New Postfunctional Method To Synthesize C_{60}-Containing Poly(ethylene oxide)

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ABSTRACT: This article reports the detailed synthesis and structural characterization of two new C_{60}-containing poly(ethylene oxide)s by a new postfunctional method. A predesigned amino end-functionalized poly(ethylene oxide) was prepared, and this reactive macromolecular intermediate was reacted with C_{60} molecules in chlorobenzene to yield the C_{60}-containing poly(ethylene oxide)s. The molecular structures of the polymers were characterized with ^{1}H-NMR, IR, and ultraviolet–visible spectra. The polymers exhibited good solubility in common organic solvents and water and were stable in air. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 867–870, 2004

Key words: functionalization of polymers; fullerene-C_{60}; synthesis; reactive polymers

INTRODUCTION

C_{60} exhibits a variety of interesting conducting, magnetic, photochemical, and electrical properties because of its unusual molecular symmetry. In the past decade, the physical properties of C_{60} have been extensively investigated. Many new C_{60} compounds have been synthesized, and some of them have shown promise as potential materials for practical applications.[1–4] However, their low solubility in common organic solvents and their poor processability limit widespread applications. Because polymers possess good processability, many C_{60}-containing polymers have been prepared, combining the outstanding characteristics of fullerenes and polymeric matrices.[5–8] The grafting of biocompatible polymers onto C_{60} is especially interesting because of the potential importance of fullerene molecules in biomedical and biotechnological fields.[9] Poly(ethylene oxide) (PEO) is well known for its remarkable biomedical properties, and some C_{60}-containing PEO have been prepared.[10–12]

Recently, we developed a new postfunctional method to synthesize C_{60}-containing polymers. This method was successfully applied to the preparation of C_{60}-containing polysiloxanes, and the resultant polysiloxanes were stable in air and exhibited good solubility in common organic solvents.[13] In this study, the method was further extended to the synthesis of C_{60}-containing PEO. Potentially functional PEO (**3**) was first synthesized and then reacted with 1,3-diaminopropane to yield amino-PEO (**4**), which reacted with C_{60} in chlorobenzene to give C_{60}-containing PEOs (**1** and **2**). These two C_{60}-containing PEOs were soluble in common organic solvents and water, the synthetic conditions were very mild, and the yield was high. Here we report the synthetic procedure and structural characterization in detail.

EXPERIMENTAL

Materials and instruments

1,3-Diaminopropane was purchased from Fluka (Buchs, Switzerland) and was used without further purification. C_{60} (99.99%), from Wuhan University (Wuhan, China), was used as received. Poly(ethylene glycol) [weight-average molecular weight (M_w) = 20,000; Shanghai Chemical Co., Shanghai, China] was used without any further treatment. Toluene was dried over and distilled from Na under an atmosphere of dry nitrogen. Pyridine was dried over and distilled from CaH_2 under an atmosphere of dry nitrogen. Dichloromethane was dried by a normal method. All the other reagents were used as received. Chlorobenzene was dried over and distilled from $CaCl_2$. All the reactions were carried out in a dry nitrogen atmosphere with a Schlenk technique.

^{1}H-NMR spectra were conducted with a Varian Mercury 300 spectrometer (Palo Alto, CA). Fourier transform infrared (FTIR) spectra were recorded on a Shimadzu Testscan FTIR 3000 series (Osaka, Japan) in the region of 3000–400 cm^{-1} on KBr pellets. Ultraviolet–visible (UV–vis) spectra were obtained with a Shi-

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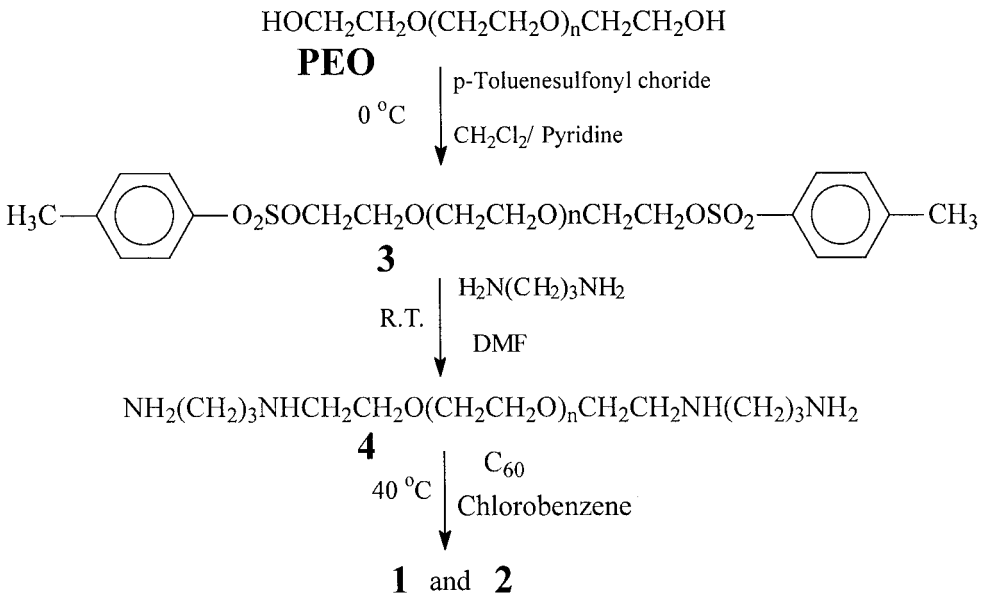

Scheme 1

madzu 160A spectrometer in a polymer dimethylformamide (DMF) solution.

Synthesis of 3

Poly(ethylene glycol) (12 g) was dissolved in 100 mL of dichloromethane, which was previously cooled to 0°C in an ice bath. Then, *p*-toluenesulfonyl chloride (0.92 g, 4.8 mmol) in 20 mL of pyridine was added to the solution dropwise in 1 h, and the reaction temperature was kept below 1°C. After the solution was added, the resultant mixture was stirred at 0°C for 4 h and then at room temperature for 12 h. After the reaction, the bulk of the solvent was removed *in vacuo*, and then the concentrated mixture was poured into diethyl ether. The white precipitate was collected and purified by several precipitations from chloroform into diethyl ether.

^{1}H-NMR (δ, $CDCl_3$): 7.71 (d, ArH), 7.19 (d, ArH), 3.62 (m, —O—CH_2—CH_2—O), 2.39 (s, —CH_3).

Synthesis of 4

3 (2.0 g) was dissolved in 10 mL of DMF, and then 1,3-diaminopropane (1 mL) was added dropwise. The resultant solution was stirred at 75°C in a nitrogen atmosphere for 30 h. Enough diethyl ether was added to precipitate the product. The product was further purified by several precipitations from chloroform into diethyl ether. At last, 1.2 g of **4** was yielded.

^{1}H-NMR (δ, $CDCl_3$): 3.62 (m, —O—CH_2—CH_2—O), 2.81 (m, CH_2—N—CH_2), 1.64 (m, N—C—CH_2—C—N).

Synthesis of 1 and 2

4 (0.50 g), C_{60} (36 mg), and 50 mL of chlorobenzene were placed in a Schlenk tube. The resultant solution was stirred at room temperature for 2 days. The solvent was removed *in vacuo*, some chloroform was added to dissolve the precipitant, and the solution was filtered. The main portion of chloroform in the filtrate was removed, diethyl ether was added to precipitate 0.4 g of the brown product (**1**), and the product was further purified by several precipitations from chloroform into diethyl ether. At last, 0.35 g of **1** was yielded.

^{1}H-NMR (δ, $CDCl_3$): 3.62 (m, —O—CH_2—CH_2—O), 2.81 (m, CH_2—N—CH_2), 1.64 (m, N—C—CH_2—C—N).

The synthetic procedure for **2** was similar to that for **1**; the only difference was that the amount of C_{60} was 18 mg instead of 36 mg in the synthesis of **1**.

^{1}H-NMR (δ, $CDCl_3$): 3.62 (m, —O—CH_2—CH_2—O), 2.81 (m, CH_2—N—CH_2), 1.64 (m, N—C—CH_2—C—N).

RESULTS AND DISCUSSION

Polymer synthesis

In the reported references, C_{60}-containing PEOs were synthesized through the reaction of C_{60} in toluene with a precursor PEO possessing an amino end group,[10] through the grafting of C_{60} onto living PEO such as PEO-K^+,[12] or through the reaction of C_{60} with a prepared azido-terminated PEO.[11] In this study, C_{60}-containing PEOs **1** and **2** were prepared by a new postfunctional method. The synthetic route is shown in Scheme 1. First, PEO (M_w = 20,000) was reacted with *p*-toluenesulfonyl chloride to yield **3**, which was

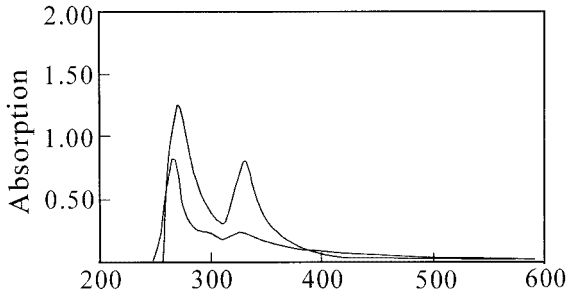

Figure 1 UV–vis spectra of **1** (top) and **2** (bottom).

then converted into a precursor PEO possessing amino end groups (**4**) in DMF in the presence of 1,3-diaminopropane. At last, **4** was reacted with C_{60} in chlorobenzene to give the C_{60}-containing PEOs (**1** and **2**), which were purified by several precipitations from chloroform into diethyl ether. These synthetic conditions were very mild, and the procedure was relatively easy. Previously, this method was successfully applied to the synthesis of C_{60}-containing polysiloxanes.[13] As the results were satisfactory, we believed that this method could be used to prepare other C_{60}-containing polymers, especially water-soluble polymers. The successful preparation of water-soluble C_{60}-containing PEOs further confirmed the usefulness of this postfunctional method, and studies on the synthesis of other C_{60}-containing polymers are now in progress.

Structural characterization

All the polymers had good solubility in common organic solvents, such as $CHCl_3$, tetrahydrofuran (THF), dimethyl sulfoxide, and DMF. They were also soluble in water. The UV–vis spectra of **1** and **2** in chloroform are shown in Figure 1. The two peaks at 269 and 330 nm have been attributed to the absorption of C_{60}.[14] These spectra showed that C_{60} was successfully covalently linked to PEO because C_{60} was not easily soluble in chloroform and PEO had no absorption in the range of 200–700 nm. The C_{60} concentrations (w/w) in **1** and **2** were 0.9 and 1.5%, respectively, which were determined by a comparison of the intensity of the absorption peak at 306 nm in toluene with that of pure C_{60} in toluene.

Figure 2 shows the IR spectra of **1** and **4**. The spectrum of **2** is similar to that of **1**. In the IR spectrum of **1**, apparently new absorption peaks appear at 528 cm^{-1}, and the intensity of another peak at 569 cm^{-1} increases. These two peaks are the characteristic peaks of C_{60},[15–17] and this further demonstrates that C_{60} was bonded to the PEO backbone. However, the other two C_{60} peaks at 1183 and 1429 cm^{-1} are masked by the absorption of PEO.

The signals of the phenyl ring of **3** in the ^{1}H-NMR spectra completely disappeared in the spectra of **4**, **1**, and **2**. This confirmed that the *p*-toluenesulfonyl groups were replaced by the amino moieties completely. Some new peaks appeared at δ = 2.81 ppm and δ = 1.64 ppm in the ^{1}H-NMR spectrum of **4**, which were assignable to the protons of the propane diamino groups. According to the reported references and our previous case, a new weak peak at 3.48 ppm, attributed to the resonance of C_{60}—H in the ^{1}H-NMR spectra of **1** and **2**, should have appeared.[18] Indeed, there was a new peak at 3.48 ppm confirming the

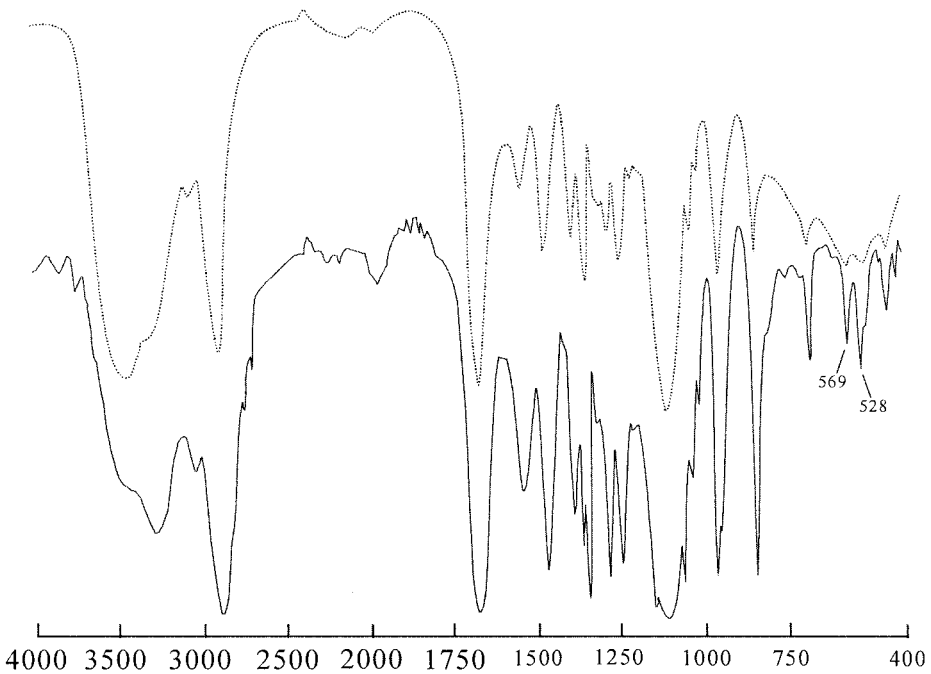

Figure 2 FTIR spectra of **4** (solid line) and **1** (dashed line)

linkage of C_{60} to PEO once more, but it was not as clear because there was a large peak of the backbone of PEO at 3.62 ppm.

The structures of **3** and **4** are shown in Scheme 1, but those of **1** and **2** are not given. During the reaction of C_{60} with **4**, one C_{60} molecule may react with not only one amino group but perhaps several amino groups from the same or different PEO chains linked to the same C_{60} moiety. Therefore, the structures of **1** and **2** may be complicated and could not easily be shown clearly. Their structural shape would be similar to what was reported previously.[18] However, their solubility was very good, and they were very stable in air. They were easily dissolved in common organic solvents and water even after they were exposed to air for half a year.

CONCLUSIONS

Two new C_{60}-containing PEOs (**1** and **2**) were successfully prepared by the reaction of C_{60} with predesigned amino end-functional PEO synthesized by a postfunctionalized approach. The synthetic procedure was relatively easy, and the reacting conditions were mild. These two C_{60}-containing PEOs were soluble in common organic solvents, such as chloroform, THF, and DMF. Also, they were very soluble in water. As PEO is a well-known and remarkable biomedical polymer, **1** and **2** may be used in biomedical applications requiring the unique properties of C_{60}. It is likely that many other polymers containing C_{60} moieties can easily be prepared by this simple synthetic strategy. Therefore, C_{60} moieties could be conveniently linked to these polymers, if needed, by the postfunctionalized method reported here. Further studies on the synthesis of other C_{60}-containing polymers, including water-soluble polymers, are now in progress.

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