

Utilization of Polyhydroxylated C₆₀ as a Molecular Core for the Synthesis of Star-Shaped Polymers

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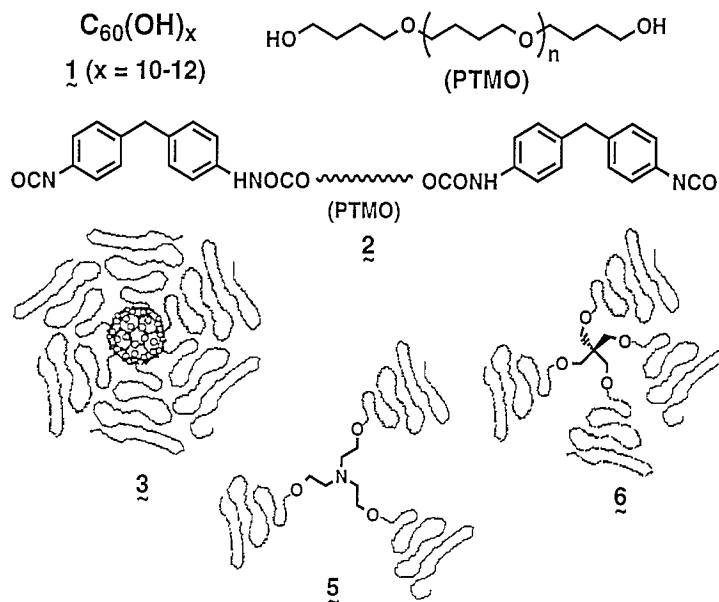
Abstract

Polyhydroxylated C₆₀ derivative (fullerenol) was used as a molecular core in the design and synthesis of poly(urethane-ether) analog star-shaped polymers. Structure of these star-polymers were characterized to consist of 6 poly(urethane-ether) arms per C₆₀, on average, in a remarkably narrow distribution of the number of arms per polymer molecule, when the reaction was performed under the described conditions.

1. INTRODUCTION

Chemical reactivity of fullerenic molecules was discovered to be unexpectedly high. Different functionalization chemistry can be selected to undergo either mono-addition or multiple-addition on fullerene molecules, giving various functionalized derivatives.[1] These derivatives provide great potential for use as versatile intermediates in the technological development of specialty chemicals. We have recently reported several synthetic methodologies for the preparation of water-soluble polyhydroxylated C₆₀ derivatives (fullerenols, **1**).[2-6] The synthetic approaches involved activation of olefinic moieties of C₆₀ molecules by electrophilic reagents, forming highly reactive carbocationic centers on C₆₀. Under such reaction conditions, these carbocationic intermediates were found to react readily with even weak nucleophiles, such as alkyl or aryl carboxylic acid and water. After hydrolysis of resulting products under mild conditions, the corresponding polyhydroxylated fullerene derivatives were obtained. Fullerenols were also generated by the reaction

of fullerenic materials with an excess of diborane, followed by the treatment of the resulting mixtures with H₂O₂-NaOH.[7] Fullerenol with multiple polar hydroxyl functions in a caged fullerene structure is suitable for utilization as an intermediate in the design of three-dimensionally



stretched polymers. The strategy involves the use of polyhydroxylated C₆₀ derivative as a molecular core for anchoring various polymer arms on C₆₀ through bonding with the hydroxyl functions. That allows us to visualize the truly star-burst

polymer molecules. An recent example of the C₆₀-based star-like polymer was synthesized by the reaction of fullerenes with living polystyrene carbanions, resulting in fullerene derivatives with the number of attached polystyrene chains in a broad distribution from 1 to 10.[8] The other closely related compound was the fullerene-bound dendrimers synthesized from the reaction of phenol-functionalized fullerenes with polyether dendrimers.[9] We demonstrated that the reaction of fullereneol **1** with a prepolymer of diisocyanated urethane polyether **2** under a mild condition, followed by a termination reaction with 1-dodecanol, afforded the corresponding C₆₀-based poly(urethane-ether) star-shaped polymers **3** in a surprisingly narrow distribution of the number of arms per molecule.

2. RESULTS AND DISCUSSION

Diisocyanated urethane polyether prepolymers **2** was prepared by the reaction of poly(tetramethylene oxide) glycol (PTMO) with 4,4'-methane diphenyl diisocyanate (MDI, 2.0 equiv.) in CDCl₃ at 60 °C under N₂. The average molecular weight of poly(tetramethylene oxide) glycol used was determined, by the gel permeation chromatographic (GPC) measurement calibrated by the PTMO standards, to be M_n 2,000 and M_w 4,500 with a polydispersity of 2.25. Proceeding of this reaction was monitored by the decrease of intensity of a hydroxyl infrared band at 3480 cm⁻¹, until its disappearance. Fullereneol **1** utilized in the study was synthesized via hydrolysis of its precursors, polycyclosulfated fullerene derivatives, which were prepared by the treatment of C₆₀ with fuming sulfuric acid at 65 °C under N₂. [6]

Structure of the resulting fullereneol was characterized to consist of 10-12 hydroxyl groups per C₆₀ on average. The condensation reaction between prepolymeric diisocyanates **2** and fullereneols was performed in a mixture of anhydrous THF and DMF (3:1) at 60 °C under N₂ for 16 h. To eliminate completely the cross-linking reaction, an excess of **2** (10 equiv. of -NCO group to each -OH group of fullereneol) was applied. At the end of the reaction period, the intermediate mixtures were allowed to react further with 1-dodecanol. Removal of bis(1-dodecanoxy) poly(urethane ether) **4**, which is the byproduct resulting from the reaction of 1-dodecanol with the unreacted prepolymer **2**, was accomplished by repeated reprecipitation of products from the THF solution into methanol, followed by washing with a mixture of THF and methanol. The corresponding C₆₀-based poly(urethane-ether) star-polymers **3** were isolated as soluble, highly viscous brownish-red semi-solids in high yield. As anticipated, the infrared spectrum of the star-polymer **3** bears a close resemblance to that of bis(1-dodecanoxy) poly(urethane ether) prepolymers **4**, showing the disappearance of a band around 2272 cm⁻¹ corresponding to the absorption of isocyanate -NCO groups. It also showed the clear disappearance of hydroxyl absorptions centered at 3550 cm⁻¹. The conversion of isocyanate functions into urethanes was evident through an observation of a band at 3300 cm⁻¹ and a strong band at 1733 cm⁻¹ corresponding to the urethanic -NH- and carbonyl absorptions, respectively.

The molecular weight of star-polymer **3** was determined mainly by its GPC (using toluene as eluent) spectrum and confirmed by light scattering

measurements. In the GPC study, the spectrum was calibrated by polystyrene standards. To ensure and examine suitability and accuracy of the calibration by linear styrene oligomers, we synthesized two polymer **3**-related star-shaped model compounds, **5** containing 3 poly(urethane-ether) arms and **6** containing 4 poly(urethane-ether) arms, by the reaction of diisocyanated urethane polyether prepolymers **2** with triethanolamine or pentaerythritol, respectively, followed by quenching with 1-dodecanol. GPC spectra of oligomers **5** and **6** indicated an average molecular weight of M_n 9,260 (M_w 15,200 with a polydispersity 1.64) and M_n 12,600 (M_w 20,300 with a polydispersity 1.61), respectively. Remarkably, these data were found to be consistent with a material having roughly 3 and 4 times the molecular weight of bis(1-dodecanoxy) poly(urethane-ether) **4** (M_n 2,600 and M_w 5,450 with a polydispersity 2.11). Considering the limited accuracy of these measurements and similarity of the chemical structure of each polymer arms in **5** and **6** to that of **4**, we concluded that the polystyrene calibration is reasonably reliable. It estimated a sensible molecular weight only 15% higher than the theoretical value. Utilizing a similar process of analysis, the average molecular weight of **3** was obtained as M_n 18,000 and M_w 26,100 that corresponds to a fullerenol-based star-polymer with 6 linear poly(urethane-ether) arms on average. Most significantly, the polydispersity (1.45) of **3** is notably narrower than that of the single polymer chain **4** (2.11). The only possibility to increase the number of polymer arms randomly bonded in a star-shaped polymer without seriously broadening the polydispersity is to restrict the number of

polymer arms in a fairly narrow distribution, as in the cases of the model polymer **5** (polydispersity 1.64) and **6** (polydispersity 1.61), both with a structure containing a fixed number of polymer arms. In addition, the average number of tetramethylene repeating unit, composed of the oligomeric PTMO segment, in structures **3**, **4**, **5**, and **6** was also determined by the ^1H NMR spectroscopic study. The chemical shift of two types of aromatic protons in the MDI derived urethane moieties can be readily identified at δ 7.08 (d , $J = 10$ Hz) and 7.28 (d , $J = 10$ Hz). The intensity of each group of peaks corresponds to 8 protons in one polymer arm. Therefore, the value of integration ratio between these aromatic protons and oxygenated methylene protons (at δ 3.40) or non-oxygenated methylene protons (at δ 1.62) in the PTMO moieties allows an accurate estimation of the average molecular weight of PTMO. As a result, each PTMO segment was found to contain 42 tetramethylene repeating units. That represents an average molecular weight of poly(urethane-ether) **4** or each polymer arm as 3,920 or 3,790 Dalton, respectively, which is positioned well in the middle of M_n (2,600) and M_w (5,450) of **4**. Furthermore, this method of calculation leads the determination of the average molecular weight of **3** as 2.4×10^4 Dalton.

One intriguing physical property of the star-polymer **3** is its thermal behavior at low temperatures. Even though the molecular weight of **3** is 6 times that of the linear poly(urethane ether) **4**, however, the glass transition temperature (T_g) of **3** was found to be -67°C in only a slightly higher temperature than that of **4** (-71°C), **5** (-70°C), and **6** (-69°C) calculated from the DSC

profiles, as shown in Fig. 1. These data clearly revealed a systematically gradual increase of the glass transition temperature going from the linear structure of **4** to **5** (three-armed star) and **6** (four-armed star) and then to the six-armed star polymer **3**. In comparison of the PTMO chain softening

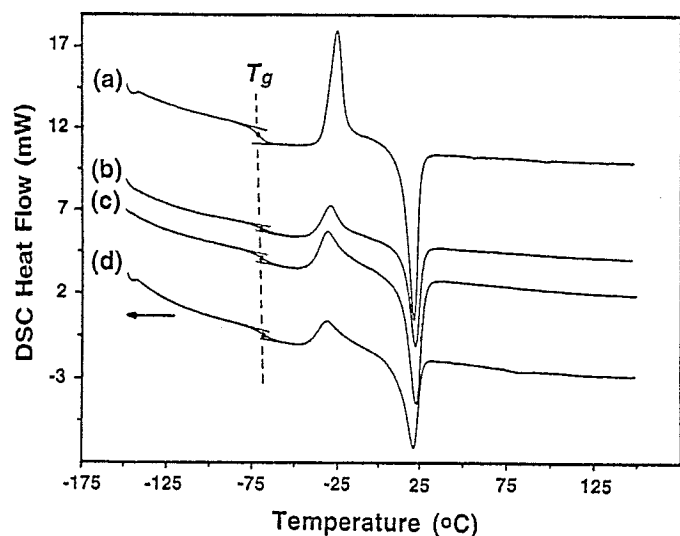


Figure 1: Differential scanning calorimetric (DSC) profiles of (a) the linear poly(urethane-ether) **4**, (b) the star model polymer **5** containing 3 urethane-connected polyether arms, (c) the star model polymer **6** containing 4 urethane-connected polyether arms, and (d) the C₆₀-based star polymer **3** containing 6 urethane-connected polyether arms.

temperature, all four polymers were found to turn into a paste-like material upon heating in a similar temperature range at 21 °C (34.3 J/g), 22 °C (45.3 J/g), 23 °C (43.5 J/g), and 23 °C (42.7 J/g) for **3**, **4**, **5**, and **6**, respectively. It also showed similar thermal properties on the recrystallization of oligomeric PTMO chains upon heating. Except the linear polymer **4** having a much intense recrystallization transition at a temperature of -25 °C (45.0 J/g), the rest of star-polymers **3**, **5**, and **6** exhibited only a moderate to weak transition at -31, -29, and -31 °C, respectively. These overall DSC

profiles implied that each polymer arm chemically bonded on the C₆₀ molecule tends to behave individually upon variation of temperatures in no difference to that of the parent linear polymer **4**.

3. CONCLUSION

We have demonstrated the synthesis of a novel class of star-shaped urethane-ether polymers, utilizing the polyhydroxylated C₆₀ fullerene derivative as a molecular core to lock polymer arms covalently on a confined fullerenic ball. Results illustrated that control of the number of polymer arms within a fairly narrow distribution is achievable. Meanwhile, the increase of the number of polymer arms as well as molecular weight in star-shaped polymers do not lead to a sharp change of their thermal behavior at low temperatures. That provides crucial advantage for processing.

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