

A New Postfunctional Method to Synthesize C₆₀-Containing Polysiloxanes

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ABSTRACT: Two new C₆₀-containing polysiloxanes were synthesized by a new postfunctional method. First, the pre-designed amino end-functionalized polysiloxane was prepared, and then the reactive macromolecular intermediate reacted with C₆₀ molecules in chlorobenzene to yield the C₆₀-containing polysiloxanes. Molecular structural characterization for the polymers was presented by ¹H-NMR, IR,

and ultraviolet-visible spectra. The polymers exhibited good solubility in common organic solvents and were air stable. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2068–2071, 2003

Key words: polysiloxanes; fullerenes; functionalization of polymers

INTRODUCTION

C₆₀ has attracted much attention due to its unique properties.^{1,2} Unfortunately, the low solubility in common organic solvents and the poor processability limit its wide applications. As the polymers possess good processability, many C₆₀-containing polymers were prepared to allow the combination of the outstanding characteristic of the fullerene with those of the polymeric matrix.^{3–6} Therefore, various methods for chemical modification of the C₆₀ to the polymers have been reported in recent years. By using these methods, the C₆₀ molecule may be introduced into the main chain of the organic polymer to form the pearl necklace polymer, in which the C₆₀ unit is a part of the polymer chain; or into the side chain of a polymer as a pendant group to form the charm bracelet polymer. Also, it may form a metallorganic macromolecule, and lattice-type polymer.⁷

However, many approaches include the complexity of the synthesis of prefunctionalized fullerenes or limit the choice of polymers that can be attached to the C₆₀ nucleus. For this reason, new ways to synthesize polymeric-modified fullerene in high yield under very mild conditions are still needed.

In this article, we present a method to prepare C₆₀-containing polysiloxanes by a postfunctionalized reaction (Scheme 1). Thus, potentially functional polysiloxane (2) was first synthesized, and then reacted with 1,3-diaminopropane to yield the amino-polysiloxane

(3), which reacted with C₆₀ in chlorobenzene to give the C₆₀-containing polysiloxanes (4 and 5). These two C₆₀-containing polysiloxanes were soluble in common organic solvents, and the synthetic conditions were very mild, the yield was high. Herein, we would like to report the synthesis procedure in detail and their structural characterization.

EXPERIMENTAL

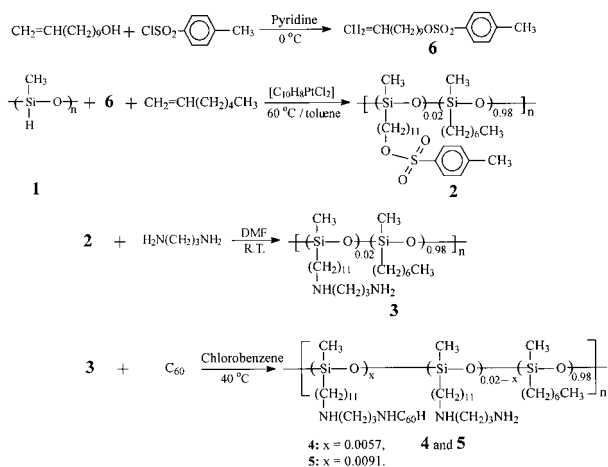
Materials and instruments

ω -Undecylenyl alcohol and 1,3-diaminopropane were purchased from Fluka and used without further purification. C₆₀ (99.99%) from Wuhan University, China, was used as received. Poly(hydrogenomethylsiloxane) was obtained from Xinhua Company, Jiangxi Province, China ($M_n = 500$). Toluene was dried over and distilled from Na under an atmosphere of dry nitrogen. Pyridine was dried over and distilled from CaH₂ under an atmosphere of dry nitrogen. Dichlorodicyclopentadiene platinum was prepared following the literature procedure.⁸ All other reagents were used as received. All the reactions were carried out in a dry nitrogen atmosphere using Schlenk technique.

¹H-NMR spectra were conducted with a Varian Mercury300 spectrometer. FTIR spectra were recorded on a Testscan Shimadzu FTIR 3000 series in the region of 3000–400 cm⁻¹ on KBr pellets. UV-visible spectra were obtained using a Shimadzu 160A spectrometer in the polymer DMF solution. Molecular weights were determined in THF solution by Waters 2960D separation Module containing Styragel HR1 THF column and Waters 2410 Refractive Index Detector with a calibration curve for polystyrene standards.

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Scheme 1

Synthesis of *p*-toluenesulfonyl ω -undecylenyloxyl ether (**6**)

p-Toluenesulfonyl chloride (34 g, 0.18 mol) was dissolved in 50 mL of pyridine, which was previously cooled to 0°C in an ice bath. Then ω -undecylenyl alcohol (25.5 g, 0.15 mol) in 30 mL of pyridine was added to the above solution dropwise in 1 h, and the reacting temperature was retained below 3°C . After the alcohol was added, the resultant solution was stirred at 0°C for 4 h. After the reaction, 50 mL of water was added, the mixture was stirred for 10 min, and then poured into 700 mL of the mixture of ice and water. The resultant mixture was placed overnight, and the organic layer was extracted by chloroform. Then the chloroform solution was washed several times by water, dried over CaCl_2 for 6 days. The solvent was distilled under vacuum to yield the product, a colorless liquid (68%). $^1\text{H-NMR}$ (δ , CDCl_3): 7.80 (d, 2H, ArH), 7.34 (d, 2H, ArH), 5.75 (m, 1H, $-\text{C}=\text{CH}-$), 4.94 (m, 2H, $-\text{C}=\text{CH}_2$), 4.01 (t, 2H, $-\text{C}-\text{CH}_2-\text{O}$), 2.45 (s, 3H, $-\text{CH}_3$), 2.02 (m, 2H, $-\text{C}=\text{C}-\text{CH}_2-\text{C}$), 1.60 (m, 2H, $-\text{C}=\text{CH}_2-\text{C}-\text{O}$), 1.34 (m, 12H, $-\text{C}-(\text{CH}_2)_6-\text{C}$).

Synthesis of **2**

Poly(hydrogenomethylsiloxane) (**1**) (1.35 g, 22.5 mmol), *p*-toluenesulfonyl ω -undecylenyloxyl ether (**6**) (0.324 g, 1 mmol) and toluene (25 mL) were placed in a Schlenk tube. After the addition of a small amount of dichlorodicyclopentadiene platinum (10^{-4} mol/mol SiH), the mixture was agitated at 60°C for 7 h. Then excess 1-heptene (3.94 g, 30 mmol) was added, and the reaction mixture was kept stirring for 40 h. Then the solvent was distilled under vacuum. The resultant product was purified by several precipitations from toluene into methanol. (3.1 g, yield: 82%) $^1\text{H-NMR}$ (δ , CDCl_3): 7.80 (d, ArH), 7.34 (d, ArH), 4.00 (t, 2H, $-\text{C}-\text{CH}_2-\text{O}$), 2.45 (m, $-\text{CH}_3$), 1.60 (m, $-\text{C}-\text{CH}_2-$

$-\text{C}-\text{O}$), 1.21 (m, $-\text{C}-(\text{CH}_2)_6-\text{C}$), 0.95 (m, $-\text{CH}_3$), 0.50 (m, $\text{Si}-\text{CH}_2-\text{C}$) 0.2 (m, $\text{Si}-\text{CH}_3$).

Synthesis of **3**

2 (3 g) was dissolved in DMF (7 mL), and then 1, 3-diaminopropane (3 mL) was added dropwise. The resultant solution was stirred at 75°C for 30 h. Enough of methanol was added to precipitate the product. The product was further purified by several precipitations from chloroform into methanol. At last, 2.25 g of **3** was yielded. $^1\text{H-NMR}$ (δ , CDCl_3): 2.94 (m, $\text{C}-\text{CH}_2-\text{N}$), 2.87 (m, $\text{CH}_2-\text{N}-\text{CH}_2$), 1.62 (m, $\text{N}-\text{C}-\text{CH}_2-\text{C}-\text{N}$), 1.21 (m, $-\text{C}-(\text{CH}_2)_6-\text{C}$), 0.95 (m, $-\text{CH}_3$), 0.50 (m, $\text{Si}-\text{CH}_2-\text{C}$) 0.2 (m, $\text{Si}-\text{CH}_3$).

Synthesis of **4** and **5**

3 (1.0 g), C_{60} (20 mg), and 20 mL of chlorobenzene were placed in a Schlenk tube. The resultant solution was stirred at 40°C for 2 days. The solvent was removed under vacuum, then some chloroform was added to dissolve the precipitant, and the solution was filtered. The main part of chloroform in the filtrate was removed, then methanol was added to precipitate 0.4 g of the black red product (**4**). $^1\text{H-NMR}$ (δ , CDCl_3): 3.48 (s, $\text{C}_{60}-\text{H}$), 2.94 (m, $\text{C}-\text{CH}_2-\text{N}$), 2.87 (m, $\text{CH}_2-\text{N}-\text{CH}_2$), 1.62 (m, $\text{N}-\text{C}-\text{CH}_2-\text{C}-\text{N}$), 1.21 (m, $-\text{C}-(\text{CH}_2)_6-\text{C}$), 0.95 (m, $-\text{CH}_3$), 0.50 (m, $\text{Si}-\text{CH}_2-\text{C}$) 0.2 (m, $\text{Si}-\text{CH}_3$).

The synthetic procedure of **5** is similar to that of **4**, the only different point was that the amount of C_{60} was 39 mg instead of 20 mg in the synthesis of **5**. $^1\text{H-NMR}$ (δ , CDCl_3): 3.48 (s, $\text{C}_{60}-\text{H}$), 2.94 (m, $\text{C}-\text{CH}_2-\text{N}$), 2.87 (m, $\text{CH}_2-\text{N}-\text{CH}_2$), 1.62 (m, $\text{N}-\text{C}-\text{CH}_2-\text{C}-\text{N}$), 1.21 (m, $-\text{C}-(\text{CH}_2)_6-\text{C}$), 0.95 (m, $-\text{CH}_3$), 0.50 (m, $\text{Si}-\text{CH}_2-\text{C}$) 0.2 (m, $\text{Si}-\text{CH}_3$).

RESULTS AND DISCUSSION

Synthesis of **2**

2 was prepared by the hydrosilylation reaction. Dichlorodicyclopentadiene platinum was chosen as the catalyst because it was soluble in toluene and its catalytic activity stays high during the period of the reaction. This was also verified by our previous examples.^{9,10} First, the controlled quantity of *p*-toluenesulfonyl ω -undecylenyloxyl ether (**6**) was added to react with poly(hydrogenomethylsiloxane) (**1**) for 7 h. The time was enough for the ether to react with **1** completely. And then, excess of 1-heptene was added to the above mixture to react for a much longer time with the remaining $\text{Si}-\text{H}$ as completely as possible. If there were some unreacted $\text{Si}-\text{H}$, the resultant polymer would crosslink after it was exposed to the air.

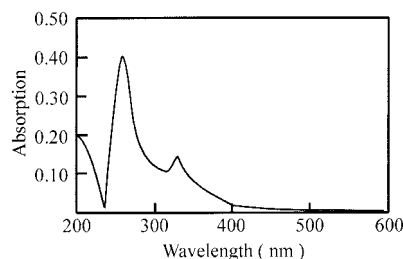


Figure 1 The UV-Vis spectrum of 4.

From the spectra of **2**, it was obvious that the signal of Si—H disappeared to indicate that there were no Si—H bonds in the polymers. Also, other functional groups could be linked to the siloxane backbone by the hydrosilylation reaction to prepare the pre-designed polymers, which contained both C_{60} moieties and the special functional groups in one polymer, for other applications.

Synthesis of 3

3 was obtained by the reaction of **2** and 1,3-diaminopropane in DMF at mild conditions. This method is a postfunctionalized approach, not like the common procedure of the synthesis of amino-containing polysiloxanes. Generally, the polysiloxanes with amino functional groups, either as pendant groups or terminated moieties, were prepared by the ring opening polymerization of cyclic siloxanes with end blockers. Also, some of these amino-containing polysiloxanes were used to react with C_{60} to yield C_{60} -containing polysiloxanes.¹¹ However, the general ring-opening conditions for the synthesis of amino-containing polysiloxanes possess some shortcomings, such as severe copolymerization, the uncontrolled amino concentration, the boring purification of the product, etc. In our method, the amino-containing polysiloxanes were synthesized by the postfunctionalized approach from a reactive polymer mediate, poly(hydrogenomethylsiloxane), and the hydrosilylation reaction can be easily controlled; also, the reaction of *p*-toluenesulfonyl ether and 1,3-diaminopropane is a mild reaction with high yield. Thus, as demonstrated in the experimental section, the amino-containing polysiloxane (**3**) with controlled amino concentration can be conveniently prepared in high yield.

The structural characterization

All the polymers have good solubility in common organic solvents, such as toluene, $CHCl_3$, THF, DMSO, and DMF, etc. The UV-Vis spectrum of **4** in chloroform was shown as an example in Figure 1. The two peaks at 258 nm and 326 nm were attributed to the absorption of C_{60} as the siloxane backbone and hep-

TABLE I

Polymer	$M_w(M_w/M_n)$	C_{60} content (wt %)
3	3000 (1.63)	—
4	2400 (1.51)	2.50
5	2200 (1.43)	3.90

tanyl moieties have no absorption in UV and visible region (200–700 nm). This spectrum confirmed that C_{60} was successfully covalently linked to the siloxane backbone because C_{60} was not soluble in chloroform.¹¹ The C_{60} concentrations in the products were determined by comparing the intensity of absorption peak at 306 nm in toluene with that of pure C_{60} in toluene (Table I).

Figure 2 showed the IR spectra of **3** and **4**. The absorption in the range of 1100–1000 cm^{-1} was assignable to the intense stretching vibration of Si—O—Si bonds, and the absorptions for the Si— CH_3 bonds were at 1260 cm^{-1} and 801 cm^{-1} . In the IR spectrum of **4**, two apparent new absorption peaks appeared at 527 and 576 cm^{-1} . **3** did not absorb in this region. These results further confirmed that C_{60} had been covalently bonded to the siloxane backbone.^{12–14} Also, the absence of the absorption peak around 2155 cm^{-1} confirmed that there were no Si—H bonds in **3** and **4**.

There was no peak at δ 4.60 ppm in the 1H -NMR spectrum of **2**, which was assigned to the proton resonance of the Si—H bonds. This confirmed that 1-heptene reacted with Si—H bonds completely and there were no Si—H bonds in **2** once more. The component concentration of **2** could be calculated from the 1H -NMR peak integration of two phenyl proton resonances of the ether group at δ 7.80 ppm, and the proton resonance of methyl group at δ 0.95 ppm. The results were shown in Scheme 1. In **4** and **5**, the molar ratio of the side groups could be calculated as the weight

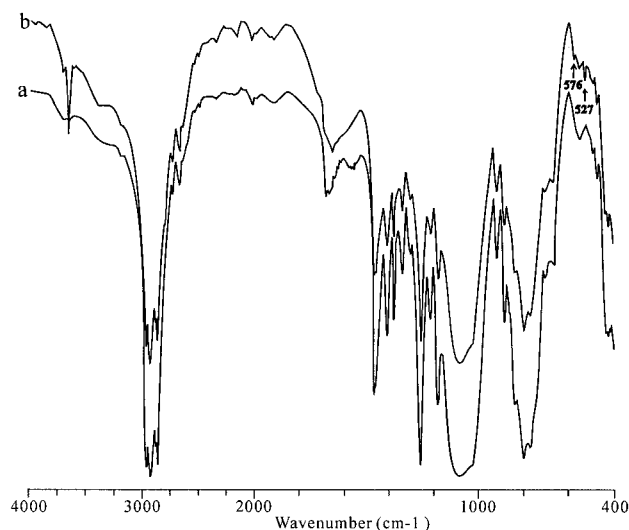


Figure 2 The FTIR spectra of 3 and 4.

concentration of C₆₀ was known in them from the UV-Vis analysis mentioned above (Scheme 1). It was shown that the resonance of the phenyl ring had completely disappeared in the ¹H-NMR spectra of **3**, **4** and **5**. This confirmed that the *p*-toluenesulfonyl groups were replaced by the amino moieties completely. Some new peaks appeared at δ2.94, 2.87, and 1.62 ppm assignable to the resonance of the protons of the diaminopropalene groups. Also, it was clear that a new weak peak at 3.48 ppm, attributed to the resonance of C₆₀-H, appeared in the ¹H-NMR spectra of **4** and **5**. This further proved that the C₆₀ moieties were really attached to the polysiloxane backbone by the postfunctional method.¹⁵

Gel Permeation Chromatography (GPC) measurements were carried out with refractive index detector (Table I). The results showed that the *M_n* of **3** was similar to those of **4** and **5**, and also the polydispersities changed a little. This suggested that the reaction conditions were mild and did not affect the properties of the polymers so much.

CONCLUSION

Two C₆₀ end-capped polysiloxanes were successfully prepared by the reaction of C₆₀ with predesigned amino end-functional polysiloxane synthesized based on a postfunctionalized approach. These two C₆₀-containing polysiloxanes are soluble in common organic solvents, such as toluene, chloroform, THF, DMF, etc.

As silicon is an element with special properties, it was introduced to the polymeric backbones in many cases. Therefore, C₆₀ moieties could be conveniently linked to these polymers if needed, by the postfunctionalized method reported here. On the other hand, many functional groups could also be bonded to the backbone of polysiloxane to yield different functionalized polysiloxanes, which also contains C₆₀ moieties, by the hydrosilylation reaction. Further studies on the synthesis of other C₆₀-containing polymers including water-soluble polymers are now in progress.

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