C_{60} end-capped polystyrene stars

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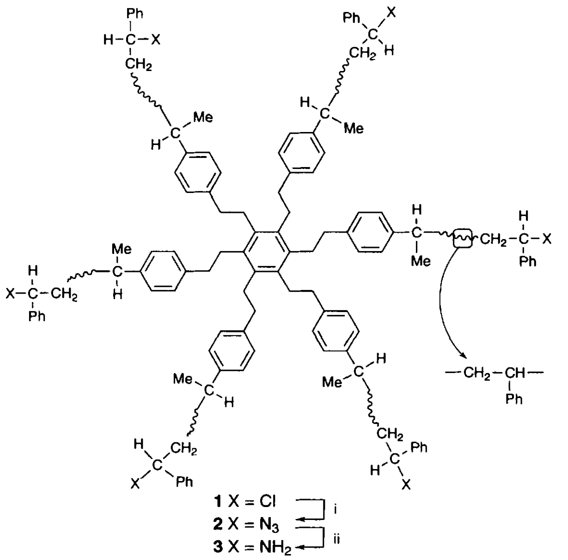
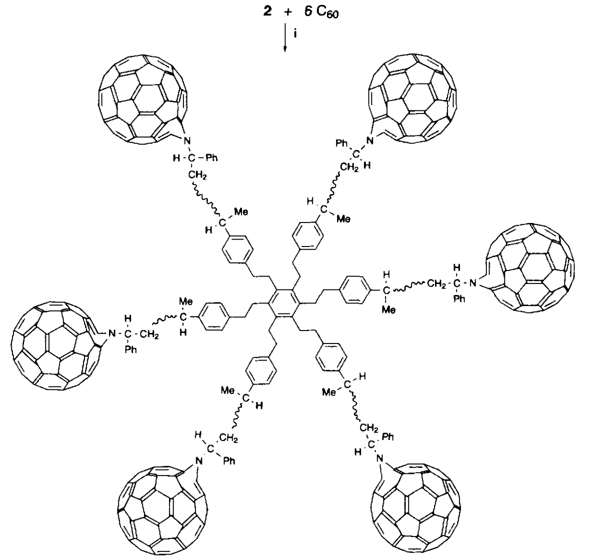
A hexaarm hexachloropolystyrene star polymer 1 ($\overline{M}_n$ = 18 000 g mol^{-1}) is functionalized by reaction with Me_3SiN_3 to give the hexaazido star polymer 2; reduction of 2 by PPh_3/H_2O leads to the hexaamine star polymer 3, and reaction of 2 with a two-fold excess of C_{60} gives the hexafullerene star polymer 4, characterized by size-exclusion chromatography, NMR, thermal-gravimetry analysis and CV.

The functionalization of polymers is of great interest *inter alia* for the syntheses of dendritic polymers,[1] for the design of electronic devices[2] and catalysts[3] and for approaches to biomaterials.[4] In particular, precisely defined star multiarm polymers constitute a new area which is promising because of their awaited specific topological and mechanical properties.[5,6] Recently, we have reported the synthesis of the hexaarm star shaped polystyrene **1** by living cationic polymerization using the core-first method.[6] The control of molecular weight was obtained for these star polymers up to 90 000 g mol^{-1}, with polydispersities around 1.1.[6] Here we report the functionalization of the six branch termini of these polymers with azido, amino and C_{60} groups. There are a number of recent interesting reports of C_{60}-derivatized polymers[7,8] and dendrimers[9] including polystyrene,[7] but this is the first example of a star polymer containing a precise number of C_{60} units. In the case of the hexaarm star polystyrene **1**,[6] the average molecular weight, determined by light scattering, is $\overline{M}_n$ = 18 000 g mol^{-1}, *i.e.* 3000 g mol^{-1} for each branch (30 styrene units per branch). The functionalization of **1** with six C_{60} units leads to a huge polyelectronic reservoir system.



Scheme 1 *Reagents and conditions*: i, Me_3SiN_3, $TiCl_4$, CH_2Cl_2, −15 °C; ii, PPh_3/H_2O, THF, room temp.

Treatment of the polymer **1**, which bears six chlorides in benzylic positions, with a 100-fold excess of Me_3SiN_3 and 20-fold excess of $TiCl_4$ in CH_2Cl_2 for 12 h at −15 °C gave the hexaazide **2** (Scheme 1). The complete replacement of the chlorides by azides can be monitored by the shift of the benzylic proton from δ_H 4.5 to 3.9 in the ^1H NMR spectrum. A strong band at 2097 cm^{-1} and a medium-intensity band at 1600 cm^{-1}



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Scheme 2 Synthesis of **4** *Reagents and conditions*: i, chlorobenzene, reflux

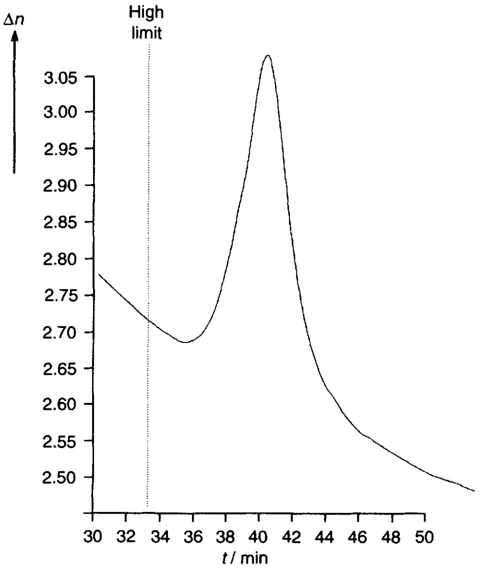

Fig. 1 GPC trace in chlorobenzene of the hexa-C_{60} polystyrene **4** ($\overline{M}_w/\overline{M}_n$ = 1.4); Δn = variation of the refractive index

appear for the azide group in the IR spectrum (CH_2Cl_2). Reduction of the hexaazide **2** by a 10-fold excess of PPh_3/H_2O at 20 °C in THF for 14 h gave the hexaamine **3**, the reaction being monitored again by the shift of the benzylic proton from δ_H 3.9 to between δ_H 1 and 2.3 also containing the CH and CH_2 protons of the polystyrene backbone. The two IR bands mentioned above disappear. The two new bands at 3430 (medium) and 1668 cm^{-1} (strong) are characteristic of the primary amine function.

Reaction of a two-fold excess of C_{60} per azide function of the hexaarm polymer **2** in refluxing PhCl for 1 d gave a brown solution of **4** (Scheme 2). After removing the solvent under vacuum, the addition of THF solubilized **4**, whereas insoluble C_{60} was filtered off. The THF solution was then concentrated and **4** was precipitated by the addition of methanol at −20 °C and **4** purified by repeated precipitation from hexane with methanol at −20 °C. Size-exclusion chromatography of **4** in PhCl indicated a monomodal distribution (Fig. 1). The ^1H NMR spectrum of **4** showed the total disappearance of the benzylic proton near to the azido group at δ_H 3.9. The main features of this spectrum are the broad absorption between δ_H 0.8 and 2.3 due to the CH and CH_2 units (including the last one) of the polystyrene backbone and the signals of the aromatic protons of the styrene units between δ_H 6.2 and 7.4 ($CDCl_3$). The peaks corresponding to C_{60} are located between δ_C 140 and 148 in the ^{13}C NMR spectrum ($CDCl_3$). This ^{13}C NMR spectrum also contains the quaternary carbon signal of the polystyrene backbone at δ_C 146–148, the aromatic CH signals at δ_C 126–128 and the aliphatic polystyrene signals at δ_C 41 (CH) and 44–46 (CH_2). This indicates that no unreacted branch remained in the C_{60}-derivatized polymer. Thermal-gravimetry analysis showed only two plateaus (Fig. 2). The polystyrene branches decomposed first at 200–450 °C and then the C_{60} units decomposed between 470 and 570 °C. The relative heights found for these two transitions (77.3 : 22.7) correspond rather well to the relative masses of the polystyrene branches and C_{60} units (80.6 : 19.4). The CV of **4** in MeCN–toluene (20 : 80) on a Pt cathode at −15 °C using Bu_4NBF_4 (10^{-3} mol dm^{-3}) as the electrolyte shows three waves at $E° = -1.00, -1.40$ and -1.90 V *vs.* ferrocene–ferricinium before the solvent front, corresponding to the three first reduction waves of C_{60}-derived compounds.[12] The shapes of the waves are in accordance with a six-electron transfer for which the redox centres are independent, *i.e.* each wave behaving as a one-electron wave[13,14] (Fig. 3). The number of electrons for the first wave (for best accuracy) can be estimated to $n_p = 5 \pm 1$ using the equation given by Bard and Anson;[13] eqn. (1), where *I*, *c* and *M*

$$n_p = \frac{I_p/c_p}{I_m/c_p}\left(\frac{M_p}{M_m}\right)^{0.275} \qquad (1)$$

are the intensity, concentration and molar mass respectively (the subscripts p and m refer to **4** and C_{60} respectively).

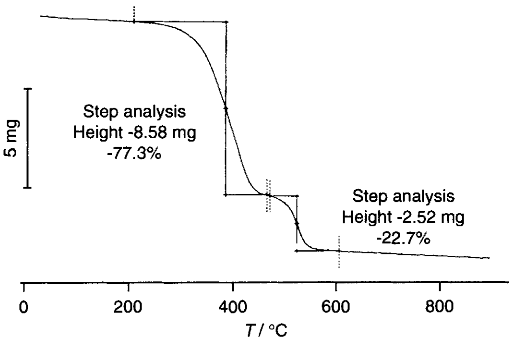

Fig. 2 Thermal gravimetric analysis of **4** heated under nitrogen at 10 °C min^{-1}

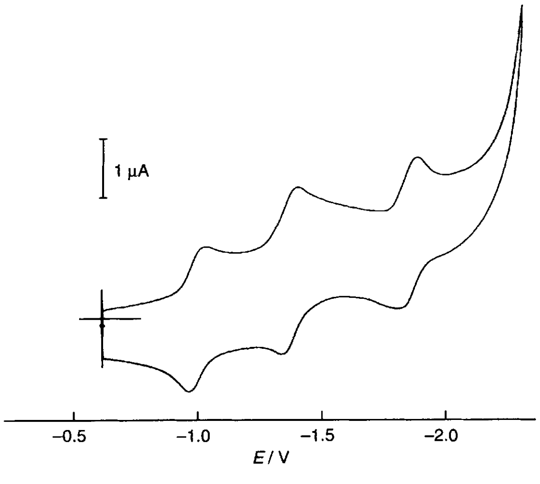

Fig. 3 Cyclic voltammogram of **4** (9 × 10^{-5} mol dm^{-3}) on Pt with Bu_4NBF_4 (10^{-3} mol dm^{-3}) in toluene : acetonitrile (1 : 4) with ferrocene–ferricinium ion as the reference redox couple. Sweep rate : 100 mV s^{-1}.

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Footnote

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