Synthesis of Linear Fullerene-Containing Polysiloxanes and Their Application to Capillary Gas Chromatography

Chen Yuanyin,* Fang Pengfei, Zeng Zhaorui, and Fan Jianhong#
Department of Chemistry, Wuhan University, Wuhan 430072, Hubei, P.R. China

(Received February 16, 1999; CL-990107)

Fullerene-containing polysiloxanes were prepared by reacting [60]fullerene with azidoalkyl polysiloxanes directly, and characterized by FT-IR, UV-Vis, ^{1}H-NMR and ^{13}C-NMR. The polymers were used as stationary phases in capillary gas chromatography. Many organic compounds, especially high boiling substance or aromatic or alcohol positional isomers, were separated effectively on these columns.

Recently, polymeric fullerene materials have received great attention.[1-3] Many types of polymers, for example, polystyrene-bound fullerene,[4-6] have been synthesized and characterized. However, fullerene-containing polysiloxanes, especially linear fullerene-containing polysiloxanes were seldom reported.[7] In fact, polysiloxanes have many advantages, such as low temperature of glass transition, good thermal and oxidative stability, low surface energies, excellent biocompatibility, etc. The combination of fullerene and polysiloxane may create a novel type of material with unique properties and wide potential technological applications. In this work, we reported the synthesis and characterization of two kinds of linear fullerene-containing polysiloxanes (Scheme 1). They were used as stationary phases in capillary gas chromatography.

Hydrosilylation of polymethylsiloxane (active hydrogen content is 0.05%) with 5-fold excess of allylbromide (or undecenyl bromide) in benzene at 60 °C catalyzed by chloroplatinic acid solution (0.1 mol/L H_2PtCl_6-i-PrOH), monitored by IR until the band at 2167 cm^{-1} for the Si-H group disappear, gave the compound **1a** (or **1b**). Their ^{1}H-NMR spectra showed that the peak of proton attached on the double bond disappeared and a peak around δ 0.5-0.6 ppm (Si-CH_2) was presented.

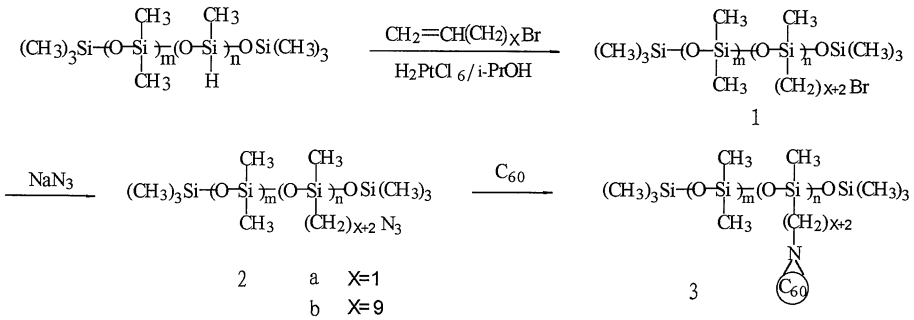
Compound **1** was dissolved in dichloromethane, then mixed with the solution of sodium azide in dimethylsulfoxide. After stirred for 24 h, the compound **2** was obtained as colorless viscous oil. A strong band at 2097 cm^{-1} appeared for the azide group in the IR spectrum (CH_2Cl_2).

Reaction of excess of [60]fullerene with compound **2** in refluxing chlorobenzene for 1 day gave a brown solution of **3**. After removing the solvent under vacuum, dichloromethane was added, and insoluble [60]fullerene was filtered off. No [60]fullerene could be detected by TLC in the filtrate. ^{1}H-NMR spectra of **3** were similar to that of **2**. But their ^{13}C-NMR spectra (125 MHz, $CDCl_3$ solution) were quite different. The ^{13}C-NMR spectra of **3** exhibited typical peaks for polymer-bound [60]fullerene,[8] i.e , a weak and broad peak in the δ 140–150 region in additional to the intense signal to polysiloxanes. FT-IR spectra of **3** was also similar to that of **2** except that the absorption band at 2097 cm^{-1} (for azide group) disappeared and the peak at 524 cm^{-1} appeared due to [60]fullerene group. The UV-Vis spectrum of **3** in dichloromethane solution showed peaks at about 231, 258, 325 nm. These results indicated that [60]fullerene had been covalently linked to the polymers. The fullerene content of **3a**, **3b** was 5.5 mg/g and 6mg/g respectively. The polymers were kept in solution to avoid cross-linking. The [η] value of **3a** and **3b** was 9.03, 9.98 mL/g respectively.

Fused-silica capillary column (0.25 mm id) was rinsed with methanol and purged with nitrogen at 250 °C for 2 h. The column was then statically coated with a solution of 0.5% (w/v) fullerene-containing polysiloxane in dichloromethane. Followed by flushing with nitrogen for 2 h, the column was conditioned at 250 °C for 4 h.

These fullerene-containing polysiloxanes stationary phases possesssed high column efficiency (over 4000 plates m^{-1}, for naphthalene at 120 °C), wide operational temperature range (100–360 °C) and outstanding thermostability. It could be used at 360 °C with a baseline drift of 4~6×10^{-15}A. Grob test mixtures eluted on these columns in the order of 2-octanone, 1-octanol, 2,6-dimethyl phenol, n-dodecane, 2,4-dimethylaniline, naphthalene. The order differed form that on column OV-1 (2-octanone, 1-octanol, 2,6-dimethylphenol, 2,4-dimethylaniline, naphthalene, n-dodecane), indicating that the strong π–π interaction of [60]fullerene with aromatic moieties played an important role in separation mechanism.

The columns exhibited unique selectivity for many organic compounds, such as alkanes, alkenes, alcohols, ketones, anilines



Scheme 1.

Table 1. Retention data for studied alcohol or aromatic positional isomers (**3a was** used as stationary phases)

Compuond	k' [a]	α [b]	Column Temperature / °C	Compuond	k'	α	Column Temperature / °C
1–Nonanol	1.93	1.00		m-Nitrochlorobenzene	2.85	1.00	
2–Nonanol	2.58	1.34	110	p-Nitrochlorobenzene	2.93	1.03	130
3–Nonanol	2.49	1.29		o-Nitrochlorobenzene	3.09	1.09	
4–Nonanol	2.36	1.22					
				o-Chlorophenol	0.25	1.00	
2,3-Butanediol	0.44	1.00		m-Chlorophenol	0.71	2.80	170
1,3-Butanediol	0.84	1.91	110	p-Chlorophenol	0.80	3.15	
1,4-Butanediol	1.53	3.48					
				o-Benzenediol	0.53	1.00	
p-Nitrotoluene	2.83	1.00		p-Benzenediol	0.66	1.24	170
m-Nitrotoluene	2.92	1.04	130	m-Benzenediol	0.88	1.66	
o-Nitrotoluene	3.11	1.11					
				p-Dinitrobenzene	1.75	1.00	
α-Methylnaphthalene	5.78	1.09	120	m-Dinitrobenzene	1.99	1.14	170
β-Methylnaphthalene	5.29	1.00		o-Dinitrobenzene	2.25	1.29	

[a] Capacity factors . [b] Separation factors (k_n/k_1).

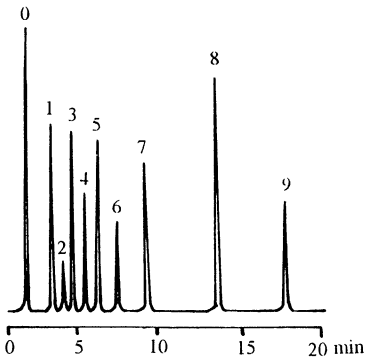


Figure 1. Chromatogram of polycyclic aromatic hydrocarbons.
Conditions: **3a** was used as stationary phase. Temperature programmed form 150 °C to 210 °C at 4 °C/min.
Peak identification: 0=solvent, 1=naphthalene, 2=β–methylnaphthalene, 3=α–methyl naphthalene, 4=biphenyl, 5=diphenyl methane, 6=acenaphthylene, 7=fluorene, 8=phenanthrene, 9= triphenyl methane.

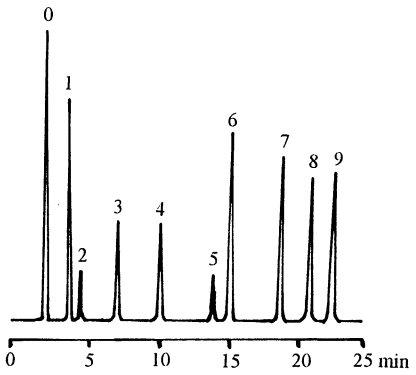


Figure 2. Chromatogram of phthalic diesters.
Conditions: **3a** was used as stationary phase. Temperature programmed form 200 °C to 290 °C at 4 °C/min.
Peak identification: 0=solvent, 1=dimethyl phthalate, 2=diethyl phthalate, 3=di-n-butyl phthalate, 4=di-n-amyl phthalate, 5=di-n-hexyl phthalate, 6=di-iso-octyl phthalate, 7=di-n-octyl phthalate, 8=di-n-nonyl phthalate, 9=di-n-decyl phthalate

and benzene homologues, etc. And they were especially suitable for separation of high boiling compounds. For example, polycyclic aromatic hydrocarbons and fatty acid methyl esters were well separated on the columns. Figure 1 showed excellent separation of some polycyclic aromatic hydrocarbons. The compounds eluted in the order of their increasing dispersion. Figure 2 showed a chromatogram of C_1~ C_{10} phthalic diesters with symmetrical peaks. These compounds are pollutants. So the fullerene-containing polysiloxane phases have significant potential application in the environment science.

It was interesting that some alcohol or aromatic positional isomers can be separated effectively on these columns. These compounds could arouse strong donor-acceptor interaction with the bonded fullerene. Table 1 showed the data of capacity factors (k') and separation factors (α) of the studied positional isomers on column using **3a** as stationary phase.

These columns have been used extensively over a period of 5 months and no significant changes in retention and selectivity have been observed.

This work was supported by National Nature Science Foundation and Fund for Ph. D. Programme from State Education Commission, P. R. China.

References and Notes

Present address: Huazhong University of Science and Technology (Hankou Division), Wuhan , P. R. China.
1 I. Amato, *Science*, **254**, 30 (1991).
2 Y. Tajima, Y. Tezuka, T. Ishii, and K. Takeuchi, *Polym. J.*, **29**, 1016 (1997).
3 L. M. Dai, A. W. H. Mau, and X. D. Zhang, *J. Mater. Chem.*, **8**, 325 (1998).
4 T. Cao and S. E. Webber, *Macromolecules*, **28**, 3741 (1995).
5 B. Liu, C. E. Bunker, and Y.-P. Sun, *Chem. Commun.*, **1996**, 1241.
6 E. Cloutet, Y. Gnanou, J.-L. Fillaut, and D. Astruc, *Chem. Commun.*, **1996**, 1565.
7 A. Glausch, A. Hirsch, I. Lamparth, and V. Schurig, *J. Chromatogr. A*, **809**, 252 (1998).
8 C. E. Bunker, G. E. Lawson, and Y.-P. Sun, *Macromolecules*, **28**, 3744 (1995).