# Polyhydroxylated $C_{60}$ Cross-Linked Polyurethanes

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Incorporation of the $C_{60}$ molecule into the main chain of organic polymers[1] or into the side chain of a polymer as a pendant group,[2–5] resulting in polymeric derivatives of $C_{60}$, has received much attention recently. In the case of uncontrolled polymerization of $C_{60}$ in the solid state[6–8] or in flash thermolysis,[9] the reaction often gave highly cross-linked intractable solids of fullerene-derived polymers. Herein we demonstrate that, with appropriate selection of highly reactive prepolymers as precursors for the polymer matrix, solubilized polyfunctional fullerenes can be utilized as molecular cores in assembling starburst polymer networks. That enhances significantly the thermal mechanical properties of the resultant polymers. In this instance, polyfunctional fullerenes resemble star-branched precursors used in the synthesis of dendritic polymers[10,11] and cross-linked polymers.[12–14] Highly polar fullerene intermediates suitable for this study are polyhydroxylated $C_{60}$ derivatives[15–19] ([60]fullerenols **1**). Structurally, fullerenols have a significant advantage over conventional hydroxylated cross-linkers such as 1,1,1-tris(hydroxymethyl)ethane and pentaerythritol. Their multiple reactive hydroxy functional groups (10 on average), covalently attached and randomly distributed on the molecular surface of the $C_{60}$ cage with a diameter of roughly 10 Å, provide a higher density of reactive sites for creating hyper-cross-linking in the fabrication of polymer networks and composites. In addition, the overall ball shape of fullerenols should facilitate the synthesis of truly three-dimensionally cross-linked polymer materials. Therefore, an increase in the tensile strength and other related mechanical properties of the resulting $C_{60}$-derived polymers can be expected.

The chemical reactivity of tertiary fullerenolic hydroxy functions is rather limited toward the nucleophilic substitution of many electron-withdrawing leaving groups under basic conditions. In one exception, they are moderately reactive with isocyanate functions, forming the corresponding urethane moieties. Thus, syntheses of $C_{60}$-derived polymer networks were performed by treating fullerenols **1**, $C_{60}(OH)_{10-12}$,[17] with diisocyanated polyether prepolymer **2** (1.0 equiv of NCO group to each OH group of fullerenols) in a mixture of anhydrous THF and DMF (3:1) at 60 °C under an atmospheric pressure of $N_2$. Diisocyanated prepolymer **2** was prepared by the treatment of poly(tetramethylene oxide) glycol (PTMO) with methylenebis(4-isocyanatobenzene) (MDI, 2.0 equiv) in $CDCl_3$ at 60 °C under an atmospheric pressure of $N_2$. The average molecular weight of poly(tetramethylene oxide) glycol used was determined to be $M_n = 2000$ and $M_w = 4500$ with a polydispersity of 2.25, which was calibrated by PTMO standards. Prior to the isocyanate–hydroxy condensation reaction, the fullerenols were dried under vacuum at 60 °C for 24 h. Complete removal of residual water from the reaction medium was accomplished by further treatment of the fullerenol-containing DMF–THF solutions with dried molecular sieves (4 Å) for at least 2 days. Reaction progress was monitored by the decrease in intensity of the IR bands centered at 3480–3550 and 2272 $cm^{-1}$, corresponding to the absorption of the hydroxy and isocyanate groups, respectively, until a minimum was reached. A gradual increase of solution viscosity and gel formation was observed during the first few hours of reaction. At the end of the reaction, unconverted isocyanate functional groups were quenched by the addition of methanol under ultrasonic treatment. Residual prepolymer **2** was then removed from the products by repeated ultrasonic solvent extraction. After evaporation of solvent and subsequent dehydration under vacuum, products of the corresponding [60]fullerenol hyper-cross-linked poly(urethane–ether) **3**, as the schematic network structure shown in Scheme 1, were isolated as free-standing, highly elastic dark-red films. The homogeneous distribution of color in the film and its shift from brown in **1** to dark-red in **3** indicated a fine dispersion of reacted fullerenol moieties in the polymer matrix.

As shown in Figure 1b, the reflective (ATR) infrared spectrum of film **3** showed the disappearance of a band around 2272 $cm^{-1}$, corresponding to the absorption of NCO groups. It also showed a large decrease in intensity of the hydroxy absorption bands centered at 3550 $cm^{-1}$, comparing to that in the IR spectrum of fullerenols **1**. The conversion of isocyanate functions into urethanes was evident via the formation of clear IR bands at 3311 and 1728 $cm^{-1}$, corresponding to the urethanic NH and carbonyl absorptions, respectively. The overall spectrum of **3** bears a close resemblance to that (Figure 1a) of linear poly(tetramethylene oxide)-based polyurethane **4**, which was synthesized from the reaction of 1,4-butanediol with diisocyanated prepolymer **2** at 60 °C under an atmospheric pressure of $N_2$. In both samples, the infrared absorptions of the fullerenic moieties in **3** were relatively low in intensity. To correlate the number of polymer arms chemically attached on each fullerenol molecule in **3**, an analogous soluble fullerenol-based poly(urethane–ether) dendritic polymer **5** was synthesized by a similar reaction procedure. In this case, an excess of diisocyanated poly(urethane–ether) prepolymer **2** was used and the termination of reaction was accomplished by the addition of 1-dodecanol. The molecular mass of dendritic polymer **5** was determined mainly by GPC and confirmed by light scattering measurements. The GPC experiments estimated the average molecular mass of **5** as $M_n = 18\,000$ and $M_w = 26\,100$. These data are consistent with the mass of fullerenol-based dendritic polymers having roughly 6 times the molecular weight of bis(1-dodecanoxy) poly(urethane–ether) **6** ($M_n = 2600$ and $M_w = 5450$ with a polydispersity of 2.11). Most significantly, the polydispersity (1.45) of **5** is notably narrower than that of the parent polymer chain **6** (2.11) and is only slightly higher than its theoretical polydispersity value[20] of 1.35, calculated from **5** with monodispersed six-arms. These reesults indicated a fairly narrow distribution of the number of polymer arms in **5**.[21] Assuming the chemical reactivity of isocyanate functions toward fullerenols is similar in both syntheses of **3** and **5**, the average number of poly(urethane–ether) arms attached on the $C_{60}$ cage in **3** may be close to six.

Variation of the cross-linking density (fullerenol concentration) or cross-linking agents has a rather limited effect on the glass-transition temperature ($T_g$) of the resulting poly(urethane–ether) elasotmers. In the low-temperature region, the differential scanning calorimetry (DSC) profile (Figure 2a) of the [60]fullerenol hyper-cross-linked network **3** shows a glass-transi-

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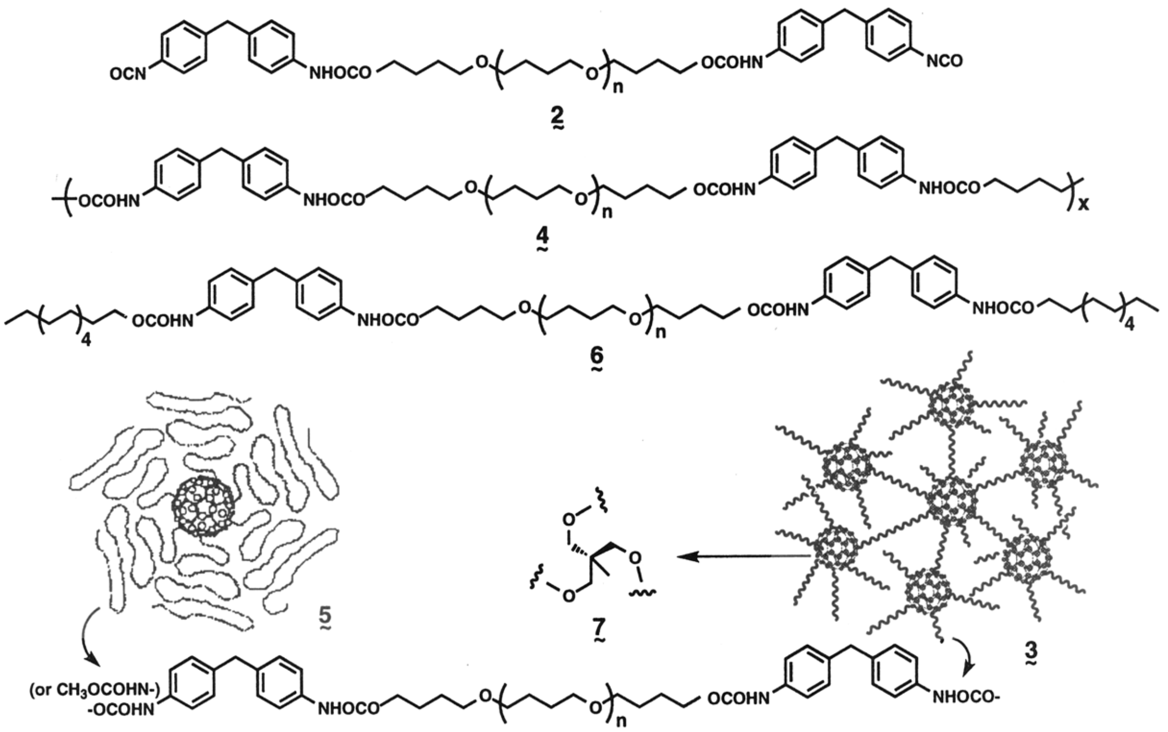
**Scheme 1**



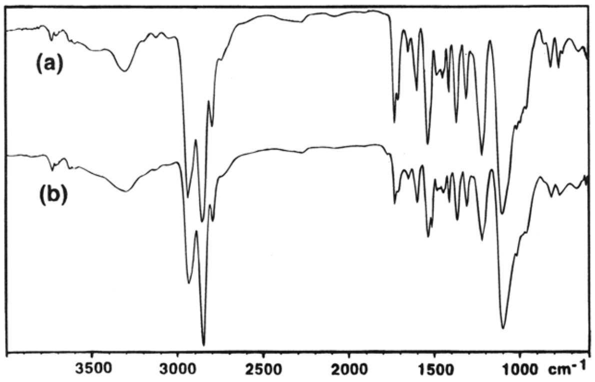


**Figure 1.** Infrared spectra of (a) linear poly(tetramethylene oxide)-based polyurethane **4** and (b) [60]fullerenol-based poly(urethane−ether) network **3**.

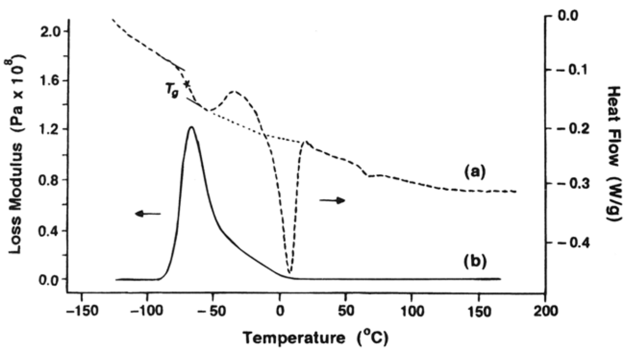


**Figure 2.** (a) Differential scanning calorimetry (DSC) profile and (b) temperature profile of loss modulus of [60]fullerenol-based poly(urethane−ether) network **3**, showing a glass-transition ($T_g$) temperature at −71 and −66 °C, respectively.

tion temperature at −70 °C, which is in a temperature range nearly identical to that ($T_g$ = −71 °C) of bis(1-dodecanoxy) poly(urethane−ether) **6**. This glass transition is also confirmed by dynamic mechanical analyses (DMA) of **3**, indicating, however, a slightly higher temperature at −66 °C in the profile of the loss modulus (Figure 2b). The exothermic recrystallization transition of **3** at −34 °C (7.8 J/g) and the endothermic chain-softening transition of poly(tetramethylene oxide) moieties in **3** at 7 °C (18.3 J/g) upon heating were found at a lower temperature than that of the corresponding transitions of **6** at −25 °C (45.0 J/g) and 22 °C (45.3 J/g), respectively. These DSC data revealed that each poly(tetramethylene oxide) urethane chain covalently interconnected with polyhydroxylated $C_{60}$ molecules in network **3** tends to behave individually in thermal terms independent of cross-linking at or below $T_g$. At temperatures above $T_g$, the effect of cross-linking becomes progressively observable. Presumably, the cross-linking sufficiently reduces the tight packing inside (chain folding) and among poly(tetramethylene oxide) urethane arms in **3** making them meltable (softening) at a lower temperature than that of un-cross-linked **6**.

At temperatures higher than 100 °C, [60]fullerenol hyper-cross-linked network **3** exhibits attractive thermal characteristcs. For the purpose of comparison, the thermal behavior of its linear polyurethane analog **4** and a polymer **3** related model network **7**, containing three poly(urethane−ether) arms at each cross-linking center, was investigated. The model network **7** was synthesized by reacting diisocyanated prepolymer **2** with the three-arm cross-linker, 1,1,1-tris(hydroxymethyl)ethane. Thermal mechanical analyses (TMA) of polymers **3**, **4**, and **7** were performed with a flat-point probe under a constant force of 0.05 N. In the case of polymer **3** as shown in Figure 3c, an increase of dimensional change of the polymer film more than its linear temperature-dependent thermal expansion was observed at an onset temperature of −70 °C, consistent with its glass transition temperature. The rate of dimensional increase of the polymer is then largely suppressed when the temperature reaches the recrystallization transition at −34 °C. As anticipated, the chain-softening transition of urethanic poly(tetramethylene oxide) segments at 7 °C induces a sharp increase in the polymer dimension. Similar phenomena were observed in the TMA data of **4** (Figure 3a) and **7** (Figure 3b), showing the PTMO chain-softening transition at a higher onset temperature

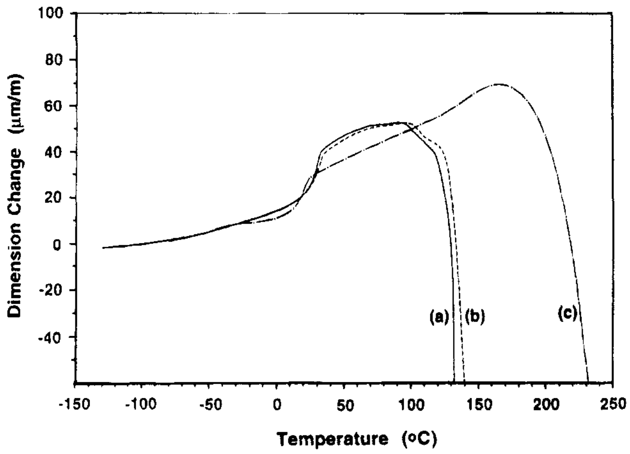


**Figure 3.** Thermal mechanical analyses (TMA) showing the penetration threshold of (a) linear poly(tetramethylene oxide)-based polyurethane **4**, (b) the model network **7** containing three poly(urethane−ether) arms at each cross-linking site, and (c) [60]fullerenol-based poly(urethane−ether) network **3**.

of 20 °C. It is subsequently followed by a linear thermal expansion at higher temperatures. The rate of the increase of polymer dimensions in this temperature region is slightly higher than that in the lower temperature region below 0 °C, as indicated by the relatively larger slope of the curves in Figure 3. Furthermore, the thermal penetration through measured polymer films by the pressurized probe was not detected until heating temperatures were above 120 °C for linear polyurethane **4**, 130 °C for the model network **7**, and 190 °C for the polymer network **3**. Above that thermal transition temperature, a rapid decline of polymer film dimensions indicated the spontaneous mechanical failure of the polymer. These TMA data clearly substantiated significant advantages in the utilization of [60]fullerenols as hyper-cross-linkers for the synthesis of polyurethane elastomers resulting in a sharp improvement of the thermal mechanical stabilities of the materials. In addition, the tensile strength of the polymers at break was found to be 0.6, 1.0, and 7.2 MPa for **4**, **7**, and **3**, respectively. A substantial increase of polymer tensile strength for **3** of roughly one order of magnitude from that of its linear polymer analog **4** is evident. In spite of the fact that the modulus of elasticity of **3** (4.8 MPa) is in a range similar to that of **4** (3.3 MPa) and **7** (4.9 MPa), the elongation at break of **3** was measured to be 580% in the range of 16 or 9 times higher than that of **4** (35%) or **7** (66%), respectively.

In conclusion, we have demonstrated the remarkable advantage of incorporating polyhydroxylated fullerenes in the synthesis of poly(urethane−ether) networks, giving high-performance elastomers with greatly enhanced tensile strength, elongation, and thermal mechanical stability, in comparison with their linear analogs or conventional polyurethane elastomers cross-linked by trihydroxylated reagents. In principle, the strategy can be generalized and applied in the synthesis of other polymer systems such as polyesters, polyethers, and polyanhydrides.

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