

Table 2. Preparation of α -Methyl β -Substituted β -Fluorovinyl Sulfides **5**

Product	R ¹	T (°C)	Yield (%) ^{a,b,c}	Z/E ^d
5d	<i>n</i> -C ₄ H ₉	-78→15	83	60/40
5e	<i>s</i> -C ₄ H ₉	-78→15	60	64/36
5f	<i>t</i> -C ₄ H ₉	-78→15	NR ^e	—
5g	C ₆ H ₅	-78→15	80	66/34
5h	H ₂ C=CH	-78→15	53	63/37
5i	C ₆ H ₁₃ C≡C	0→15	81	67/33
5j	C ₆ H ₅ C≡C	0→15	80	68/32

^aIsolated yield. ^bAll products are (E) and (Z) isomeric mixtures. ^cAll products were isolated by column chromatography. ^dRatio was determined by ¹H-NMR and ¹⁹F-NMR spectrum. ^eNo reaction.

of **2c** with alkylolithium, vinylolithium, phenyllithium, and lithium alkyl or aryl acetylide at -78°C , followed by slow warming to ambient temperature, resulted in the formation of corresponding vinyl sulfides **5** in moderate to high yields. However, reaction of **2c** with *t*-BuLi did not occur even at room temperature. The results of these reactions are summarized in Table 2. In particular, compound **2c** can be utilized in the addition-elimination reaction¹⁶ with various types of nitrogen and oxygen nucleophiles which can not be reacted with compound **1c**. Although reactions of **1c** with organolithium compounds except for lithium phenyl acetylide and *t*-BuLi provided the corresponding vinyl sulfides **5**, the use of intermediate **2** in these reactions resulted in the clean formation and easy isolation of **5**.

In a typical procedure, a 250 ml two-neck flask equipped with a septum, a magnetic stir bar and a nitrogen tee connected to a source of argon, was charged with 1,1-bis(phenylthio)-2,2,2-trifluoroethylbenzene (3.76 g, 10.0 mmol) and 50 ml dry THF. The reaction mixture was cooled to -78°C by using dry-ice/isopropanol slush and phenyllithium (1.8 M solution, 11.2 ml, 20.2 mmol) was added dropwise at -78°C , followed by slow warming to ambient temperature. The reaction mixture was quenched with water (50 ml) and extracted with ether (50 ml \times 2). After the ether layer was dried with anhydrous MgSO₄, column chromatography (hexane) provided 2.87 g (94% yield) of 1,2-diphenyl-2-fluorovinyl phenyl sulfide **3g**: m.p. 53°C ; ¹H-NMR (CDCl₃) δ 7.83-7.50 (m, 5H), 7.41-7.07 (m, 10H); ¹⁹F-NMR (CCl₄, external standard CF₃COOH) δ -6.67 (s, 1F), -10.57 (s, 1F); IR (KBr) 3050 (w), 1616 (m, C=C), 1577 (m, aromatic C=C), 1473 (m, aromatic C=C), 1438 (m, aromatic C=C), 1215 (m, C-F), 1064 (m), 1022 (m), 929 (m), 736 (s, =C-H OOP), 690 (s, =C-H OOP) cm⁻¹; MS, m/e (relative intensity) 306 (M⁺, 100), 196 (43), 185 (25), 121 (32).

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Separation of Fullerene with Poly-p-Phenylene

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Because of its various chemical reactivity and applicability,

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Figure 1. SEM photograph of poly-p-phenylene (PPP).

fullerene, a new form of solid carbon allotropes, has been required for macroscopic quantities in order to satisfy the growing interests of many researchers in this area.¹⁻⁴ Fullerene, however, is obtained from the soots in the form of mixture mainly consisting of C₆₀ and C₇₀ in toluene extracts. Therefore complete separation of C₆₀ from C₇₀ is essential in the fullerene chemistry.

Several separation methods using various chromatographic techniques such as normal/reversed phase and gel permeation columns have already been reported.⁵⁻¹³ One of the conventional methods in the preparation of pure C₆₀ and C₇₀ until now, is to use an alumina/hexane system.⁷⁻¹¹ Because the dissolving power of *n*-hexane for fullerene is so poor to be used in the preparative scale that the separation of C₇₀ in this system is incomplete, there are lots of efforts to find a chromatographic system utilizing toluene itself as a solvent. One of the promising techniques recently reported is the system utilizing a ground graphite¹² or activated charcoal¹³ as the stationary phase. W. A. Scrivens *et al.* developed an activated charcoal-silicagel/toluene system which demonstrated an excellent separation efficiency for C₆₀.¹³ Even in this method, the separation of C₇₀ was incomplete and some of the fullerenes were irreversibly adsorbed into the charcoal.

On the other hands, the fullerene compounds have unique geometrical structures. They are consisted of 12 pentagonal faces, but have different number of hexagonal faces; C₆₀ has 20 six-membered rings while C₇₀ has 25 six-membered rings. As a result, C₆₀ is spherical and C₇₀ is ellipsoidal. As the symmetrical difference due to the number of six-membered rings between C₆₀ and C₇₀ could play an important role in their separation, we examine the poly-p-phenylene (PPP) as the stationary phase which is a typical compound with six-membered ring only.¹⁴ Fortunately, since PPP is a fine particle which is insoluble in organic solvent and thermally stable, it can be selected as a packing material for the chromatographic column.¹⁵ Namely, in this communication, in order to obtain the complete separation of C₆₀ and C₇₀ in the fullerene mixture, we developed a new liquid chromatographic system with PPP as the stationary phase and pure toluene as the mobile phase respectively.

PPP was prepared from polymerization of benzene according to Kovacic's method¹⁶ and characterized by Fourier trans-

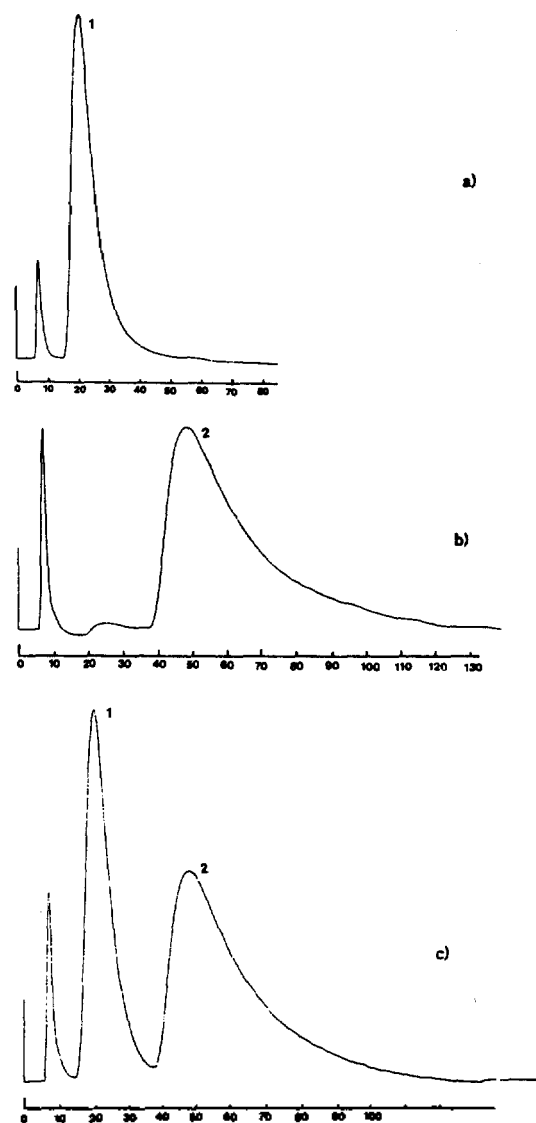


Figure 2. Typical chromatogram of a) standard C₆₀; b) standard C₇₀; and c) fullerene mixture. (1) C₆₀, (2) C₇₀

Conditions: PPP as the stationary phase; Toluene as the mobile phase; flowrate 0.7 ml/min; UV detection at 330 nm.

form infrared spectroscopy (FTIR, IFS-48, Bruke Co.), X-ray powder diffractometer (XRD, PW-1710, Philips), and thermal analyzer (TA, TA-9200 system, 951 TGA, 2910 DSC, TA Instruments). It was grounded in the mortar and its size was determined by scanning electron microscope (SEM, JSM-35 CF, JEOL). The column was packed with PPP into a stainless steel tubing (4.6 mm I.D., 30 cm length) under flowing of toluene at 100 psi. A single-piston reciprocating pump (Waters 510, Millipore Co.) was used to deliver toluene as the mobile phase at the flow rate of 0.7 ml/min. Fullerene mixtures were prepared by mixing C₆₀ (2×10^{-4} M, 50 μ l) and C₇₀ (2×10^{-4} M, 100 μ l).¹⁷ Each C₆₀, C₇₀ and mixture was introduced into the column by using a 200 μ l¹⁸ injection valve (C10U, Valco Instruments). The eluent from the column flowing through a UV-absorbance detector (Waters 486, Millipore, Milford, MA) at the wavelength of 330 nm and the signal was displayed on a chart recorder (Model 585, Linear instru-

ments).

The instrumental data of PPP obtained from FTIR, XRD, and TA are well agreed with those of Kovacic. From the result of SEM showing in Figure 1, the particle diameter of PPP is about 10 μm , but irregularly large particles are observed, too. As PPP particles have weak cohesive property, it is difficult to make their size be uniform. The chromatograms for the separation of C_{60} and C_{70} in PPP/toluene system are plotted in Figure 2. In Figure 2a, the retention time of air¹⁸ and C_{60} at the flow rate of 70 ml/min is 7 and 20 minutes respectively. In Figure 2b, retention time of C_{70} is 48 minutes and the impurity peak of C_{60} ¹⁷ in C_{70} is also observed. The resolution capacity factor of C_{70} is about 3 times higher than that of C_{60} , so the chromatogram of C_{70} is much broader than that of C_{60} . Figure 2c shows the separation of C_{60} from C_{70} in its mixture. The retention times of C_{60} and C_{70} in the mixture are exactly the same as those of individual compound, that is, 20 and 48 min respectively. The complete separation of C_{60} and C_{70} with the resolution of about 1.5 was achieved. And C_{70} is retained over twice longer than C_{60} . As mentioned above, it is anticipated that the spherical C_{60} seems to elute faster than ellipsoidal C_{70} in the present chromatographic condition. It is, however, insufficient to describe the retention mechanism of fullerenes in this system. We hope to perform more detailed investigation for the separation mechanism in further study.

Note that our experimental conditions were not optimized for the separation of fullerene in the standard mixture or in the toluene extracts. However the separation ability preliminarily reported here was found to be superior to the existing methods at least by obtaining complete separation of C_{60} and C_{70} with pure toluene solvent. Clearly, this method could separate larger quantities of raw material from the toluene extracts rapidly using much smaller volume of solvent. Additionally, because the pressure of this system was selected at 100 psi, it is possible to make to pump free system.¹⁹ In the condition of high-pressure packing of PPP, the separation efficiency could be significantly improved.

In conclusion, based on the ideas and data described above, the PPP/toluene system promises a strong possibility that can be used for the separation method of fullerene in toluene extracts. This system can also be extended into a preparatory scale and be an alternative for the conventional activated charcoal/toluene system due to its high separation ability of C_{70} .

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- Of course, graphite and active charcoal are also another example of this type compound.
- As far as we know, The use of PPP as a stationary phase in liquid chromatography has not been reported yet.
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- The standard solutions were made using conventional separation method of alumina/hexane system. In general, the C_{70} solution obtained from this technique, contains about 5% of C_{60} as impurities due to incomplete separation of fullerene.
- When the solvents has been used as mobile phase, in order to make the reference peak, the air was injected with sample using the injection valve.
- 100 psi is the obtainable pressure from conventional N_2 regulator. So ordinary nitrogen tank could substitute the expensive high pressure pump.

Effect of Fe(II)-Tetradentate Schiff Base Complex on the Electrochemical Reduction of Thionyl Chloride

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The lithium thionyl chloride system has emerged as one of the best primary batteries having combined characteristics of high rate capability, high energy density, long shelf life, and efficient low temperature operation. The electrochemical reduction of thionyl chloride has been studied extensively