Fullerenol Derived Urethane-connected Polyether Dendritic Polymers

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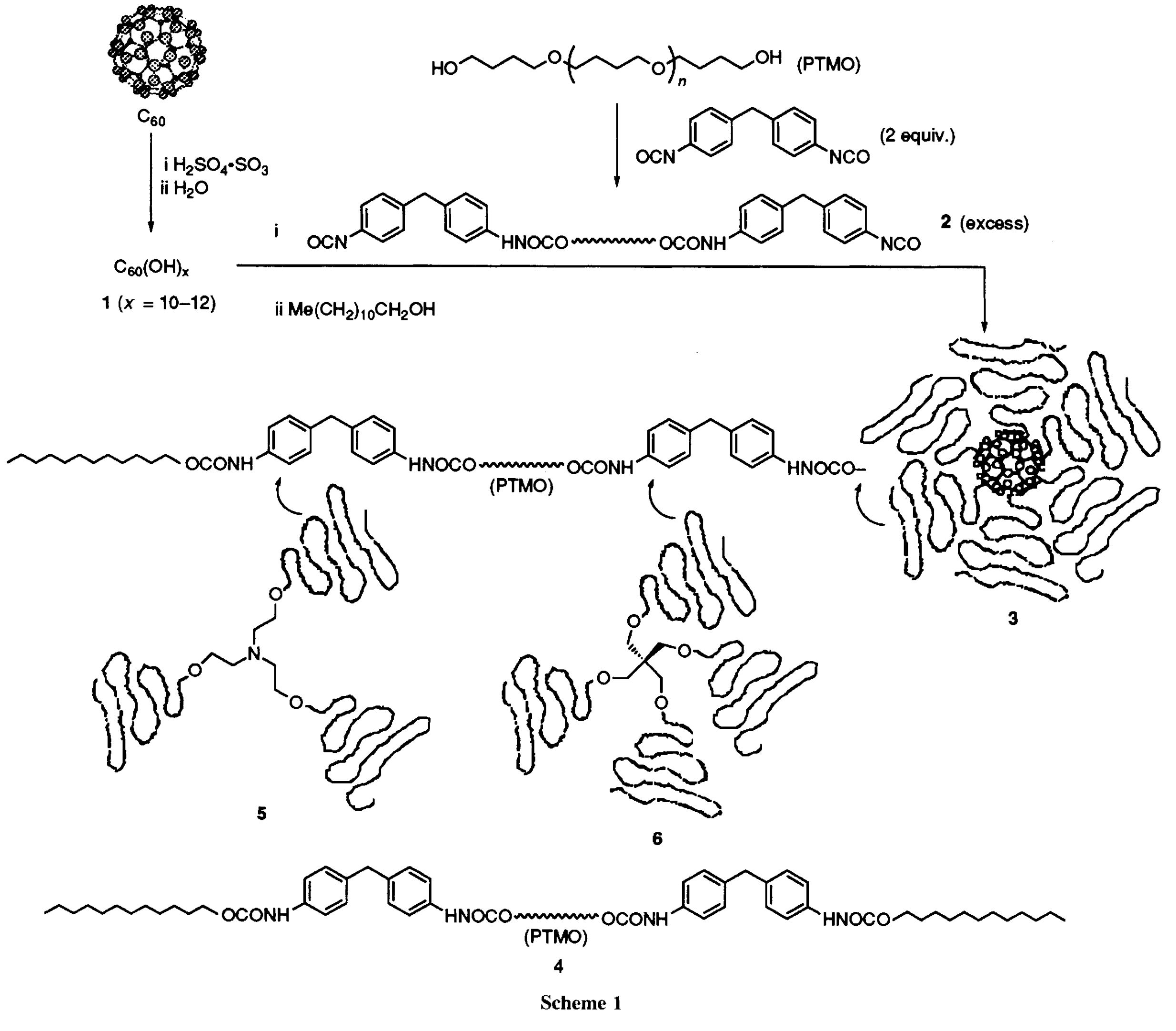
Urethane-connected polyether star polymers utilizing fullerenol as a molecular core are synthesized as a soluble material containing six chemically bonded polymer arms per C_{60} on average, with a narrow distribution of the number of arms per molecule and a polydispersity index of 1.45.

Synthetic methods leading to the preparation of water soluble polyhydroxylated C_{60} derivatives (fullerenols **1**) have been extensively investigated.[1-6] These molecules, which contain multiple polar hydroxy functions in a ball-shaped fullerene structure, are utilizable as versatile intermediates in the prospective design of the three-dimensionally stretched polymers. The strategy involves anchoring various polymer arms onto the C_{60} cage as a molecular core through bonding with the hydroxy functions. Since the overall diameter of fullerenol is approximately 13 Å, dendritic polymer molecules can be formulated. A recent example of a C_{60}-based star-like polymer was synthesized by treating fullerenes with living polystyrene carbanions, resulting in fullerene derivatives with a broad distribution of 1–10 in the number of the attached polystyrene chains.[7] Closely related are the fullerene-bound dendrimers synthesized from the reaction of phenol-functionalized fullerenes with polyether dendrimers.[8] Here we report that treatment of fullerenols **1** with a prepolymer of diisocyanated urethane polyether **2** under mild conditions, followed by a termination reaction with dodecan-1-ol, afforded the corresponding C_{60}-based urethane-connected polyether dendritic polymers **3**, possessing a narrow distribution of the number of arms per molecule (Scheme 1).

Preparation of the diisocyanated urethane polyether prepolymers **2** was carried out by treating poly(tetramethylene oxide) glycol (PTMO) with 4,4′-methane diphenyl diisocyanate (MDI, 2.0 equiv.) in $CDCl_3$ at 60 °C under N_2. The average molecular mass of poly(tetramethylene oxide) glycol used was determined by gel permeation chromatographic (GPC) measurements, calibrated by PTMO standards, to be M_n 2000 and M_w 4500 with a polydispersity of 2.25. Reaction progress was monitored by the decrease in intensity of the hydroxy IR band at 3480 cm^{-1}, until its disappearance. The fullerenols **1** used in this study were synthesized *via* the hydrolysis of their polycyclosulfated fullerene precursors, prepared by the treatment of C_{60} with fuming sulfuric acid at



Scheme 1

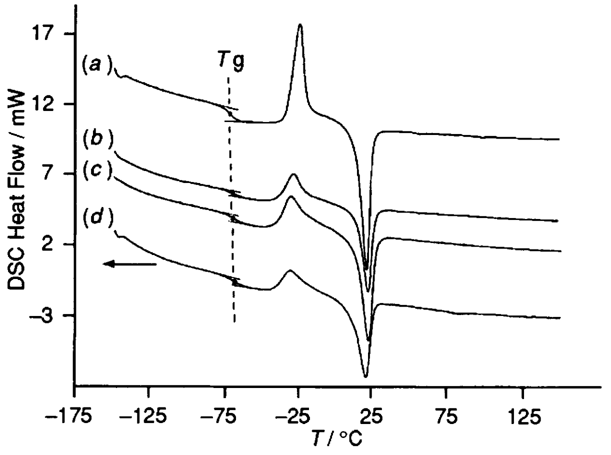


Fig 1 The DSC profiles of (*a*) the linear poly(urethaneether) **4**, (*b*) the dendritic polymer **5** containing three urethane-connected polyether arms, (*c*) the dendritic polymer **6** containing four urethane-connected polyether arms, and (*d*) the C_{60}-based dendritic polymer **3** containing six urethane-connected polyether arms

65 °C under N_2.[5] The structure of the resulting fullerenol was shown by various spectroscopic methods to consist of an average of 10–12 hydroxy groups per C_{60}. The condensation reaction between prepolymeric diisocyanates **2** and fullerenols was performed in a mixture of anhydrous THF and DMF (3 : 1) at 60 °C under N_2 for 16 h. To completely eliminate the cross-linking reaction, an excess of **2** (10 equiv. of NCO group to each OH group of fullerenol) was used. At the end of the reaction period, the intermediate mixtures were allowed to react further with dodecan-1-ol or 2,2′-dichloroethanol. In the former case, the removal of bis(dodecan-1-oxy) poly(urethane ether) **4**, which is the byproduct resulting from the reaction of dodecan-1-ol with the unconverted prepolymer **2**, was accomplished by repeated precipitation of products from the THF solution into MeOH, followed by washing with a mixture of THF and MeOH. The corresponding C_{60}-based urethane-connected polyether dendritic polymers **3** were thus isolated as soluble, highly viscous brownish-red semi-solids in high yield (more than 15 times the mass of the starting fullerenol was obtained). As anticipated, the IR spectrum of the dendritic polymer products **3** bears a close resemblance to that of the bis(dodecan-1-oxy) 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 hydroxy absorptions centred 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 mass of dendritic polymers **3** was determined mainly by GPC (toluene as eluent) and confirmed by light scattering measurements; the spectrum was calibrated by polystyrene standards. To confirm the accuracy of calibration by the linear styrene oligomers, we synthesized two polymer **3**-related star shaped model compounds, **5** (containing three urethane-connected polyether arms) and **6** (containing four urethane-connected polyether arms), by reacting diisocyanated urethane polyether prepolymers **2** with triethanolamine or pentaerythritol, respectively, followed by quenching with dodecan-1-ol. The GPC spectra of oligomers **5** and **6** indicated an average molecular mass of M_n 9260 (M_w 15 200, polydispersity 1.64) and M_n 12 600 (M_w 20 300, polydispersity 1.61), respectively. Remarkably, these data were found to be consistent with a material having roughly 3 and 4 times the molecular mass of bis(dodecan-1-oxy) poly(urethane ether) **4** (M_n 2600 and M_w 5450, polydispersity 2.11). Considering the limited accuracy of these measurements and the similarity of the chemical structure of each of the polymer arms in **5** and **6** to that of **4**, we conclude that the polystyrene calibration is reasonably reliable. It estimated a sensible molecular mass range only 15–20% (M_n) or 7% (M_w) higher than the theoretical value. Nevertheless, the detected polydispersities of **5** and **6** are considerably higher than their theoretical values[9] of 1.37 and 1.28, respectively. Utilizing a similar process of analysis, the average molecular mass of **3** was obtained as M_n 18 000 and M_w 26 100, which corresponds to a fullerenol-based dendritic polymer with six linear urethane-connected polyether arms on average. Most significantly, the polydispersity (1.45) of **3** is narrower than that of the single polymer chain **4** (2.11). By taking the percentage deviations of the polydispersities of **5** and **6** from their theoretical values into account, we conclude that the only possible way to increase the number of polymer arms randomly bonded in **3** without seriously broadening its polydispersity is to restrict the number of polymer arms in a fairly narrow distribution.

One intriguing physical property of the dendritic polymer **3** is its thermal behaviour at low temp. Even though the molecular mass of **3** is six times that of the linear poly(urethane ether) **4**, the glass transition temp. (T_g) of **3** was found to be −67 °C, only a slightly higher temp. than that of **4** (−71 °C), **5** (−70 °C), and **6** (−69 °C), as shown in Fig. 1. These DSC data clearly revealed a systematically gradual increase of the glass transition temperature on going from the linear structure of **4** to **5** (three-armed dendrimer) and **6** (four-armed dendrimer) and then the six-armed dendrimer polymer **3**. In comparing the PTMO chain-softening temperature, all four polymers were found to turn into a paste-like material upon heating in the temperature range at 21 (34.3), 22 (45.3), 23 (43.5), and 23 °C (42.7 J g^{-1}) for **3**, **4**, **5**, and **6**, respectively. They also showed similar thermal properties on the recrystallization of oligomeric PTMO chains upon heating, except that the linear polymer **4** has a more intense recrystallization transition at a temperature of −25 °C (45.0 J g^{-1}); the dendritic polymers **3**, **5**, and **6** exhibited only a moderate to weak transition at −31, −29 and −31 °C, respectively. These DSC profiles imply that each polymer arm chemically bonded to the C_{60} molecule tends to behave individually upon variation of temperature in a similar manner to that of the parent linear polymer **4**. Owing to the star-burst shape of **3**, **5** and **6**, the possibility for their soft polymer arms to recrystallize decreases significantly.

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