C$_{60}$ end-functionalized four-armed polymers: synthesis and optical limiting properties

Hui-Xia Wu · Wei-Man Cao · Rui-Fang Cai · Ying-Lin Song · Li Zhao

Abstract A series of bromo-terminated four-armed homopolymers [polystyrene (PSt) and poly(methyl methacrylate) (PMMA)], prepared by atom transfer radical polymerization (ATRP), were subsequently functionalized with fullerene C$_{60}$ by atom transfer radical addition (ATRA) reaction using CuBr/2,2′-bipyridine (bipy) as the catalyst system. The C$_{60}$ end-capped four-armed polymer derivatives were then characterized by gel permeation chromatography (GPC), UV–vis, FT-IR, thermal gravimetric analyses (TGA) and differential scanning calorimeter (DSC). Another technique of synthesizing C$_{60}$-functionalized four-armed polymers from azide functional polymers was also applied for comparison. The optical limiting behavior of C$_{60}$ end-capped four-armed polymers prepared via ATRA reaction were measured in THF solution at 532 nm. Both groups of fullerene-functionalized polymers (C$_{60}$-PSts and C$_{60}$-PMMAs) are provided with optical limiting properties.

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Introduction

In recent years, the materialization of fullerenes and their application in the field of optical and electrical devices have been a focal point of the research on chemistry and physics of fullerenes. To synthesize various kinds of fullerenated polymer derivatives with specific structure is one of important branches for preparing fullerene functional materials [1]. Among all the patterns of polymer derivatives modified with fullerene, the frameworks of branched, star-shaped and dendritic structure have special significance for designing fullerene-functionalized polymer materials. Compared with linear polymers of the same molecular weight, these kinds of star-shaped polymers probably possess some distinctive properties, including some material physical properties such as solubility and film forming properties.

There have been some reports on the syntheses and characterization of the fullerenated star-shaped polymer derivatives. Ederle and Mathis [2] produced a six-arm star-shaped fullerene derivative with six polystyrene (PSt) chains grafting onto a C$_{60}$ core by the reaction between C$_{60}$ and ''living'' polystyrene anion in an apolar solvent. They also prepared high functionality PSt stars with each branch bearing at its end a carbanion, and the star-shaped ''living'' PSt anions were allowed to react with C$_{60}$, however, the products were three dimensional network structures of PSt with C$_{60}$ molecules as knots due to the multiaddition of C$_{60}$ [3]. Our research group also synthesized star-shaped C$_{60}$-polyacrylonitrile [4] and C$_{60}$-poly(α-methylstyrene) [5] derivatives via the addition reaction of ''living'' polymer carbanions and C$_{60}$. Recently, Mathis et al. [6] synthesized asymmetric and mikto-arm stars (PS$_a$)$_2$C$_{60}$(PS$_b$)$_2$ and (PS$_a$)$_2$C$_{60}$(PI)$_2$ by the stepwise addition of macro-radicals or anionic polymer chains onto C$_{60}$.

During the process of preparing the star-shaped polymers with C_{60} as the core, the number of the polymer chains grafted onto a C_{60} core was difficult to be controlled, because multiadditional reactions occurred easily for C_{60}. Furthermore, the C_{60} content in the star-shaped polymers with C_{60} as the core is relatively low for the desire of C_{60}/polymer functional composite materials. Therefore, to solve these problems, another way was used, in which star-shaped polymer compounds were designed and synthesized in advance, then C_{60} molecules were linked at the end of each polymer chain. Cloutet et al. [7, 8] first successfully synthesized six-arm star-shaped polystyrene derivatives with each arm end-capped with one C_{60} cage. A hexaarm hexachloropolystyrene star polymer was functionalized by reaction with Me_3SiN_3 to give a hexaazido star polymer, which then reacted with a two fold excess of C_{60} to give the hexafullerene star polymer. Meanwhile, Gnanou et al. [9] reported the synthesis of a C_{60} derivatized triarm poly(ethylene oxide) (PEO) copolymer. A tri-arm PEO end-capped with azide function was allowed to react with 5-fold excess of C_{60} per azide function to achieve C_{60} end-capped star-shaped PEO.

As part of our research on preparing fullerene-functionalized materials with special-structure, in this work, we report the synthesis of C_{60} end-capped four-armed polymers. The bromo-terminated four-armed polymer precursors, synthesized via atom transfer radical polymerization (ATRP) in toluene using initiating system of 1,2,4,5-tetrakis(bromomethyl) benzene (TBMB)/CuBr/ 2,2′-bipyridine (bipy), were subsequently functionalized with C_{60} through atom transfer radical addition (ATRA) reaction using CuBr/bipy as catalyst system. The synthetic route was shown in Scheme 1. Another technique of synthesizing C_{60} end-capped four-armed polymers from azide functional polymers was also applied for comparison. The C_{60} end-capped four-armed polymers were characterized, and their optical limiting properties were measured.
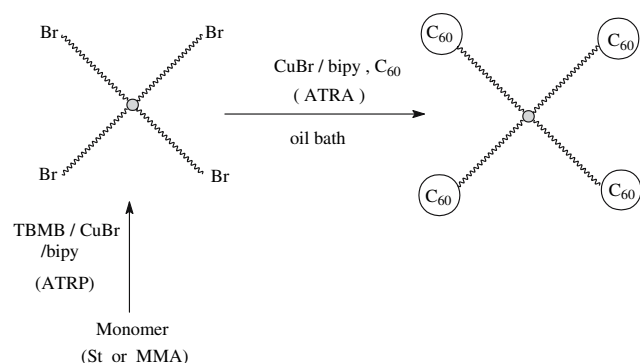
Scheme 1

Experimental

Reagents and instrumentation

C_{60} (99.9%) were obtained from Yin-Han fullerene High-Tech. Co. Ltd., Wuhan University of China. Styrene (St) and methyl methacrylate (MMA) were dried over CaH_2, and distilled under vacuum. 1,2,4,5-Tetrakis(bromomethyl) benzene (TBMB) (Aldrich, 97%) was recrystallized from $CHCl_3$, and dried at room temperature under vacuum. CuBr was washed subsequently by acetic acid and ethanol, and then dried under vacuum. 2,2′-Bipyridine (bipy) was used as received. Sodium azide (NaN_3) was recrystallized from ethanol. Toluene was distilled under purified nitrogen in the presence of Na and benzophenone before use. 1,2-Dichlorobenzene was distilled over CaH_2 under vacuum. All other reagents were used as received without further purification. All polymerization reactions were conducted under purified nitrogen by use of standard Schlenk tubes.

UV–vis absorption spectra were taken on a HP8452 spectrophotometer. The FT-IR spectra were recorded on a nicolet FTIR-5DX spectrometer using KBr pellets. The apparent molecular weight of the polymers was analyzed by a HP series 1100 gel permeation chromatography (GPC) equipped with Zorbax columns and refractive index (RI)/ultraviolet dual-mode detectors. The elution rate of tetrahydrofuran (THF) was 1 mL/min and standard PSt was used for calibration. The absolute molecular weights were determined in THF on a Waters 150 SEC apparatus, equipped with an Optilab DSP differential refractometer and a miniDAWN multi-angle (18-angles) laser light scatter detector (MALLS) (Wyatt Technology Co.), and operating at $\lambda = 690$ nm. Thermogravimetric measurements were made with a Perkin–Elemer Pyris 1 DTA-TGA instrument under nitrogen at a heating rate of 10 °C/min. Glass-transition temperature were measured on a Perkin–Elemer Pyris 1 differential scanning calorimeter at a heating rate of 10 °C/min. Optical limiting measurements were performed by the use of the 8 ns duration laser pulses at 532 nm generated from a Q-switched, frequency-doubled Nd:YAG pulse laser system. The laser was operated at 10 Hz repetition rate. The laser beams were focused by a 30 cm-focal-length lens into the sample solution. The incident and transmitted pulse energy were measured simultaneously by two energy detectors.

Synthesis of bromo-terminated four-armed polymer precursors

A dry glass Schlenk tube was charged with TBMB, CuBr and bipy (feed molar ratio = 1:4:12), and then was sealed with a rubber septum. After the mixture was degassed three

times, the monomer (St or MMA) and 10 mL of toluene was added. The polymerization was carried out in an oil bath (110 °C for St and 90 °C for MMA) for a period of time. After the polymerization was stopped, the crude polymer was obtained by precipitation with methanol. The precipitate was redissolved in THF, and filtered through a neutral alumina column to remove the catalyst. The polymer was recovered by precipitation with a large excess of methanol and then dried under vacuum.

Synthesis of C_{60} end-capped four-armed polymers via ATRA reaction

C_{60}, CuBr, bipy and 0.5 g of bromo-terminated four-armed polymer precursor were introduced into a two-neck round-bottom flask. The feed molar ratio was bromo-terminated polymer:CuBr:bipy:C_{60} = 1:4:12:10. After deoxygenizing three times, 50 mL of 1,2-dichlorobenzene was added. The mixture was then refluxed at desired temperature (120 °C for PSt; 100 °C for PMMA) in an oil bath for 24 h. After cooling to room temperature, the reaction mixture was filtered to remove the initiator residues and the solvent was evaporated under vacuum. The solid residue was taken up in THF and filtered again. The THF filtrate was concentrated under reduced pressure and precipitated with methanol. The crude product was repeatedly dissolved in THF, and then precipitated with methanol. Then the product was further purified by repeated precipitation in hexane, a solvent of C_{60} but not a solvent of the polymer, until the hexane supernatant was colorless and UV analysis showed no absorption peaks from C_{60}, indicating that the unreacted C_{60} has been removed. The purified product was dried under vacuum as brown powder.

Synthesis of C_{60} end-capped four-armed PSt from azide functional PSt

At first, azide end-functional PSt was synthesized according to the literature method [10]. A 1:15 (molar ratio) of bromo-terminated four-armed PSt and NaN$_3$ were weighted into a round bottom flask, then 15 mL of N,N-dimethylformamide (DMF) was added into the flask. The solution was stirred and allowed to react at room temperature for 48 h. The obtained azide end-functional polystyrene precursor was subsequently used to synthesize C_{60} end-capped polystyrene. A round-bottom flask equipped with a spiral condenser was charged with azide end-functional PSt (0.5 g), C_{60} and 50 mL of 1,2-dichlorobenzene. The feed molar ratio was azide end-functional PSt:C_{60} = 1:10. The flask was immersed in an oil bath and stirred at 130 °C under nitrogen for 72 h. After cooling to room temperature, the solvent was evaporated and the residue was dissolved in THF and filtered, then precipitated with hexane. The crude product was purified repeatedly by being redissolved in THF, filtered and reprecipitated with hexane. The final brown powder was dried under vacuum.

Results and discussion

Synthesis of bromo-terminated four-armed polymer precursors

ATRP is a useful method for most of vinyl monomers to prepare well-defined polymers under ordinary radical polymerization conditions. Several kinds of star-shaped polymers of styrene and acrylates with low molecular weight distributions, including 3, 4, 6, 8 and more arms, were produced via ATRP using multifunctional initiators in a controlled manner [11–16]. These results encourage us to design and prepare star-shaped polymers with a ''living'' end group in each arm using active polyfunctional-group initiators. Moschogianni et al. [15] used TBMB as a tetrafunctional initiator for the synthesis of four-armed star PMMA via ATRP with CuBr/bipy as catalytic system and benzene as solvent. The star shaped polymers had relatively low polydispersities, and their experimental molecular weights were in agreement with the theoretical ones. In this study, we prepared a series of bromo-terminated four-armed star PMMA and PSt in toluene via ATRP process using TBMB/CuBr/bipy initiating system according to the method reported by Moschogianni [15]. The molecular characterization results of the four-armed star polymers were given in Table 1. All the bromo-end-capped polymers given in Table 1 have narrow polydispersities and the GPC traces were monomodal, showing that the polymerization can be well controlled. Furthermore, their absolute molecular weight, determined by SEC/MALLS, is close to their corresponding theoretical molecular weight, implying the characteristic of living polymerization. The molecular weight values determined by GPC/RI detector were lower than those obtained by MALLS measurements. This is just a characteristic of star-shaped polymers, because star polymers have smaller hydrodynamic volumes

Table 1 Results of bromo-terminated four-armed polymers prepared by ATRP

Polymer	$\overline{M}_n$ (GPC/RI) Kg mol^{-1}	$\overline{M}_w/\overline{M}_n$ (GPC/RI)	$\overline{M}_n$ (theo) Kg mol^{-1}	Tg °C
PSt-1	13.8	1.18	15.5	100.5
PSt-2	21.0	1.18	23.4	103.4
PMMA-1	20.6	1.35	22.5	120.7
PMMA-2	46.4	1.40	49.4	126.4

than linear polymers with similar molecular weight and composition, bringing on longer retention times and a lower apparent molecular weight [11, 15].

Synthesis and characterization of C_{60} end-capped four-armed polymers via ATRA

Li Fumian et al. [17, 18] prepared well-defined bromo-terminated PSt and PMMA by ATRP in the presence of CuBr/bipy. Then these bromo-terminated polymers were allowed to react with excess C_{60} under ATRP conditions (CuBr/bipy) to yield C_{60} end-bonded PSt and PMMA with controlled molecular weight and narrow molecular weight distributions. Meanwhile, Hadziioannou et al. [19] described their results on the C_{60} functionalization of styrene-type copolymers via ATRA reaction using similar catalyst system of Cu/CuBr/bipy. Afterwards, Mathis et al. [20] reported that Br-terminated polystyrenes can be converted to macroradicals using CuBr/bipy catalyst system, and the radical addition of the polystyrene macroradicals to C_{60} favored the grafting of even number of PSt chains onto C_{60} core (100–110 °C, 45–160 h). Very recently, K. C. Tam et al. [21–24] synthesized a series of well-defined fullerene C_{60} containing polymers by ATRP technique, all the C_{60} end-capped polymers were testified to be monoadditional, and their self-assembly behavior were characterized. Therefore, it has been demonstrated that ATRP is a versatile technique for the preparation of well-defined C_{60}-containing polymers. In this work, we applied ATRA reaction to synthesize C_{60} end-capped four-armed polymers. The precursor bromo-terminated four-armed polymers synthesized via ATRP were subsequently functionalized with C_{60} using CuBr/bipy as catalyst system.

The details of synthesizing C_{60} end-capped four-armed polymers have been described in the Experimental part. To avoid multiple substitutions of polymer chains onto C_{60}, a ratio of 10:1 C_{60}/bromo-terminated four-armed polymer was used in all ATRA reactions. The excessive C_{60} was removed by dissolving the products in THF and then filtrating, since the solubility of C_{60} in THF is negligible. The products were further purified with hexane to remove the physically absorbed C_{60}. All of the C_{60} chemically modified polymers were obtained as brown powders. They are soluble not only in fullerene solvent such as benzene and toluene but also in fullerene nonsolvent such as THF, giving dark brown solutions. Various techniques were used to confirm the covalent attachment of C_{60} to the four-armed polymers, including UV–vis spectra, FT-IR spectra, GPC, thermal gravimetric analyses (TGA) and differential scanning calorimeter (DSC).

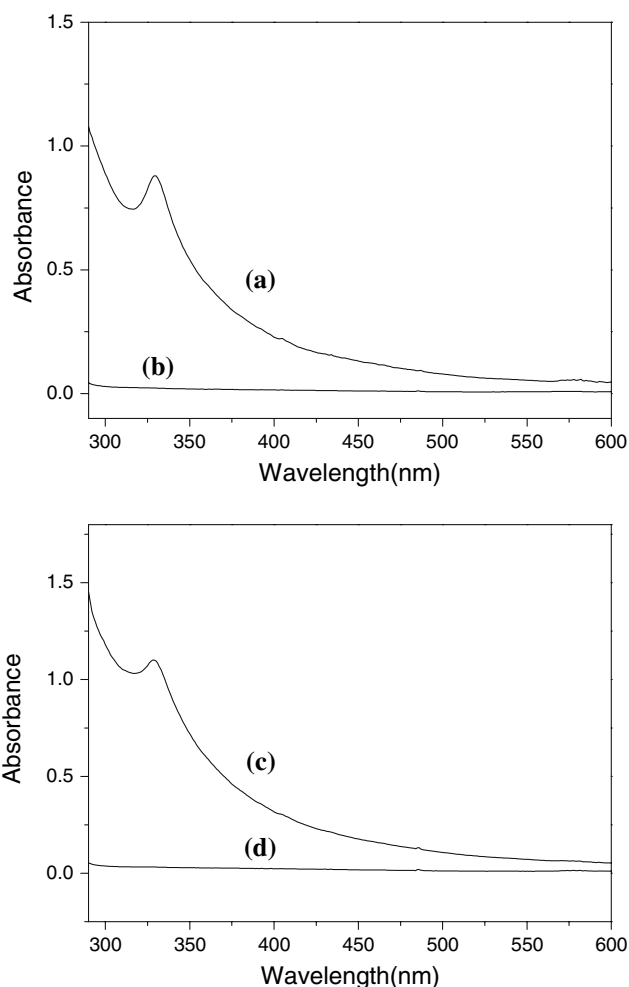The UV–vis spectra of C_{60}-functionalized products and their corresponding precursors in THF are shown in Fig. 1.

Fig. 1 UV–vis spectra of (a) C_{60}-PSt-2, (b) PSt-2, (c) C_{60}-PMMA-2 and (d) PMMA-2 in THF

The bromo-terminated star-shaped PSt and PMMA are essentially transparent at wavelength more than 280 nm, while the absorption bands of corresponding C_{60}-functionalized polymer derivatives are somewhat like those of pure C_{60}, with a peak appearing at about 330 nm. The UV–vis spectra of C_{60} end-capped four-armed polymers show that C_{60} was covalently bonded with polymer because free C_{60} should have been removed after repeated washings with hexane.

Unlike the UV–vis absorption spectra, the FT-IR spectra of the fullerene-bonded four-armed polymers show less information. Because of the relatively low C_{60} content and the overwhelming contributions of polymer chains in the polymer structure, the observed IR spectra (shown in Fig. 2) of C_{60} end-capped four-armed polymer derivatives and their corresponding bromo-terminated precursors were basically similar. Only two new weak absorption bands at about 528 cm^{-1} and 577 cm^{-1} were discovered for fullerene-bonded polymers, which was interpreted as being
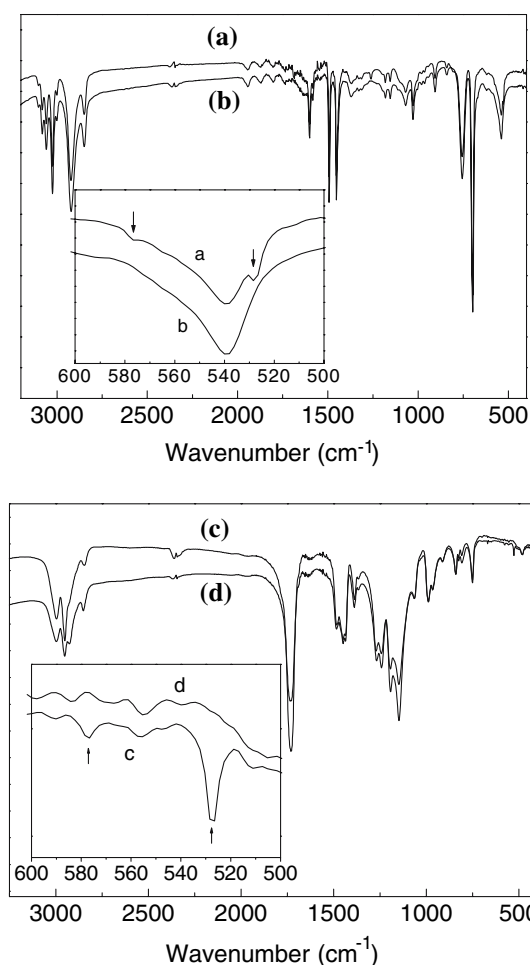
Fig. 2 IR spectra of (a) C_{60}-PSt-1 (b) PSt-1 (c) C_{60}-PMMA-1 and (d) PMMA-1

Fig. 3 GPC profiles of C_{60}-bonded polymer products and their bromo-terminated parent polymers obtained by refractive index and UV dual detectors. The working wavelength for the UV detector was set at 330 nm

associated with the characteristic infrared absorption arising from functionalized C_{60} cages [25].

The molecular weights of C_{60} end-capped polymers (Table 2) were measured by GPC equipped with both RI and UV (330 nm) dual detectors. The UV detector was set at 330 nm where the bromo-terminated polymer precursors could not be detected but only C_{60} and its derivatives could
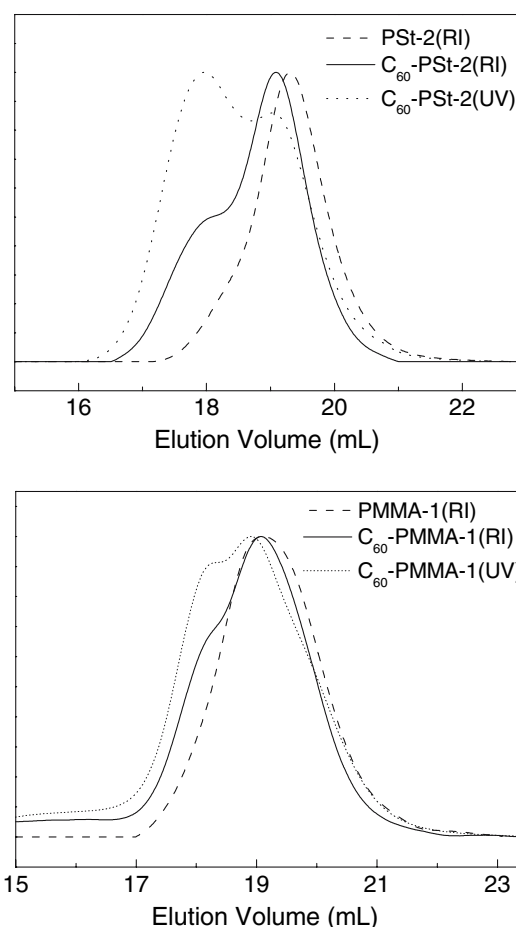
be recorded. The GPC profiles of C_{60} end-capped polymers detected at 330 nm strongly confirmed the covalent bond between C_{60} and polymer. Nevertheless, the GPC traces of all C_{60}-functionalized polymers (Fig. 3) in THF exhibited a shoulder in the high molar mass region. E. Cloutet and Y. Gnanou et.al. [7–9] found that the SEC traces of tri-arm and six-arm star-shaped fullerene-end-capped polymers in

Table 2 Results of the C_{60} end-capped four-armed polymer derivatives

Product	Precursor	$\overline{M}_n$[a] Kg mol^{-1}	$\overline{M}_w/\overline{M}_n$[a]	C_{60} content[b] wt.%	Tg°C
C_{60}-PSt-1	PSt-1	18.8	1.48	13.8 (15.7)	103.3
C_{60}-PSt-2	PSt-2	28.7	1.38	9.4 (11.0)	104.5
C_{60}-PMMA-1	PMMA-1	24.3	1.38	10.4 (11.3)	122.9
C_{60}-PMMA-2	PMMA-2	48.2	1.63	6.2 (5.5)	128.0

[a] $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ were obtained by GPC (RI detector) on the basis of a polystyrene calibration

[b] C_{60} content was measured by TGA. The data in parentheses are the theoretical C_{60} content value based on $\overline{M}_n$ (theo) of bromo-terminated star-shaped polymer precursor and four-armed C_{60}-monoadduct structure

THF exhibited a shoulder in the high molar mass region, whereas showed a smooth monomodal distribution with PhCl as eluent. They inferred that the shoulder observed in THF is likely caused by the aggregation of C_{60} termini, because THF is a nonsolvent for the C_{60} parts. Li Fumian et al. [17, 18] prepared C_{60} end-bonded PSt and PMMA via the ATRA reaction between bromo-terminated polymers and C_{60}. GPC profiles obtained by UV and RI dual detectors indicated that C_{60} had been covalently bonded to the polymers, and most of the C_{60} end-bonded polymers were monosubstituents. Mathis et al. [20] also studied the ATRA reaction between Br-terminated polystyrene and C_{60} using CuBr/bipy as catalyst system. They detected the grafting of even number of PSt chains onto C_{60} core. However, only monoadditional C_{60} end-bonded PMMA could be obtained for the ATRA reaction between Br-terminated PMMA and C_{60} using the same catalyst system whatever the stoichiometry PMMABr/C_{60} or the reaction time [6]. We once synthesized fullerene-end functionalized PMMA via reverse ATRP. The GPC profiles of C_{60}-PMMA obtained by both UV and RI dual detectors were almost the same with no shoulder in the high molar mass region, showing the monoaddition of C_{60} cage [26]. Therefore, we consider that most C_{60} end-capped four-armed PMMA derivatives were C_{60} monoadducts in which each C_{60} cage was bonded with only a polymer chain, and the shoulder in the high molar mass region was caused mainly by the aggregation of C_{60} termini. But for C_{60} end-capped four-armed PSt, the peak in the high molar mass region of the GPC traces detected by UV detector is more intense than that in the low molar mass region. This can be attributable to the multiadditon of some C_{60} cages and the aggregation of C_{60} termini as well. In this study, the large excess of C_{60} and the steric barrier of four-arm star-shaped polymer may hinder the formation of cross-linking product due to multiadditional reaction of C_{60}. Furthermore, the fact that all C_{60} functionalized polymer derivatives can easily dissolve in THF suggests that the multiadditon of PSt to C_{60} cages was well under controlled and had not led to the formation of cross-linking product.

The C_{60} contents of C_{60} end-capped star-shaped polymers were estimated by TGA (Fig. 4). Bromo-terminated four-armed PSt and PMMA decompose completely at 450 and 410 °C, respectively. Comparing with their corresponding precursor, the existence of C_{60} cages did not increase the thermal stability of C_{60} functionalized star-shaped polymers. The weight of C_{60}-PSt and C_{60}-PMMA decreased rapidly near 400 °C and 330 °C, respectively. Fullerene C_{60} is stable up to 550 °C [19], whereas the polymers start to decompose at much lower temperatures. Since the decomposition of PSt and PMMA is complete at 550 °C, it is safe to consider the residue at this temperature as C_{60} cages. The C_{60} wt.% estimated by TGA was listed in
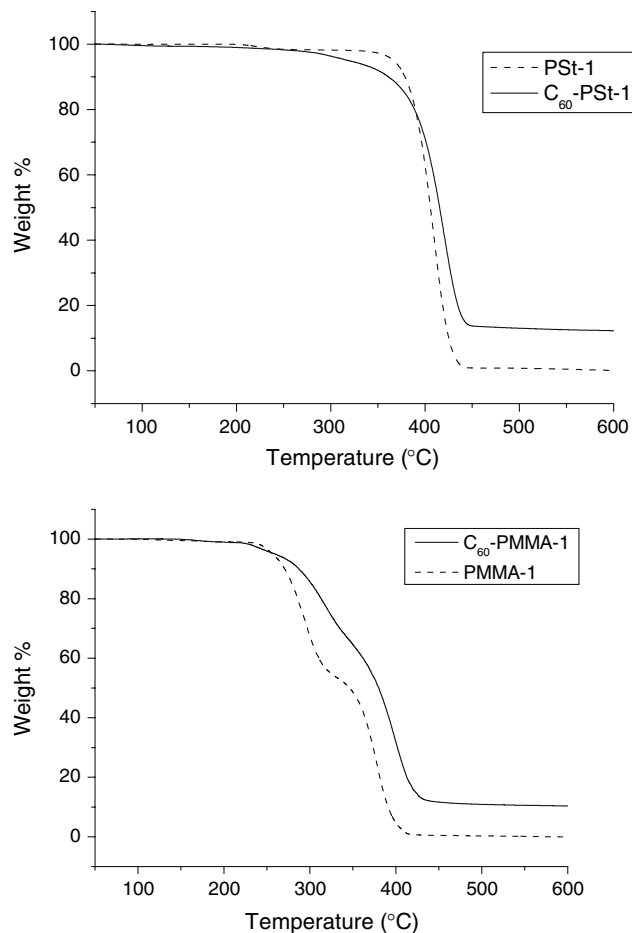

Fig. 4 TGA weight loss curves of PSt-1, C_{60}-PSt-1, PMMA-1 and C_{60}-PMMA-1

Table 2. It can be seen from Table 2 that the content of C_{60} in fullerenated PMMA determined by TGA was roughly close to the theoretical value calculated based on $\overline{M}_n$ (theo) of bromo-terminated star-shaped PMMA precursor and four-armed C_{60}-monoadduct structure. The results showed that most of the star-shaped PMMA was bonded with one C_{60} molecule per polymer arm. The C_{60} content in C_{60}-PSt measured by TGA is slightly less than the corresponding theoretical value, which may result from a partial coupling reaction between bromo-terminated four-armed PSt stars through the possible grafting of even number of PSt chains onto C_{60} core as mentioned by Mathis et al. [20].

All C_{60}-functionalized star-shaped polymers and their corresponding bromo-terminated parent polymers exhibit single glass transition temperature (Tg) (Fig. 5), suggesting no phase separation in the resultant polymer system. The Tg values of C_{60}-functionalized products and their corresponding precursors were listed in Tables 1 and 2. Several research groups have reported that when C_{60} content increases, the Tg of C_{60}-containing polymers increases regularly, decreases slightly, or almost does not change.
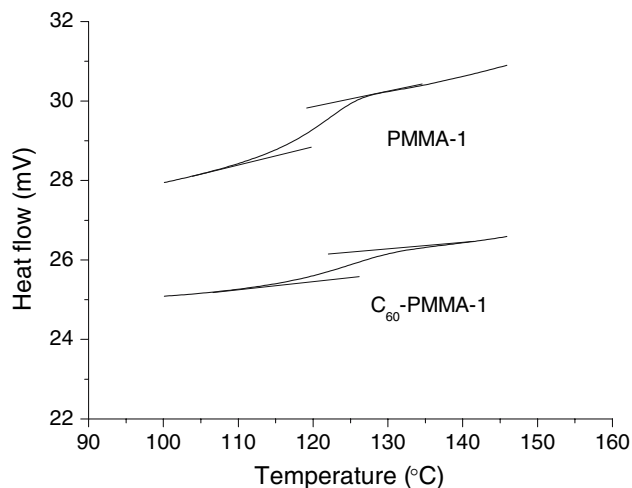
Fig. 5 DSC curves of PMMA-1 and C_{60}-PMMA-1

Fig. 6 IR spectra of (**a**) C_{60}-PSt-2′ (**b**) PSt-2-N3 (**c**) PSt-2. The fullerenated polymer from azide functional polymer PSt-2-N$_3$ is marked as C_{60}-PSt-2′

[27–29] In our case, all the C_{60}-functionalized products have Tg value higher than their corresponding precursors, showing that the incorporation of C_{60} may restrict the movement of polymer chain segments and result in the increase of the Tg value.

Comparing with C_{60} end-capped four-armed PSt prepared from azide functional star-shaped PSt

Another efficient method to synthesize C_{60} end-capped polymers is the reaction of excessive C_{60} with azide functional polymers, which are reported to react selectively with C_{60} through a monoaddition reaction without noticeable side reactions. [8, 9, 30, 31] Considering the possible multiaddition of some C_{60} cages during the ATRA reaction between bromo-terminated four-armed PSt and C_{60}, we also applied this technique to synthesize C_{60} end-capped four-armed PSt for comparison. This method includes a two step sequence. First, to replace bromo group with azide group, the bromo-terminated four-armed PSt was allowed to react with a 15-fold excess of NaN_3 at room temperature for 2 days. The appearance of the strong band at 2,092 cm^{-1} for the azide group gives an evidence of the successful replace of the azide group at the end of the polymer (Fig. 6b). The GPC trace of the recovered azide functional PSt was basically the same as that of the starting bromo-terminated PSt. Then, the fullerenation was carried out through the reaction of azide terminated four-armed PSt and 2.5-fold excessive C_{60} per azide function in 1,2-dichlorobenzene at 130 °C for 72 h. The final product is brown-colored powder, and can be easily dissolved in various organic solvents such as CHCl$_3$ and THF.

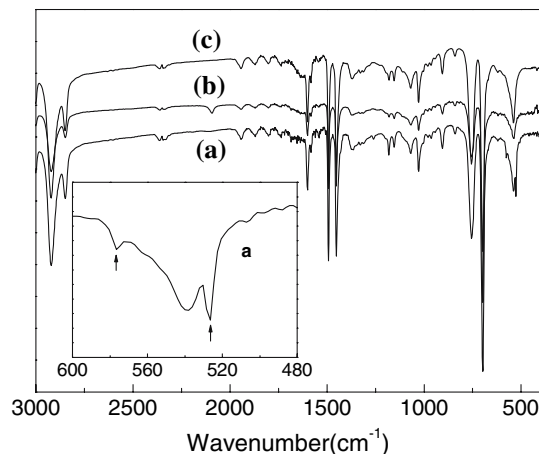The FT-IR spectrum of the fullerenated four-armed PSt from azide functional PSt showed the complete disappearance of the band at 2,092 cm^{-1} and the appearance of two weak bands at 526 cm^{-1} and 576 cm^{-1} characteristic of the vibration of fullerenes (Fig. 6).

The C_{60} content of the fullerenated four-armed PSt synthesized from azide functional PSt can be estimated by TGA likewise. According to the TGA weight loss curve of C_{60}-PSt-2′, the C_{60} content was estimated to be 12.2% (550 °C). The molecular weight of C_{60}-PSt-2′ measured by GPC trace from the RI detector revealed that its $\overline{M}_n$ was 22.4 kg mol^{-1} with $\overline{M}_w/\overline{M}_n = 1.22$. The GPC profile of C_{60}-PSt-2′ also showed a shoulder in the high molar mass region (Fig. 7), but the shoulder minished obviously in comparison with that of C_{60}-PSt-2. Therefore, it is obvious that the fullerenation product via the reaction of azide functional polymer with excessive C_{60} was basically C_{60} monoadduct, with a better purity. Considering that this fullerenation technique includes a two-step sequence and requires long reaction time, while the ATRA reaction procedure possesses only one step, we consider that ATRA reaction is still an efficient technique for synthesizing well-defined fullerene-functionalized polymers, especially for fullerene end-capped PMMA.

Optical limiting

Optical limiters are devices that strongly attenuate optical beams at high intensities while exhibit higher transmittance at low intensities. Therefore, they are useful for protecting the human eyes and optical sensors from intense laser beams. C_{60} is an excellent optical limiter operating in a reverse saturable absorption mode [32, 33]. However, the ability to fabricate optical limiting devices based on fullerene has been limited due to its poor solubility and processibility. The combination of this eminent optical limiting characteristic of fullerene with good processibility
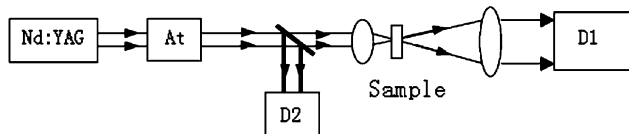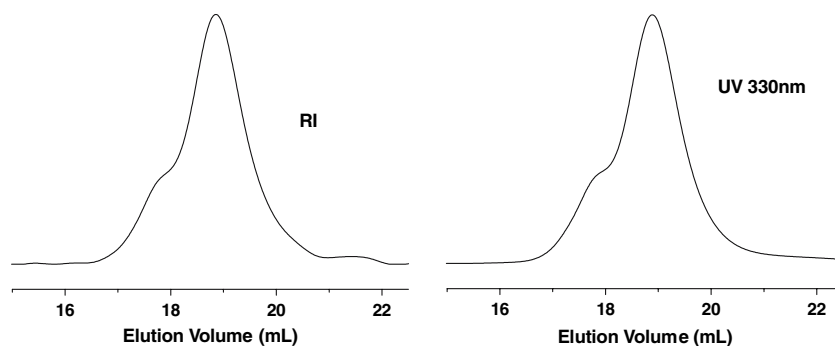
Fig. 8 Experimental setup for optical limiting measurements

of polymer materials through chemical syntheses of fullerene-containing polymers would open up the application of C_{60} in the field of optical limiting.
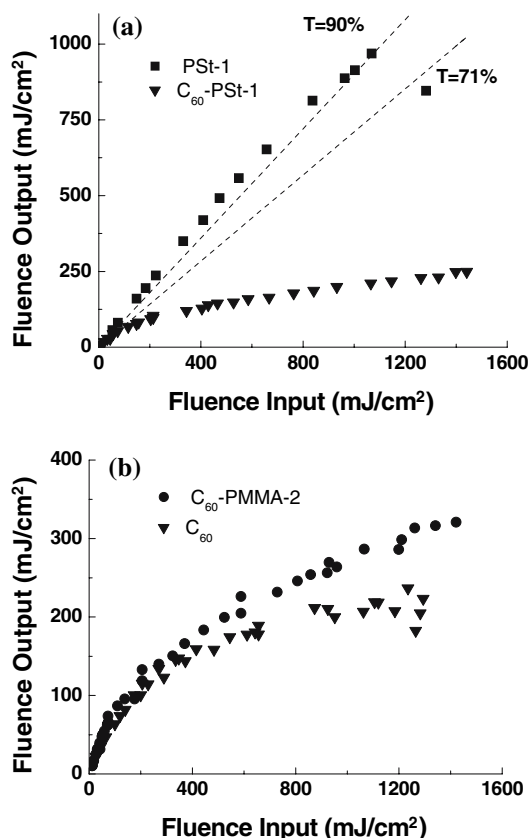

Fig. 9 Optical limiting response of (**a**) C_{60}-PSt-1 and PSt-1 (Linear transmittance: 71% and 90%, respectively) (**b**) C_{60}-PMMA-2 and C_{60} (Linear transmittance: 85%) to 8ns laser pulses at 532nm

The optical limiting properties of C_{60} end-capped four-armed polymers were measured using the setup shown in Fig. 8. Optical limiting measurements were carried out with 8 ns duration laser pulses at 532 nm in THF solution. At very low fluences, the optical response of C_{60} end-capped four-armed polymers obeys Beer's law and the transmittance is roughly constant. At high input fluence, the transmittance decreased with input fluence and optical limiting property with saturated output fluence was observed. Figure 9a showed the optical limiting response of C_{60}-PSt-1 and its corresponding precursor PSt-1. At an input fluence of about 100 mJ/cm^2, the transmittance of C_{60}-PSt-1 began to decrease markedly. When the incident fluence became very high, the transmitted fluence leveled off at about 250 mJ/cm^2. For C_{60}-PMMA-2 in THF (Fig. 9b) at a linear transmittance of 85%, the transmittance began to decrease at an input energy of about 120 mJ/cm^2, and the output energy leveled off at about 350 mJ/cm^2. The saturation fluences of C_{60} toluene solution at linear transmittance of 70% and 85% were about 90 mJ/cm^2 and 240 mJ/cm^2, respectively. Although the optical properties of these samples were inferior to that of C_{60}, considering the improved solubility and easily processibility, the C_{60} end-capped four-armed polymers can be applied as effective optical limiters. The linear transmittance versus input laser energy of these samples was also determined. It was found that the transmittance began to drop off significantly at very low input energy. Therefore, the optical limiting properties of C_{60} end-capped four-armed polymers may be attributed to the reverse saturable absorption, namely, these samples have a much higher absorption cross section of excited state than the ground state [34].

Conclusion

In this article, bromo-terminated four-armed polymers synthesized via ATRP were allowed to react directly with excessive fullerene C_{60} by ATRA reaction using CuBr/bipy as the catalyst system to yield C_{60} end-capped four-

armed polymer derivatives. The resulting products, which can be well dissolved in common organic solvents such as THF, toluene and CHCl$_3$, were characterized by UV–vis, FT-IR, GPC, TGA, and DSC. The results showed that each four-armed star-shaped PMMA was mainly bonded with one C$_{60}$ molecule per polymer arm, whereas there existed a certain multiadditon of some C$_{60}$ cages in fullerenated four-armed star-shaped PSt. A two-step technique of synthesizing C$_{60}$ end-capped four-armed PSt from azide functional PSt precursor was also applied for comparison. We conclude that ATRA reaction is still an efficient technique for synthesizing well-defined fullerene-functionalized polymers, especially for fullerene end-capped PMMA. The optical limiting behavior of C$_{60}$ end-capped four-armed polymers in THF solution were investigated at 532 nm. Both two groups of fullerene functionalized star-shaped polymers (C$_{60}$-PSts and C$_{60}$-PMMAs) synthesized via ATRA reaction still showed optical limiting response. Although the optical limiting properties of these samples in THF were inferior to that of C$_{60}$ in toluene, considering the improved solubility and easily processibility, they can be applied as effective optical limiters.

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