Synthesis of C_{60}-End-Bonded Polymers with Designed Molecular Weights and Narrow Molecular Weight Distributions via Atom Transfer Radical Polymerization

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ABSTRACT: Bromo-terminated polystyrene (PSt−Br) and poly(methyl methacrylate) (PMMA−Br) with designed molecular weights and narrow molecular weight distributions were prepared by atom transfer radical polymerization (ATRP). These bromo-terminated polymers were allowed to react with C_{60} under ATRP conditions to yield C_{60}-end-bonded PSt (PSt−C_{60}−Br) and PMMA (PMMA−C_{60}−Br). The polymers were characterized by gel permeation chromatography (GPC), UV−vis, FT-IR, and fluorescence spectra. 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. Furthermore, 2-aminoacetonitrile (AAN) was used as an IR label to react with PSt−C_{60}−B; the products thus obtained show a characteristic absorption of CN group at 2369 cm^{-1}. This result reinforces the conclusion that C_{60} has been covalently bonded into the polymer. The fluorescence of PMMA−C_{60}−Br and PSt−C_{60}−Br can be quenched by triethylamine or fumaronitrile, indicating that C_{60} still keeps its strong electron-accepting and strong electron-donating property after it was modified by macromolecules. A possible mechanism of the formation of C_{60}-end-bonded PSt was deduced tentatively.

Introduction

C_{60}, the representative of the fullerene family, possesses uniquely attractive properties in physics, photophysics, photochemistry, and so on.[1] Since the large-scale preparative method for C_{60} was developed, there have been considerable reports on the macromolecular modification of C_{60} aiming at the materialization of C_{60} for the practical purpose.[2] It is obvious that C_{60}-bonded polymers obtained by introducing C_{60} to the polymers led to the improvement of the solubility and processability of C_{60}. Because of the multifunctionality and the activity of C_{60} in chemical reaction, the introduction of C_{60} to polymers by ordinary radical polymerization usually makes the C_{60}-bound polymers with broader distribution in molecular weight and shape; some are even cross-linked.[3,4]

So far, some efforts have been devoted to the synthesis of well-defined polymeric C_{60} derivatives. Frey et al.[5] synthesized polystyrene monosubstituted C_{60} by the reaction of C_{60} with an amino-functionalized polystyrene which was obtained via living anionic polymerization. Astruc et al.[6] prepared C_{60}-end-capped polystyrene stars by reacting C_{60} with a hexaarm hexaazidepolystyrene star-shaped polymer. Wang et al.[7] and Fukuda et al.[8] separately reported on the preparation of C_{60}-containing PSt with narrow molecular weight distribution by reaction of C_{60} with PSt−TEMPO (polystyrene adducts with 2,2,6,6-tetramethylpiperidinyl-1-oxy).

Recently, the precise polymerizations have been developed persistently and attracted much interest in order to gain well-defined polymers in topologic aspects—among which newly developed atom transfer radical polymerization (ATRP) is a starred one.[9] The advantage of ATRP is that the polymerization can be performed according to the ordinary free-radical polymerization procedure and thus can avoid the stringent polymerization condition like living anionic polymerization needed. This encourages the introduction of C_{60} to polymer via controlled radical polymerization to obtain C_{60}-involved polymers with designed molecular weight and narrow molecular weight distribution. This article deals with the synthesis of C_{60}-end-bonded well-defined polystyrene (PSt) and poly(methyl methacrylate) (PMMA) via ATRP. The existence of C_{60} covalently bonded in the polymer was also evidently confirmed by labeling with 2-aminoacetonitrile whose characteristic peak in the IR spectrum does not interfere with those of C_{60} and phenyl group in the copolymer.

In the first step, the Br-terminated polystyrene (PSt−Br) or poly(methyl methacrylate) (PMMA−Br) was prepared via ATRP with designed molecular weights, which can be "awoke" from the dormant state to radical at high temperature in the presence of CuBr/2,2′-bipy, and then a solution of C_{60} was added to it. Since C_{60} is chemically considered to behave like an electron-deficient polyolefin,[2] the addition of aforementioned PSt (or PMMA) radicals to C_{60} took place readily. Simultaneously, C_{60} abstracted the halogen atom from Cu(II) complex, thus completing the reaction cycle and giving out the product of C_{60}-end-bonded well-defined PSt or PMMA as shown in Scheme 1.

Experimental Section

Materials. 1-Phenylethyl bromide (1-PEBr), $n_D^{20} = 1.5614$ (lit. 1.5600) was prepared according to the literature.[10] Methyl 2-bromopropionate (MBP, Aldrich) was used as received. Styrene and MMA (A.R., Beijing Chemicals Co.) were distilled under reduced pressure over CaH_2. CuBr (C. P., Beijing Chemicals Co.) was purified by subsequently washing with acetic acid and ethanol and then dried in vacuo. C_{60} was

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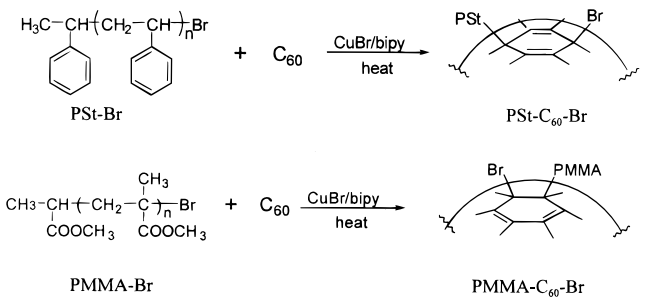
Scheme 1



prepared by an arcing method with a homemade apparatus, whose purity was 99.5%. 2,2′-Bipyridine (bipy, A. R., Beijing Chemicals Co.), 2-aminoacetonitrile hydrochloride (AAN, Aldrich), and other reagents were used as received.

Atom Transfer Radical Polymerization of St and MMA. The polymerizations of styrene and MMA were conducted in bulk in sealed glass tubes. The feed molar ratio was 1-PEBr:CuBr:bipy = 1:1:2 (MBP was used as an initiator in the polymerization of MMA). After the mixture was degassed three times, the tube was sealed under vacuum, and the polymerization was carried out in an oil bath (for styrene, 110 °C, 12 h; for MMA, 90 °C, 8 h). The crude polymer was obtained by precipitation from methanol and then was dissolved in $CHCl_3$; the solution was 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 white fine powdery polymer was obtained.

Synthesis of PSt−C_{60}−Br and PMMA−C_{60}−Br. In a typical run, C_{60}, CuBr, bipy, and PSt−Br (or PMMA−Br) were dissolved in 20 mL of chlorobenzene and charged in the glass tube in the molar ratio of 2:1:2:1. After the mixture was degassed three times, the tube was sealed under vacuum and then kept in an oil bath of 110 °C for 12 h (for PMMA−Br, the temperature was kept at 90 °C for 8 h). Then the tube was broken, the solvent was distilled out, and the residue was dissolved with $CHCl_3$ and precipitated in a large excess of methanol. The polymer was purified by dissolution in THF and reprecipitation from methanol.

Chemically Labeling of PSt−C_{60}−Br. To a solution of 100 mg of PSt−C_{60}−Br ($M_n = 3.32 \times 10^3$) in 5.0 mL of THF was added 0.2 mL of free 2-aminoacetonitrile (AAN) in 1.0 mL of THF. The addition reaction was kept at room temperature under argon atmosphere with stirring for 20 h, and then the reaction mixture was poured into large amount of methanol. A brown precipitate was obtained. The precipitate was washed thoroughly with methanol until no unreacted AAN was detected by UV−vis spectrometry and dried in vacuo.

Characterization. The UV−vis absorption spectra were recorded on a Shimadzu UV2101PC UV−vis scanning spectrophotometer using a 1.0 cm square quartz cell. The FT-IR spectra were recorded on a Nicolet 750 FT-IR spectrometer (KBr). The molecular weights of the polymers were estimated by a Waters-515 gel permeation chromatograph (GPC) equipped with three Styragel columns (HT2 + HT3 + HT4), a Waters 2410 refractive index (RI) detector, and a Waters 2487 UV detector. The working wavelength of the UV detector was set at 350 nm. Degassed THF was used as an eluent at a flow rate of 1.0 mL/min. Calibration was based on low distribution polystyrene standards. Data analysis was made on Millenium 32 software. Thermalgravimetric (TGA) analyses were measured on a Universal V1.9D TA instrument. The fluorescence emission spectra were recorded on a F-4500 fluorescence spectrophotometer with PMT voltage of 700 V. The slit widths of the monochromators were both 5 nm. The solvents were purified to eliminate the interfering impurities for florescence.

Results and Discussion

Synthesis of PSt−Br and PMMA−Br. ATRP is a useful method for most of vinyl monomers to prepare well-defined polymers under ordinary radical polymerization conditions. It had been demonstrated that PSt and PMMA obtained via ATRP possess well-controlled molecular weights and narrow molecular weight distributions. Here we prepared PSt and PMMA via ATRP based on the procedure reported by Matyjaszewski et al.[9] It can be seen from Table 1 and Table 2 that the molecular weight distributions of PSt and PMMA are narrow. These well-defined prepolymers were used to prepare PSt−C_{60}−Br and PMMA−C_{60}−Br in the presence of ATRP catalyst $CuBr_2$/bipy.

Synthesis of PSt−C_{60}−Br and PMMA−C_{60}−Br. It has been demonstrated that the electronic properties of C_{60} were perturbed as the its conjugated structure was destroyed.[11] So it is important to prepare monosubstituted C_{60}-bonded polymer, which can increase the solubility while retain the intriguing properties of C_{60} to the greatest extent. To optimize the synthesis of monosubstituted C_{60}-bonded polymer in all reactions, a ratio of C_{60}:polymer = 2:1 was used to minimize the fraction of higher substituted products. As the reaction proceeded, the characteristic purple color of C_{60} in chlorobenzene turned to dark brown, indicating that the reaction occurs. Excess of C_{60} was removed by dissolving the product s in THF since the solubility of C_{60} in THF is so small that it is negligible. All of the C_{60} chemically modified polymers were obtained as brittle powders with brown color, which was changed depending on the amount of C_{60} incorporated. The C_{60}-end-bonded polymers are soluble not only in fullerene solvent such as benzene, toluene, and CS_2 but also in fullerene nonsolvent such as THF and $CHCl_3$, giving a dark brown solution.

Characterization of PSt−C_{60}−Br and PMMA−C_{60}−Br. Tables 1 and 2 summarize the molecular weights and molecular weight distributions for PSt−Br and PMMA−Br before and after reacted with C_{60}, respectively. It can be seen that the molecular weight distributions of the PSt−Br and PMMA−Br remain almost unchanged after the reaction with C_{60}. The molecular weights of both polymers increase a little. The increase is not equal to the molecular weight of C_{60}, which may be attributed to the fact that the compact shape of C_{60} moiety in the copolymer contributes little to the hydrodynamic volume of the polymer.

Although the existence of C_{60} increases the thermal stability of C_{60}-end-capped polymers, we can still assume that the weight percent of C_{60} incorporated into the polymers could be determined by DTA because PSt and PMMA decompose at 450 and 405 °C, respectively. The residue left could be deemed as C_{60}. Comparison with prepolymers and physical mixtures confirmed the TGA results. We can see in Table 1 that the content of C_{60} was roughly close to the theoretical value which was calculated under the premise that the C_{60}-end-capped polymer was a monoadduct.

After PSt−Br was reacted with C_{60}, there should be one Br atom bonded at the end of each polymer chain. But elemental analysis result shows that the content of bromine in the polymer was lower than the theoretical value. Since the bromine atom directly linked to C_{60} is very active, it can be displaced by other functional groups. For example, methanol and trace water leads to the debromination process of PSt−C_{60}−Br; a similar result was previously reported by Heymann et al.[12] Furthermore, the fact that C_{60} derivatives cannot be burned completely during the elemental analyses may also resulted in an inaccurate measurement. This

Table 1. Molecular Weights and Molecular Weight Distributions of PSt−Br and PSt−C_{60}−Br[a]

	PSt−Br			PSt−C_{60}−Br				
run	$M_n(10^3)$[b]	$M_w(10^3)$[b]	M_w/M_n	$M_n(10^3)$[b]	$M_w(10^3)$[b]	M_w/M_n	Br (%)[c]	C_{60} cont (%)[d]
1	2.52	3.35	1.33	3.32	4.61	1.39	2.01 (2.41)	18.8 (21.6)
2	4.80	5.72	1.19	5.46	6.66	1.22	0.56 (1.46)	11.9 (13.2)
3	8.01	9.02	1.12	8.29	9.62	1.16	0.38 (0.96)	7.6 (8.6)

[a] Polymerization condition: 1-PEBr:CuBr:bipy = 1:1:2 (in molar ratio), 110 °C, 8 h. Reaction condition: C_{60}:CuBr:bipy:PSt−Br = 2:1:2:1 (in molar ratio), 110 °C, 12 h. [b] Determined by GPC analysis in THF; monodisperse polystyrene standards were used as the molecular weight reference. [c] Measured by elemental analysis; the data in parentheses are the calculated values based on M_n, and each polymer chain contains one bromine atom. [d] Measured by DTA on the prepolymers and the C_{60}-end-capped polymers; the data in parentheses are the theoretical value based on M_n and C_{60}-monoadduct structure.

Table 2. Molecular Weights and Molecular Weight Distributions of PMMA−Br and PMMA−C_{60}−Br[a]

	PMMA−Br			PMMA−C_{60}−B			
run	M_n (10^4)[b]	M_w (10^4)[b]	M_w/M_n	M_n (10^4)[b]	M_w (10^4)[b]	M_w/M_n	C_{60} cont (%)[c]
1	1.70	2.26	1.32	2.57	3.37	1.31	2.9 (2.8)
2	3.09	4.12	1.34	3.51	4.94	1.41	1.9 (2.1)
3	4.06	5.67	1.39	4.65	6.62	1.42	1.8 (1.5)

[a] Polymerization conditions: MBP:CuBr:bipy = 1:1:2 (in molar ratio), 90 °C, 8 h. Reaction conditions: C_{60}:CuBr:bipy:PMMA−Br = 2:1:2:1 (in molar ratio), 110 °C, 8 h. [b] Determined by GPC analysis in THF; monodisperse polystyrene standards were used as molecular weight reference. [c] Measured by DTA on the prepolymers and the C_{60}-end-capped polymers; the data in parentheses are the theoretical value based on M_n and C_{60}-monoadduct structure.

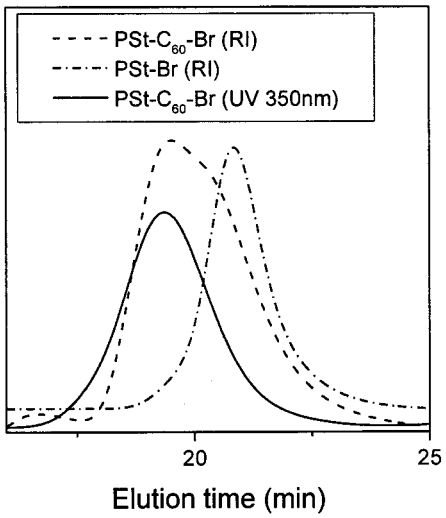


Figure 1. GPC profiles of PSt−C_{60}−Br and PSt−Br obtained by refractive index and UV−vis dual detector; the working wavelength for the UV detector was set at 350 nm.

explanation is also verified by the elemental analysis of the model compound of PSt−C_{60}−Br, Br−C_{60}−CH-(C_6H_5)CH_3.

The molecular weights and molecular weight distributions of PMMA−Br before and after the reaction with C_{60} are listed in Table 2. These results share the same rule with those of PSt−Br and PSt−C_{60}−Br listed in Table 1.

Figure 1 and Figure 2 show the GPC profiles of PSt−C_{60}−Br and PMMA−C_{60}−Br obtained by UV and RI dual detectors. The UV detector was set at 350 nm where the PSt and PMMA could not be detected and only C_{60} and its derivatives can be recorded. Comparing the GPC profiles of PSt−C_{60}−Br (or PMMA−C_{60}−Br), the profiles thus obtained are very similar, and their peaks almost share the same elution time.

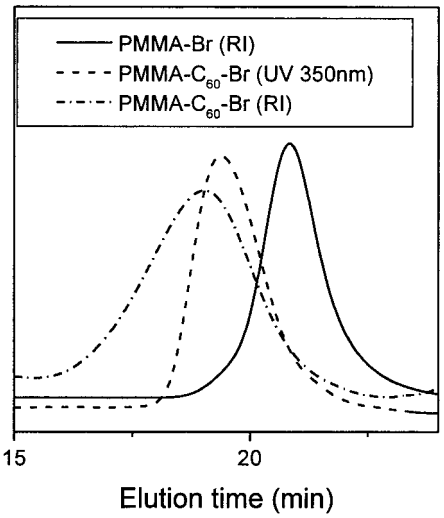


Figure 2. GPC profiles of PMMA−C_{60}−Br and PMMA−Br obtained by refractive index and UV−vis dual detector; the working wavelength for the UV detector was set at 350 nm.

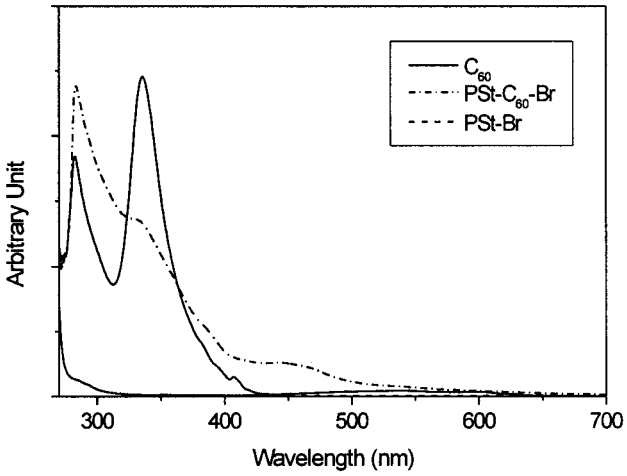


Figure 3. UV−vis spectra of PSt−C_{60}−Br ($M_n = 8.29 \times 10^3$), PSt−Br ($M_n = 8.01 \times 10^3$), and C_{60} in cyclohexane.

It is obvious that there is a shoulder peak in the GPC profiles of PSt−C_{60}−Br obtained by the refractive index detector. This indicates that the sample was a mixture of PSt−C_{60}−Br and PSt homopolymer. Since PSt−C_{60}−Br and PSt homopolymer possess similar solubility in organic solvent, it is difficult to separate PSt−C_{60}−Br from PSt homopolymer in the mixture. So the profiles obtained by the RI detector is less symmetry than that obtained by UV detector, and the molecular weight distribution obtained by RI detector are slightly boarder than that obtained by the UV detector.

Figure 3 shows the UV−vis spectra of PSt−Br, PSt−C_{60}−Br, and C_{60} in cyclohexane. It is seen that one of

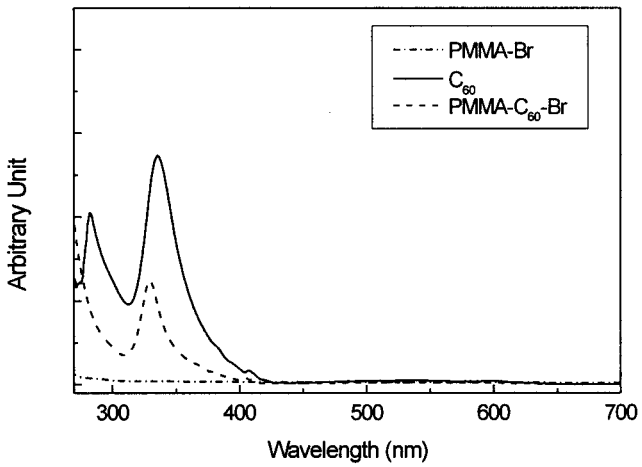
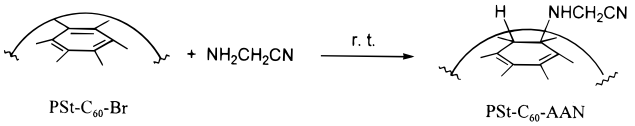


Figure 4. UV−vis spectra of PMMA−C_{60}−Br (M_n = 2.57 × 10^4) and PMMA−Br (M_n = 1.70 × 10^4) in THF and C_{60} in cyclohexane.

the characteristic absorption peaks of C_{60} at 272 nm remains, and the other strong absorption band of C_{60} at 336 nm is replaced by a steadily decreasing curve of typical substituted C_{60}. It is caused by the breakage of the symmetry and electronic structure of C_{60} after its reaction with PSt−Br. Generally, monosubstituted C_{60} derivatives show characteristic UV−vis absorption as described by Hirsch et al., Murata et al., and Okamura et al. separately.[13] The broad band that appeared at 434 nm indicates that PSt−C_{60}−Br is a 1,4-substituted derivative.[13]

Figure 4 shows the UV−vis spectra of PMMA−Br, PMMA−C_{60}−Br, and C_{60} in cyclohexane. The absorption bands of PMMA−C_{60}−Br are similar to that of parent C_{60} but different from PSt−C_{60}−Br, especially in the disappearance of a broad band at 434 nm. This indicates that PMMA−C_{60}−Br may be a 1,2-substituted derivative, as Hirsch et al. pointed out.[13]



It is noticeable that the FT-IR spectra of both PSt−Br and PSt−C_{60}−Br do not exhibit any absorption peak in the range 2000−2600 cm^{-1}. Considering that the cyano group would display a characteristic peak at around 2250 cm^{-1} and the aliphatic primary amino group can react readily with C_{60} under mild conditions via a single electron transfer process, 2-aminoacetonitrile (AAN) was elaborately chosen for the chemically labeling of PSt−C_{60}−Br.

Figure 5 shows the IR spectra of PSt−C_{60}−Br, and the product after it was treated by 2-aminoacetonitrile. In the IR spectrum of NH_2CH_2CN-labeled PSt−C_{60}−Br, 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 extendedly used to label other C_{60} derivatives.

It is known that spherical shape molecule hardly displays fluorescence. Because of the high symmetry of C_{60} in three dimensions, bare C_{60} does not display florescence in solution at room temperature. However,

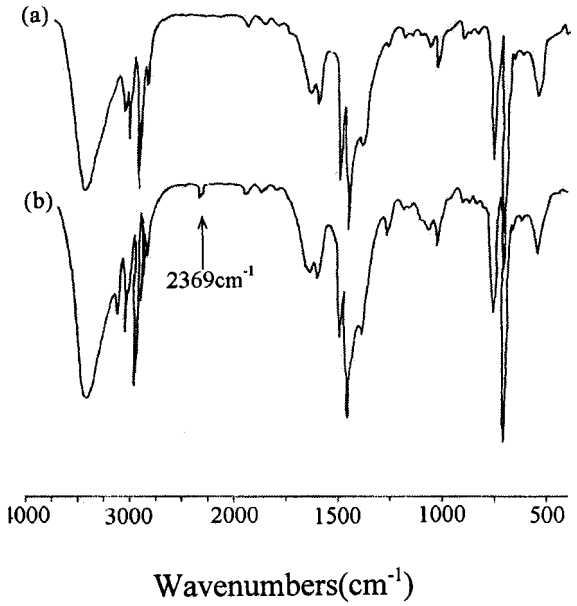


Figure 5. IR spectra of (a) PSt−C_{60}−Br and (b) NH_2CH_2CN-labeled PSt−C_{60}−Br.

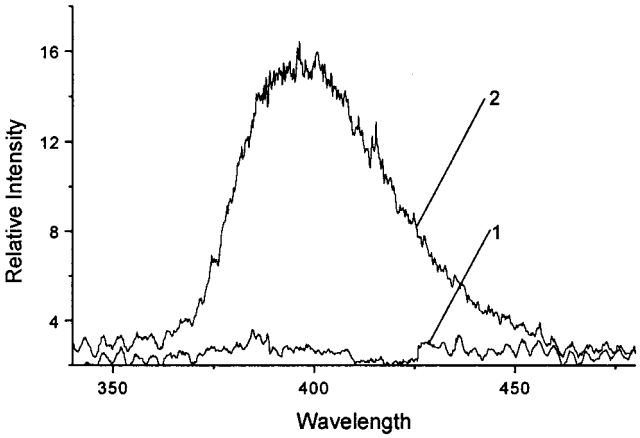


Figure 6. Fluorescence spectra of PMMA−Br (1) (M_n = 1.70 × 10^4) and PMMA−C_{60}−Br (2) (M_n = 2.57 × 10^4) in dichloromethane at room temperature. λ_{ex} = 248 nm.

after C_{60} was modified by other compounds such as isobutylamine and polymers such as poly(allylamine), the adducts obtained displayed fluorescence in solution at room temperature.[15,16] This may be due to the lessening of the highly symmetric shape of C_{60}.[17]

Both PMMA−C_{60}−Br and PSt−C_{60}−Br displayed fluorescence in dichloromethane at room temperature. Figure 6 and Figure 9 show the fluorescence spectra of PMMA−C_{60}−Br and PSt−C_{60}−Br with the same polymerization degree at the same mass concentration by the excitation wavelength of 248 nm. It can be seen from Figure 6 that PMMA−C_{60}−Br displayed fluorescence even though it is weak. Obviously, PMMA does not have any chromophore moieties, so it is difficult to absorb enough energy to transfer to C_{60}. Thus, the fluorescence of PMMA−C_{60}−Br supports the concept that the lessening of the highly symmetric shape of modified C_{60} would be a crucial factor for the display of fluorescence.[17]

One of the intriguing properties of C_{60} is that whose ionization potential and electron affinity are 7.51 eV and 2.56 eV, respectively, meaning that C_{60} acts as both strong electron acceptor and strong electron donor.

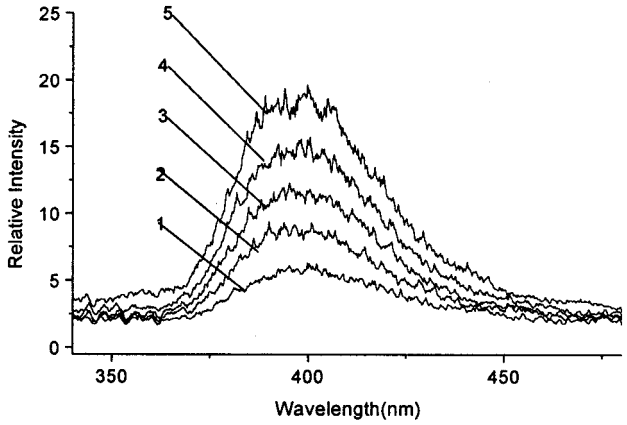


Figure 7. Fluorescence quenching of PMMA−C_{60}−Br by triethylamine in dichloromethane, $\lambda_{ex} = 248$ nm. From top to bottom, concentration of triethylamine (mol/L): 0, 0.0050, 0.0150, 0.0450, 0.0090.

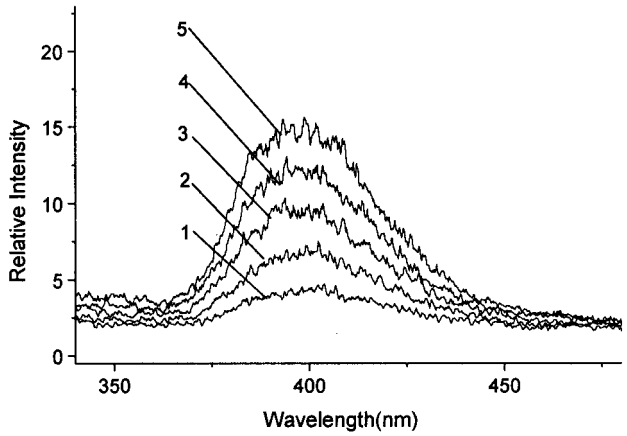


Figure 8. Fluorescence quenching of PMMA−C_{60}−Br by fumaronitrile in dichloromethane, $\lambda_{ex} = 248$ nm. From top to bottom, concentration of fumaronitrile (mol/L): 0, 0.0050, 0.0100, 0.0300, 0.0500.

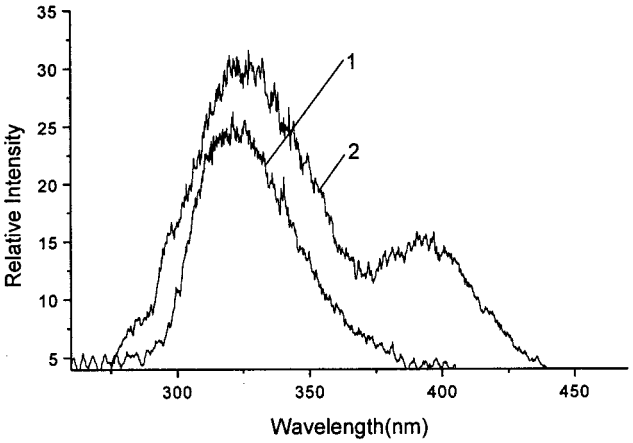


Figure 9. Fluorescence spectra of PSt−Br (1) ($M_n = 2.52 \times 10^3$) and PSt−C_{60}−Br (2) ($M_n = 3.32 \times 10^3$) in dichloromethane at room temperature. $\lambda_{ex} = 248$ nm.

Accordingly, whether C_{60} can maintain its proper electronic properties after it was covalently bonded to the polymers is of our concern. That the fluorescence of PMMA−C_{60}−Br can be quenched by either strong electron donors such as triethylamine or strong electron acceptors such as fumaronitrile is shown in Figures 7 and 8, indicating that C_{60} still keeps its strong electron-accepting and strong electron-donating property after it was modified by macromolecules.

Figure 9-(2) shows the fluorescence spectrum of PSt−C_{60}−Br in dichloromethane at room temperature. It can be seen that there are two peaks at 314 and 395 nm. It is known that styrene homopolymers displays fluorescence caused by its benzene ring. The peak at 314 nm should be ascribed to the benzene rings of the PSt chains which was clarified by the recorded fluorescence spectrum of styrene homopolymer as shown in Figure 9-(1). The energy absorbed by benzene rings of PSt may transfer to the $C_{60}-CH_2-CH-$ moiety, and the peak at 395 nm may be the excimers formed by the C_{60} and the PSt segments. This implies that PSt chains enhance the fluorescence of C_{60} moieties. That the fluorescence peak of PSt−C_{60}−Br and PMMA−C_{60}−Br at 395 nm can be quenched by triethylamine and fumaronitrile also proved that this peak was contributed by $C_{60}-CH_2-CH-$. The invariance of the emission wavelength firmly supported this opinion.

Webber et al.[4] reported on the preparation of copolymer of C_{60} and styrene by ordinary free-radical polymerization initiated by using AIBN. The copolymer was denoted as P(C_{60}−St)$_n$, and its fluorescence behavior was explored. The profile of fluorescence emission spectra of PSt−C_{60}−Br recorded by us is different from the P(C_{60}−St)$_n$. The excitation wavelengths of P(C_{60}−St)$_n$ and PSt−C_{60}−Br are 577 and 248 nm, and the fluorescence maxima are observed at 620 and 395 nm, respectively. This can be explained by the difference of the structure of P(C_{60}−St)$_n$ and PSt−C_{60}−Br. For PSt−C_{60}−Br only one C_{60} was terminated at the end of each chain as designed, meaning the PSt segment occupied almost the whole chain as showed in Scheme 1. As regards P(C_{60}−St)$_n$, there are much more "antenna" effects of PSt chains that absorb energy and transfer to the $C_{60}-CH_2-CH-$ moiety as illustrated in Figure 10. Compared to PSt−C_{60}−Br, P(C_{60}−St)$_n$ requires less radiation energy than does PSt−C_{60}−Br. This is also explained by the difference of excitation wavelength of PSt−C_{60}−Br and P(C_{60}−St)$_n$, whose excitation wavelengths are 248 and 577 nm, respectively, meaning that the fluorescence emission of the latter need lower energy than does PSt−C_{60}−Br.

Mechanism. The mechanism of the preparation of the C_{60}-end-bonded polymers is deduced tentatively as shown in the following. In reaction 1, a catalytic amount of the CuBr/bipy coordination complex reversibly abstracts the bromine atoms from the polymer chain ends switching them from a dormant state to an active state and generates a small concentration of polymer-based radicals and the corresponding $CuBr_2$/bipy complex. Since the CuBr/bipy complex is only slightly soluble in chlorobenzene, reaction 1 is a heterogeneous process.

Thermodynamically, the equilibrium must lie toward the side of dormant chain end to maintain a sufficiently low concentration of PSt*, so the bimolecular termination between radicals was suppressed. Kinetically, reaction 1 is a fast reaction, thus keeping the concentration of radicals in a steady state. Reaction 2 is the addition of radicals to C_{60}, and PSt−C_{60}* was thus produced. In reaction 3, PSt−C_{60}* abstracts a bromine atom from the $CuBr_2$/bipy complex, yielding the final product PSt−C_{60}−Br. Because of an excess of C_{60} relative to PSt−Br in the feed and the potential barrier of the PSt moieties, the monoadduct was the dominant product in this system.

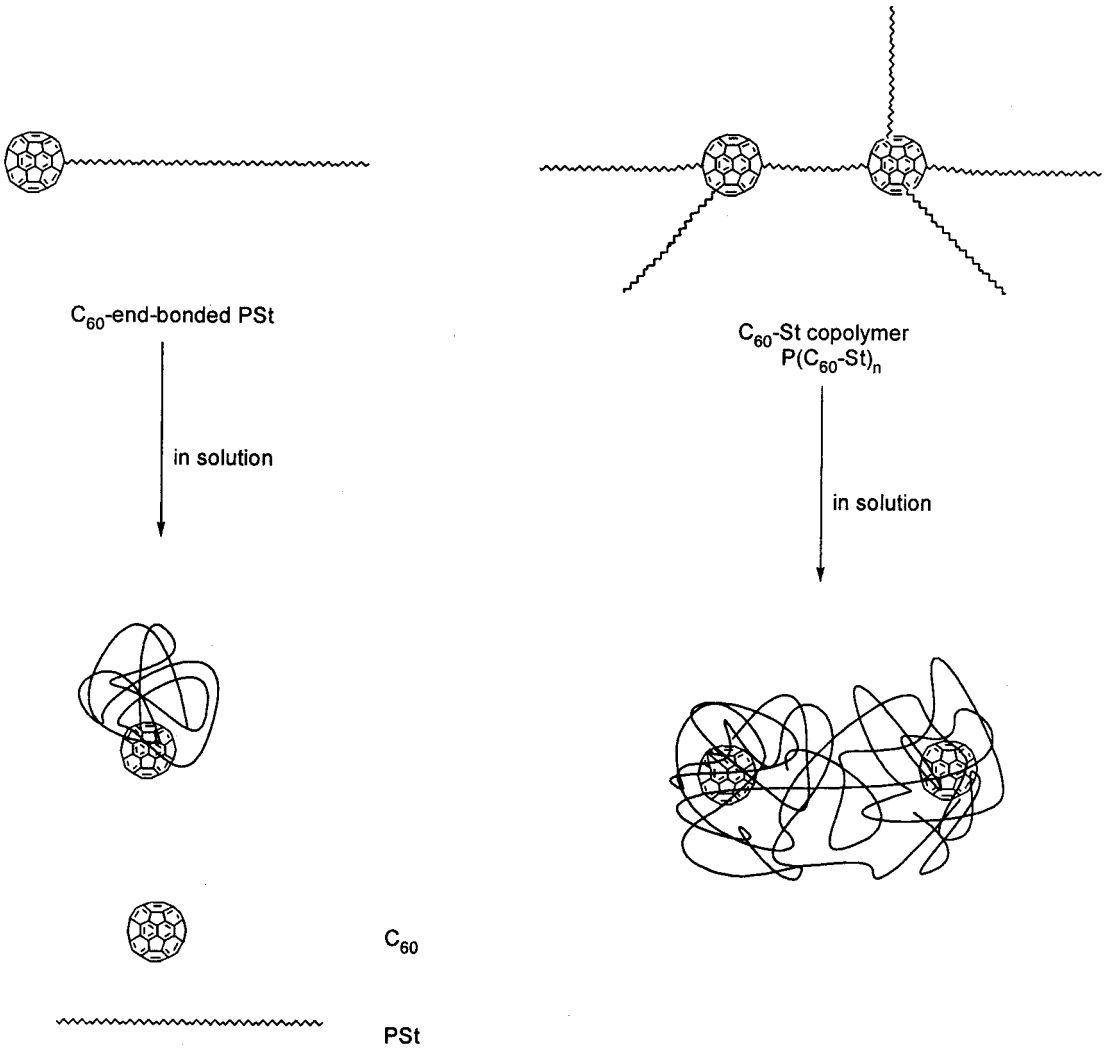
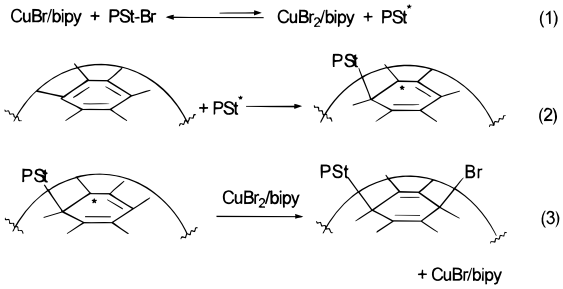
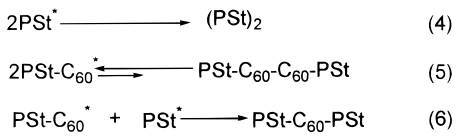


Figure 10. Schematic illustration of the "antenna effect" of PSt chains for C_{60}.



At the same time, the terminations between following radicals were unavoidable:



Reaction can occur competitively to reaction 2, yet reaction 4 is much less important, because [PSt*] is small enough and $[C_{60}] \gg [PSt^*]$. Reaction 5 is a process of dimerization, which is reversible. Because of the steric effect, the C_{60} dimer is unstable at high temperature,[15] making the equilibrium more incline toward the radical side. In contrast to reaction 6, which happened between polymer radicals, reaction 3 proceeds far more easily for the reason that it takes place between polymer radicals and the ambient $CuBr_2$/bipy complex, so reaction 3 is the main termination process.

Conclusion

Bromo-terminated polystyrene (PSt−Br) and poly(methyl methacrylate) (PMMA−Br) with designed molecular weights and narrow molecular weight distributions, prepared by atom transfer radical polymerization (ATRP), were heated with C_{60} in chlorobenzene in the presence of CuBr and 2,2′-bipyridine complex to yield C_{60}-end-bonded PSt (PSt−C_{60}−Br) and PMMA (PMMA−C_{60}−Br). GPC measurements equipped with UV and RI detectors indicate that C_{60} had been covalently bonded to the polymers, and most of the C_{60}-end-bonded polymers were monosubstituted. The main reasons for the selectively production of monosubstituted C_{60} are contributed to the excess of C_{60} in feed relative to PSt−Br or PMMA−Br, the steric hindrance of PSt−Br or PMMA−Br, and the low concentration of polymer-based radicals in the system. Furthermore, 2-aminoacetonitrile (AAN) was used as an IR label to react with PSt−C_{60}−Br; the products thus obtained show a characteristic absorption of the CN group at 2369 cm^{-1}, avoiding the interfering with those of benzene rings of PSt and C_{60}. This result confirmed that C_{60} had been covalently bonded to PSt, and this method can be extendedly used to label other C_{60} derivatives. The fluorescence of

PMMA−C_{60}−Br and PSt−C_{60}−Br can be quenched by triethylamine or fumaronitrile, indicating that C_{60} still maintains its strong electron-accepting and strong electron-donating property after it was modified by macromolecules.

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