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Synthesis of hammer-like macromolecules of C_{60} with well-defined polystyrene chains *via* atom transfer radical polymerization (ATRP) using a C_{60}-monoadduct initiator

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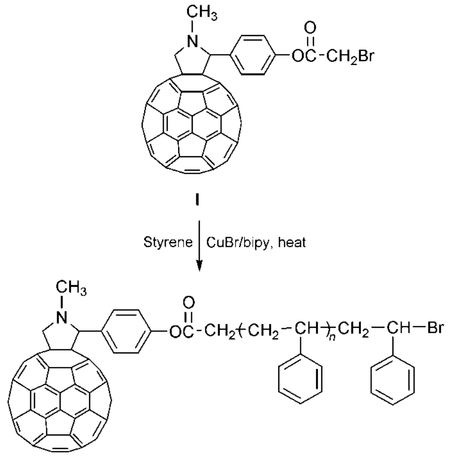
A new preparation of uniform hammer-like macromolecules of C_{60} with designed molecular weight and narrow molecular weight distributions in the range of 1.13–1.37 is developed by using C_{60}-monoadduct initiator (I) in a copper-mediated atom transfer radical polymerization (ATRP).

Recently, C_{60} (fullerene) has attracted much interest in the field of chemistry, physics and materials owing to its uniquely caged shape and intriguing properties. The structure, physical properties and photophysical behavior of C_{60} have been extensively studied.[1] Since the large-scale preparation of C_{60} was developed, there have been considerable reports on the macromolecular modification of C_{60} for practical purposes.[2–6,9–12] Since block polymers whose segments with different properties can be used as building units for aggregates,[7,8] it can be expected that an asymmetric hammer-like polymer containing C_{60} would self-assemble into a highly ordered supramolecular architecture with special electrical and optical properties. On the other hand, in order to establish the structure–property relationship of C_{60}-containing polymers, it is necessary to know the accurate content of C_{60} in the polymers. However, this has been proven to not be an easy task. The amount of C_{60} present estimated by thermogravimetry (TG), UV–VIS spectroscopy and gel permeation chromatography (GPC) do not agree well. In general, the actual amount of C_{60} incorporated in the polymer is usually much less than that in the feed.[5] Thus, there is an increasing need to synthesize well-defined C_{60}-containing polymers. This goal has been achieved partially by using different methods.[9–12] Recently, we tried an approach to synthesise well-defined C_{60}-containing polymers. In previous work,[12] well-defined bromo-terminated polymers obtained by ATRP[13] were treated with C_{60} under ATRP conditions to yield C_{60}-end-bonded PSt (PSt-C_{60}-Br) and PMMA (PMMA-C_{60}-Br). The final products were characterized to be mainly monoadducts and had controlled molecular weight with narrow molecular weight distributions, however, it was difficult to separate them from homopolymers. Here, we synthesized C_{60}-monoadduct **I** first, then it was used as an initiator for the ATRP of styrene to obtain uniform hammer-like macromolecules of C_{60} with designed molecular weight and narrow molecular weight distributions, Scheme 1.

Shown in Fig. 1 is the $\ln([M_0]/[M])$ *vs.* polymerization time plot. It can be seen that when the polymerization conversion was lower than 5%, it showed a linear relationship, meaning that the number of active species during the polymerization is constant under these conditions. This observation together with the linear evolution of molecular weight with conversion (as shown in Fig. 2) indicates that the initiation is fast so the contribution of chain breaking, transfer and termination is negligible; thus, when the conversion is lower than 5%, the process is controlled. When the conversion is higher than 5%, there is a deviation from the semilogarithmic kinetic plot, the consumption of styrene is faster than the initial stage, thus the termination on the C_{60} core can not be neglected, and the product obtained is no more well defined. The reason can be traced to the mechanism of ATRP. The initial stage of ATRP that generates radicals is a rate-determining step. In this step, a catalytic amount of the CuBr/bipy coordination complex reversibly abstracts the bromine atoms from the C_{60}-monoadduct initiator **I**, switching them from a dormant state to an active state, and generates a low concentration of C_{60}-based radicals. Since the concentration of



Scheme 1

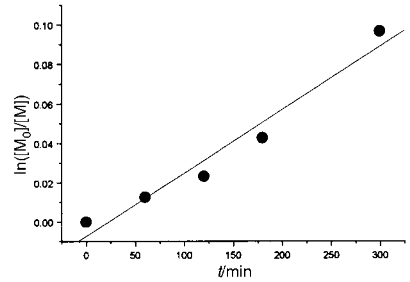


Fig. 1 Semilogarithmic kinetic plot of the preparation of C_{60}-end-bonded polystyrene *via* ATRP using C_{60}-monoadduct **I** as an initiator.

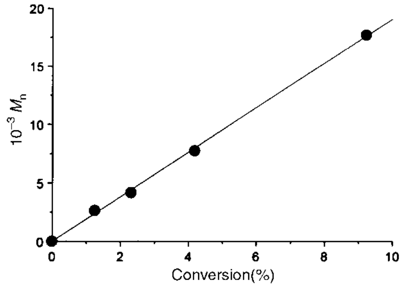


Fig. 2 Dependence of molecular weight on conversion of the preparation of C_{60}-end-bonded polystyrene *via* ATRP using C_{60}-monoadduct **I** as an initiator.

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Table 1 A summary of the conversion, molecular weight and molecular weight distribution of C_{60}-end-bonded polystyrene prepared *via* ATRP using C_{60}-monoadduct **I** as initiator

Run	Polymerization time/min	Conversion (%)	$M_{n,\,th}$ $(10^{-3})^a$	$M_{n,\,GPC}{}^b$ (10^{-3})	$M_w/M_n{}^b$
1	60	1.3	2.57	2.64	1.37
2	120	2.3	4.75	4.18	1.18
3	180	4.2	8.61	7.75	1.13
4	300	9.2	19.0	17.7	1.32

[a] Polymerization conditions for the bulk ATRP of St at 110 °C using C_{60}-monoadduct **I** as an initiator: $[St]_0 = 9.26$ M, $[CuBr]_0 = [bipy]_0/2 = [\mathbf{I}]_0 = 4.63 \times 10^{-2}$ M. [b] As determined by GPC in THF, low distribution polystyrenes were used as standards.

styrene is much higher than C_{60}-monoaduct initiator **I**, the addition of radicals to styrene double bonds occurs almost exclusively. As the polymer chains propagate, the relative concentration of styrene against C_{60}-monoaduct initiator **I** decrease, and the possibility of termination on the double bonds of C_{60} increase, thus making the molecular weight distribution broader. From the above observation, it is concluded that hammer-like macromolecules of C_{60} with designed molecular weight could be obtained by this method with low conversion.

The presence of C_{60} in polymers can be characterized by UV–VIS, DSC and NMR *etc.* Here we use 2-aminoacetonitrile (AAN) as an IR label of C_{60} in the polymers as we had reported previously.[15] Since the reaction between C_{60} and the aliphatic primary amino group of AAN proceeded smoothly under mild conditions *via* single electron transfer, the cyano group would display a characteristic peak at around 2250 cm^{-1}, while both PSt and PSt-C_{60} do not exhibit any absorption peak in the range 2000–2600 cm^{-1}. In the IR spectrum of NH_2CH_2CN-labeled PSt-C_{60}, an apparent new absorption peak appears at 2369 cm^{-1}. In a control experiment, the reaction product of pure PSt with NH_2CH_2CN does not absorb in this region. The result thus confirmed that C_{60} had been covalently bonded to PSt and this method can be extended to label other C_{60} derivatives.

Table 1 demonstrates that narrow molecular weight distribution C_{60}-bonded polystyrenes with high content of C_{60} can be obtained *via* this method. Since in ATRP, the molecular weight depends on the polymerization conversion, and the change of polymer chain length lead to the change of C_{60} content in the polymers, then by tailoring the polymer chain length, the content of C_{60} in the polymers can be well controlled.

Fig. 3(a) shows the GPC profiles of PSt-C_{60} with different molecular weight prepared by using C_{60}-monoadduct initiator **I** in THF. In all the GPC profiles the shapes are symmetrical, and there is no shoulder peak on the profiles of the PSt-C_{60} samples 2, 3 and 4 obtained by this method as compared to those obtained by preformed PSt which reacts with C_{60}.[15] This indicates that the sample possesses the designed hammer-like structure, not a mixture of PSt-C_{60} and PSt homopolymer.

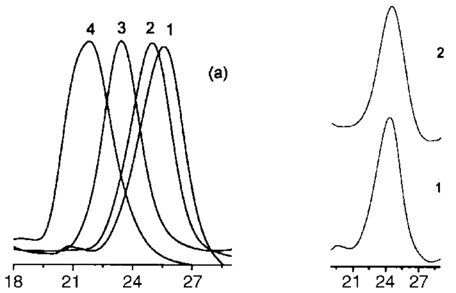

Fig. 3 (a) GPC profiles of C_{60}-end-bonded PSt prepared by using C_{60} monoadduct initiator (**I**) *via* ATRP (sample 1: $M_n = 2.64 \times 10^3$, sample 2: $M_n = 4.18 \times 10^3$, sample 3: $M_n = 7.75 \times 10^3$, sample 4: $M_n = 17.7 \times 10^3$) (b) GPC profiles of C_{60}-end-bonded polystyrene (sample 1, $M_n = 2.64 \times 10^3$) obtained by refractive index (1) and UV–VIS (2) dual detector, the working wavelength for the UV detector was set at 350 nm.

Fig. 3(b) shows the GPC profiles of C_{60}-end-bonded polystyrene (sample 1, $M_n = 2.64 \times 10^3$) obtained by UV and RI dual detector. The working wavelength of the UV detector was set at 350 nm where the PSt could not be detected and only derivatives of C_{60} can be recorded. Comparing the GPC profiles of C_{60}-end-bonded polystyrene, the profiles thus obtained are almost the same. The slight difference between the peaks at elution time is due to the different distance that the polymers passed from the pump to the detectors. This result indicates that C_{60} is bonded evenly in the polymers and the C_{60}-end bonded polystyrenes are monoadducts with well-defined structure.

Since the structure of C_{60}-end-bonded polystyrene obtained was defined with one C_{60} per polymer chain end, *i.e.* hammer shaped, by controlling the polymer chain length, the content of C_{60} in the polymers can be altered and the quantification of C_{60} in the polymers can be achieved thus aiding to establish the structure–property relationship of the C_{60}-containing polymers.

The preparation and the study of self-assembled aggregation behavior of these hammer-like macromolecules with well-defined flexible polymer chains including hydrophilic and amphiphilic chains are underway.

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Notes and references

The C_{60}-monoadduct initiator **I** was synthesized according to the literature[14,15] as shown in Scheme 1. In a typical run, a mixture of *N*-methylglycine and 4-bromoacetoxybenzaldehyde was refluxed in toluene in the presence of C_{60}. The reaction proceeded readily over 8 h, affording the monoadduct **I** of the C_{60} *N*-methylpyrrolidine derivative in 35% yield after chromatography and recrystallization (70% based on C_{60} conversion). ^{1}H NMR of C_{60} monoadduct ($CDCl_3/CS_2$) δ 7.82 (br, 2H), 7.12 (d, 2H), 4.94 (s, 1H), 4.84 (d, 1H), 4.18 (d, 1H), 3.99 (s, 2H), 2.69 (s, 3H). UV–VIS (cyclohexane): 213.8, 257.2, 317.4, 430.5 nm.

The polymerizations of styrene were conducted in bulk in sealed glass tubes. The feed molar ratio was **I** : CuBr : bipy = 1 : 1 : 2. After the mixture was degassed three times, the tube was sealed under vacuum, and the polymerization was carried out in an oil bath of 110 °C for given times. The crude polymer was obtained by precipitation from methanol, dissolved in $CHCl_3$, and the solution then passed through a silica column to remove the catalysts. The polymer was recovered by precipitation from a large excess of methanol, and then dried under vacuum. A yellow to brown fine powdery polymer was obtained. UV–VIS (cyclohexane): 215.2, 259.3 nm.

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