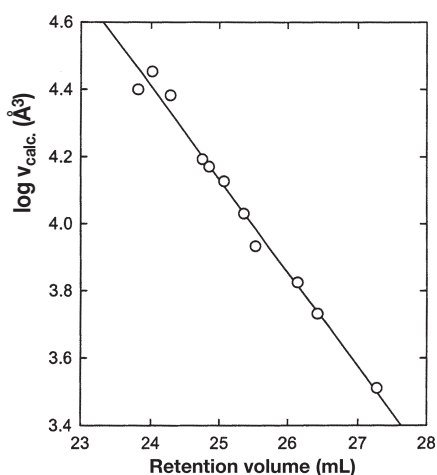


Figure 2. A semilogarithmic plot of the calculated molecular volumes against the experimental GPC retention volumes for macromolecules in both series.

## Supporting Information

Supporting information including details on the synthesis and characterization of the fullerene-centered macromolecules is available from the author.

## Acknowledgments

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  - Details on the synthesis and characterization of the fullerene-centered macromolecules are provided in the Supporting Information.
  - Hyperchem software. Hypercube, Inc., Gainesville, FL.

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