

# Synthesis of Telechelic C<sub>60</sub> End-Capped Polymers Under Microwave Irradiation

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**ABSTRACT:** Bromo-Double-Terminated polystyrene (Br-PSt-Br) and poly(methyl methacrylate) (Br-PMMA-Br) with pre-designed molecular weight and narrow polydispersity were prepared by atom transfer radical polymerization (ATRP) using the initiating system *aa'*-dibromo-*p*-xylylene(DBX) / CuBr/2,2'-bipyridine(bipy). The precursor bromo-terminated polymers were subsequently functionalized with fullerene C<sub>60</sub> using CuBr/bipy as the catalyst system under microwave irradiation (MI). The telechelic C<sub>60</sub> end-capped products were characterized by gel permeation chromatography (GPC), UV-vis, FT-IR, TGA, DSC, <sup>1</sup>H NMR, and

<sup>13</sup>C NMR. The results showed that microwave irradiation could significantly increase the rate of fullerene reaction, and the physical properties and structure of the C<sub>60</sub> end-capped polymers are not modified by the use of the microwave. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 828–834, 2006

**Key words:** atom transfer radical polymerization (ATRP); fullerene; functionalization of polymer; microwave irradiation; telechelics

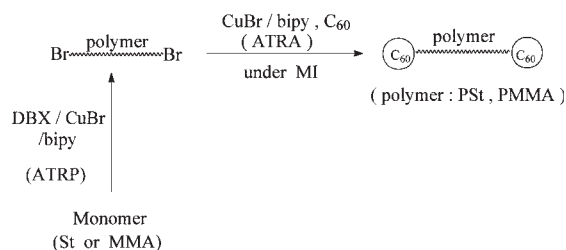
## INTRODUCTION

Fullerene has attracted much attention due to its unique electronic conducting, magnetic, and photo-physical properties. However, the ability to fabricate devices based on fullerene has been limited due to its poor solubility and processibility. The combination of the unique molecular characteristics of fullerene with good processibility of polymers through chemical syntheses of fullerene-containing polymers would open up the possibility for making advanced polymeric materials with peculiar physicochemical properties and good processibility.

Conventional radical polymerization is one of the simple and useful methods for introduction of fullerene to polymers.<sup>1–5</sup> Many attempts have been made for the preparation of suitably designed fullerene chemically modified polymers with controlled molecular weights and narrow molecular weight distributions.<sup>6</sup> Recently, well-defined polymers with narrow polydispersities and complex architectures can be achieved by a newly developed method of living/controlled radical polymerization, atom transfer radical polymerization (ATRP).<sup>7</sup> With the dynamic equilibrium of the halogen atom transfer between dormant polymer chains and ligands, the polymerization of styrene and MMA could be well

controlled by the use of the ATRP method. 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 conditions that living anionic polymerization needs. This encourages the introduction of C<sub>60</sub> to polymers via controlled radical polymerization to obtain C<sub>60</sub>-involved polymers with designed molecular weight and narrow molecular weight distribution. Zhou et al.<sup>8,9</sup> prepared well-defined bromo-terminated polystyrene and poly(methyl methacrylate) by ATRP in the presence of CuBr/bipy. These bromo-terminated polymers were allowed to react with C<sub>60</sub> under ATRP conditions (CuBr/bipy) to yield C<sub>60</sub> end-bonded PSt and PMMA with controlled molecular weight and narrow molecular weight distributions. Meanwhile, Hadziioannou et al.<sup>10</sup> described their results on the C<sub>60</sub> functionalization of styrene-type copolymers via an atom-transfer radical addition (ATRA) reaction using a similar catalyst system, Cu/CuBr/bipy. Very recently, Mathis et al.<sup>11</sup> reported that Br-terminated polystyrenes can be converted to macroradicals using the CuBr/bipy catalyst system, and the radical addition of the polystyrene macroradicals to C<sub>60</sub> favored the grafting of an even number of PS chains onto the C<sub>60</sub> core (100–110°C, 45–160 h). All the products mentioned above were prepared under a conventional heating process, which usually required high temperature (110–130°C) and long reaction time (at least 6 h).

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Scheme 1

It is known that microwave irradiation (MI) is a nonconventional energy source that can significantly accelerate many chemical reactions. As to the reason of acceleration, some authors attribute it to the "specific microwave effect"<sup>12,13</sup>; others attribute it to the "dielectric heating effect."<sup>14</sup> Many results<sup>15–17</sup> have shown that, in comparison with conventional heating processes, reactions under MI have the advantages of higher reaction rate and greater yield within a shorter period of time, so MI is an effective, less energy exhaustive, and no environmental pollution method. Therefore, the combination of microwave heating technology and ATRP seems a logical consequence of both the good control/"livingness" offered by ATRP and the increased rate and effectiveness offered by MI. Cheng et al. and Chen et al.<sup>18,19</sup> reported the homogeneous polymerization of methyl methacrylate through ATRP reaction under MI. The results showed that MI not only increased the polymerization rate, but also narrowed the polydispersity index of polymers.

Encouraged by the above results, as a part of our research to prepare well-defined fullerene chemically modified polymers, in this work, we report the synthesis of telechelic C<sub>60</sub> end-capped polymers by using ATRA reaction conditions under microwave irradiation. The bromo-double-terminated polymers were synthesized through ATRP using the DBX/CuBr/bipy initiating system<sup>20</sup> in bulk. The precursor bromo-terminated polymers were subsequently functionalized with C<sub>60</sub> using CuBr/bipy as the catalyst system under microwave irradiation. The synthetic route is shown in Scheme 1.

## EXPERIMENTAL

### Reagents and instrumentation

C<sub>60</sub> (99.9%) was obtained from Yin-Han Fullerene High-Tech. Co. Ltd., Wuhan University, China. Styrene and methyl methacrylate were dried over CaH<sub>2</sub> and distilled under vacuum. DBX (Aldrich, 97%) was recrystallized from CHCl<sub>3</sub>, and dried at room temperature under vacuum. CuBr was washed subsequently by acetic acid and ethanol and then dried under vacuum. Bipy was used as received. Toluene and THF were dried, deoxygenated, and distilled from Na/

benzophenone ketyl before use. *N,N*-dimethylformamide (DMF) was distilled from P<sub>2</sub>O<sub>5</sub> three times before use. All other reagents were used as received without further purification.

All experiments for polymerization reactions were conducted under purified nitrogen by use of standard Schlenk tubes. The reactions under microwave irradiation for preparing telechelic C<sub>60</sub> end-capped polymers were performed in a self-improved domestic microwave oven, a WP750L23–6 Galanz with irradiation frequency of 2.45GHz. The microwave irradiation power was adjustable to constant at 300W.

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 molecular weight of the polymers was analyzed by an HP series 1100 gel permeation chromatograph (GPC) equipped with Zorbax columns and refractive index/ultraviolet dual-mode detectors. The elution rate of THF was 1mL/min, and standard PSt was used for calibration. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> with a Bruker-AM 500 apparatus. Thermogravimetric measurements were made with a Perkin-Elmer Pyris 1 DTA-TGA instrument under nitrogen at a heating rate of 10°C/min. Glass-transition temperature was measured on a Perkin-Elmer Pyris 1 differential scanning calorimeter at a heating rate of 10°C/min.

### Synthesis of homopolymers of St and MMA

The synthesis of Br-PSt-Br and Br-PMMA-Br were carried out via ATRP conditions under a conventional heating process. A dry glass Schlenk tube was charged with DBX/CuBr/bipy (mole ratio, 1 : 2 : 6), and then was sealed with a rubber septum. After the mixture was degassed three times, the monomer (St or MMA) was added using a flamed syringe. The polymerization was carried out in an oil bath at the desired temperature (for styrene, 110°C; for MMA, 90°C) for a period of time. The polymerizations were stopped by cooling the tube in ice water. Afterwards, the reaction mixture was diluted with THF, and the crude polymer was obtained by precipitation from methanol. The solid product was dissolved in THF, and the solution was filtered through a neutral alumina column to remove the catalyst. The polymer was recovered by precipitation from a large excess of methanol and then dried under vacuum.

### Synthesis of telechelic C<sub>60</sub> end-capped polymer

*Microwave irradiation.* In a typical run, C<sub>60</sub>, CuBr, bipy, and bromo-terminated polymer were introduced into a two-neck round bottom flask (250mL). The feed molar ratio was bromo-terminated polymer : CuBr : bipy : C<sub>60</sub> = 1 : 2 : 6 : 4. After the mixture was deoxy-

**TABLE I**  
**Results of Bromo-Double-Terminated Polymers Prepared by ATRP**

Polymer	$M_n (\times 10^4)$	$M_w/M_n$	$T_g$ ( $^{\circ}\text{C}$ )
Br-PSt-Br	0.955	1.243	95.0
Br-PMMA-Br	2.140	1.387	122.7

generated three times, 40mL of toluene and 10mL of DMF were added via a flamed syringe. The round bottom flask with the mixture was then placed into the self-improved microwave oven equipped with reflux apparatus. The reaction was carried out under nitrogen with a preset microwave power (300W) and then stopped at a desired time. After being cooled to room temperature, the reaction mixture was filtered to remove the initiator residues and the solvent evaporated under vacuum. The solid residue was taken up in THF and filtered again. The THF filtrate was concentrated under reduced pressure and precipitated from methanol. The crude product was redissolved in THF, filtered, and reprecipitated with methanol. The purified product was dried under vacuum as brown powder.

*Conventional heating process.*  $\text{C}_{60}$ , CuBr, bipy, and bromo-terminated polymer were introduced into another two-neck flask with the same feed molar ratio as that for MI. After the mixture was deoxygenated three times, the mixed solvent (40mL toluene and 10mL DMF) was added. The reaction was then carried out in an oil bath under nitrogen at the desired temperature (for styrene,  $110^{\circ}\text{C}$ ; for MMA,  $90^{\circ}\text{C}$ ) for 8 h. The other procedures are the same as those used for microwave irradiation.

## RESULTS AND DISCUSSION

### Synthesis of Br-PSt-Br and Br-PMMA-Br

ATRP is a useful method for most vinyl monomers to prepare well-defined polymers under ordinary radical polymerization conditions. Gao et al.<sup>20</sup> prepared well-defined telechelic bromo-double-terminated polystyrene in bulk under ATRP conditions using the initiating system DBX/CuBr/bipy. Here, we prepare the well-defined bromo-terminated telechelic PMMA (or PSt) via ATRP by using a DBX/CuBr/bipy initiating system based on the procedure described by Gao. It can be seen from Table I that the molecular weights and polydispersities of bromo-terminated PMMA and PSt can be well controlled by the initiating system for ATRP.

### Synthesis of telechelic $\text{C}_{60}$ end-capped polymer under MI

Since the atom transfer radical addition (ATRA) reaction of active halogeno-terminated polymers with

fullerene  $\text{C}_{60}$  required high temperature and long reaction time,<sup>9–11</sup> in this work, we report for the first time the successful synthesis of telechelic  $\text{C}_{60}$  end-capped polymers by ATRA reactions of difunctional bromo-terminated polymers with  $\text{C}_{60}$  using a CuBr/bipy catalyst system under microwave irradiation. Application of microwave greatly enhanced the rate of addition reactions and the reactions are easily performed. The optimal reaction conditions were determined as follows.

*Mole ratios of  $\text{C}_{60}$ /bromo-terminated polymer.* It has been demonstrated that the electronic properties of  $\text{C}_{60}$  would be perturbed if its conjugated structure was destroyed.<sup>21</sup> So it is important to prepare mono-substituted  $\text{C}_{60}$ -bonded polymer, which can increase solubility while retaining the intriguing properties of  $\text{C}_{60}$  to the greatest extent. To optimize the synthesis of monosubstituted  $\text{C}_{60}$ -bonded polymer from difunctional polymers with active bromine end group structures (Br-PSt-Br and Br-PMMA-Br) by atom transfer radical addition (ATRA), an excess of  $\text{C}_{60}$  was used. In all reactions, a mole ratio 4 : 1 of  $\text{C}_{60}$ /bromo-terminated polymer was employed. Excess of  $\text{C}_{60}$  could be removed by dissolving the products in THF since the solubility of  $\text{C}_{60}$  in THF is negligible.

*Effect of solvent system.* For MI ATRA reactions, the solvent effects are of particular importance. If toluene, a nonpolar solvent, was used as the solvent for preparing  $\text{C}_{60}$  end-capped polymers under MI, the reaction did not occur and the purple color of  $\text{C}_{60}$  in toluene remained unchanged after 20 min of microwave irradiation. The main reason may be that, as a nonpolar solvent, toluene is transparent to microwaves and only weakly absorbs microwaves, and the temperature of the reaction mixture is too low for the reaction to occur. For this reason, some polar aprotic solvent was selected to add into the reaction mixture. When 10mL of DMF and 40mL of toluene were used as the mixed solvent, the solution began to reflux after only 1 min of irradiation. As the reaction proceeded, the characteristic purple color of  $\text{C}_{60}$  in toluene gradually turned to dark brown, indicating the occurrence of the reaction. Another solvent, 1,2-dichlorobenzene, was also selected as the solvent for the reaction. When a mixed solvent of 10mL 1,2-dichlorobenzene and 40mL toluene was used as the solvent for the reaction, the solution also boiled after a few minutes of irradiation. But the color of the solution changed only a little after 20 min of microwave irradiation, so the  $\text{C}_{60}$  content of the product is lower than that prepared in the mixed solvent of DMF and toluene with the same irradiation time. Therefore, in this work, the mixed solvent of DMF and toluene was used as the reaction solvent to prepare telechelic  $\text{C}_{60}$  end-capped polymers.

*Irradiation time.* Since the MI did prove to work for the ATRA reaction, the radiation-assisted fullerenation

TABLE II  
Results of the Telechelic C<sub>60</sub> End-Capped Products

Product	Reaction time	<i>Mn</i> (× 10 <sup>4</sup> )	<i>Mw/Mn</i>	C <sub>60</sub> Content (wt %)	T <sub>g</sub> (°C)
C <sub>60</sub> -PSt-C <sub>60</sub> (MI)	20 min	1.129	1.150	10.03 <sup>a</sup> 10.25 <sup>b</sup> (12.75)	97.7
C <sub>60</sub> -PMMA-C <sub>60</sub> (MI)	15 min	2.511	1.532	6.35 <sup>a</sup> 5.51 <sup>b</sup> (5.73)	124.4
C <sub>60</sub> -PSt-C <sub>60</sub> (CH)	8h	1.195	1.311	11.55 <sup>a</sup> 12.41 <sup>b</sup> (12.05)	98.0
C <sub>60</sub> -PMMA-C <sub>60</sub> (CH)	8h	2.457	1.502	4.88 <sup>a</sup> 5.41 <sup>b</sup> (5.86)	123.9

<sup>a</sup> Calculated on the basis of the UV absorbance at 330 nm.

<sup>b</sup> Measured by TGA on the parent polymers and the C<sub>60</sub> end-capped polymers; the data in parentheses are the theoretical value based on Mn and telechelic C<sub>60</sub>-monoadduct structure.

behavior was further investigated by changing the irradiation time from 5 to 35 min. The solution of the reaction mixture remained purple color for 5 min of irradiation. The color of the solution changed gradually by increasing the time of irradiation. If the reaction time is long enough, the reaction solution turned to dark brown at last (15–20 min). Too long a reaction time will result in the decomposition of the polymer, especially for PMMA. Thus, the irradiation time shown in Table II was applied to the reactions as the optimum reaction time.

#### Characterization of telechelic C<sub>60</sub> end-capped polymers prepared by microwave irradiation

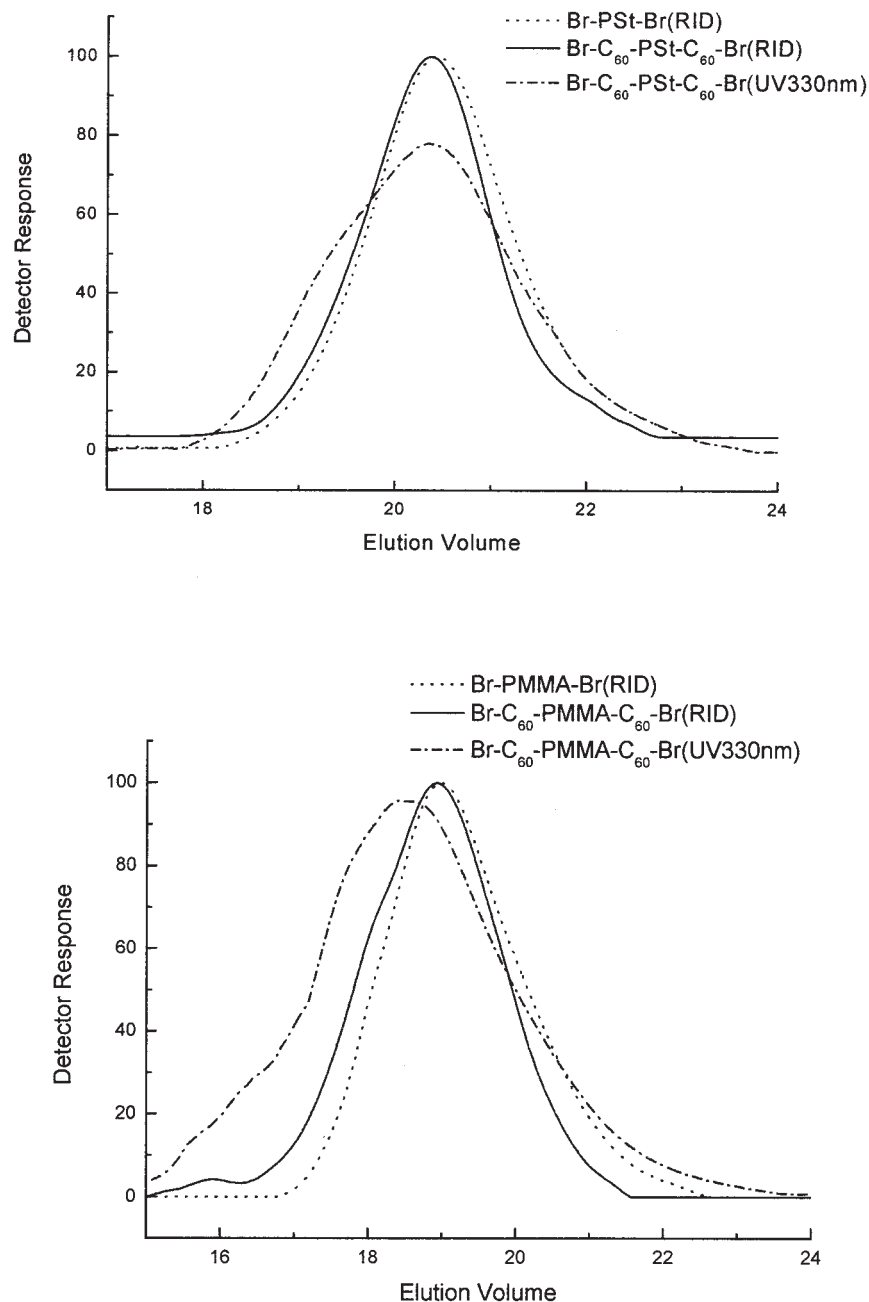
Tables I and II summarize the molecular weights and molecular weight distributions for bromo-terminated polymers and their corresponding C<sub>60</sub>-bonded products. It can be seen that the molecular weights of C<sub>60</sub>-functionalized polymers rose slightly and the molecular weight distributions of polymers remained almost unchanged after reaction with C<sub>60</sub>. To compare the MI ATRA reaction with the conventional thermal heating process, the fullerenation reactions were also carried out in an oil bath for the same time interval (15–20 min) as that for MI; however, the reaction did not proceed at all. By the use of regular heating, the reactions were complete after at least 8h of heating. Therefore, compared with the conventional heating process (listed in Table II), microwave irradiation can greatly increase the reaction rate, and maintains a low polydispersity.

The molecular weights of C<sub>60</sub> end-capped polymers were measured by GPC with both RI and UV (330nm) dual detectors, and the bromo-terminated polymer precursors could not be detected by the UV(330nm) detector. Figure 1 shows the GPC profiles of C<sub>60</sub>-bonded products and their bromo-terminated precursor polymers. The GPC profiles of C<sub>60</sub> end-capped polystyrene detected by both UV and RI dual detectors were almost the same and very similar to that of the Br-PSt-Br precursor obtained by the RI detector. The GPC results strongly confirmed covalent bonding between C<sub>60</sub> and the polymer. In the GPC profile of Br-C<sub>60</sub>-PMMA-C<sub>60</sub>-Br obtained by the UV-330 detec-

tor, there was a shoulder peak in the high molecular weight region, indicating that some PMMA molecules may decompose under the irradiation of microwaves. The decomposition of some PMMA molecules may result in the multiaddition or possibly some side reactions, forming C<sub>60</sub> containing high molecular weight species. These C<sub>60</sub> containing multiadducts might be responsible for the left side shoulder peak of the GPC curve obtained by the UV-330nm detector. However, according to the RI detected curve, the shoulder peak is a minor fraction of the mass. Comparing the molecular weights of bromo-terminated polymers and their corresponding C<sub>60</sub>-bonded products in Tables I and II, it can be concluded that the main products were C<sub>60</sub> monoadducts, in which each polymer chain was end-bonded with two C<sub>60</sub> cores. The telechelic C<sub>60</sub> end-capped polymers are soluble not only in fullerene solvents, such as benzene and toluene, but also in fullerene nonsolvents, such as THF, giving a dark brown solution. The solubility of the products further suggests that the possible crosslinking reaction in the fullerenation process may be negligible.

Figure 2 shows the UV-vis spectra of Br-PSt-Br and Br-C<sub>60</sub>-PSt-C<sub>60</sub>-Br in THF. The Br-PSt-Br spectra are essentially transparent at wavelengths longer than 280nm, while the absorption bands of Br-C<sub>60</sub>-PSt-C<sub>60</sub>-Br are somewhat like those of pure C<sub>60</sub>; the characteristic absorption peaks of C<sub>60</sub> at 272nm and 336nm remain, and at 430nm appears a broad band that indicates that Br-C<sub>60</sub>-PSt-C<sub>60</sub>-Br is a 1,4-substituted derivative.<sup>9</sup> Figure 3 shows the UV-vis spectra of Br-PMMA-Br and Br-C<sub>60</sub>-PMMA-C<sub>60</sub>-Br in THF. The absorption bands of Br-C<sub>60</sub>-PMMA-C<sub>60</sub>-Br are similar to those of pure C<sub>60</sub>; there was a sharp band peak at nearly 340nm. The absence of the weak broad peak at 430nm indicated the possible 1,2-substituted structure of PMMA-C<sub>60</sub>.<sup>9</sup> Since bromo-terminated polymers show no absorption at 330nm, the C<sub>60</sub> contents in the C<sub>60</sub> end-capped polymers can be calculated based on the absorbance peak at 330nm (Table II).

Although the existence of C<sub>60</sub> increases the thermal stability of C<sub>60</sub> end-capped polymers, the weight percent of C<sub>60</sub> incorporated into the polymers could still be determined by TGA because PSt and PMMA de-

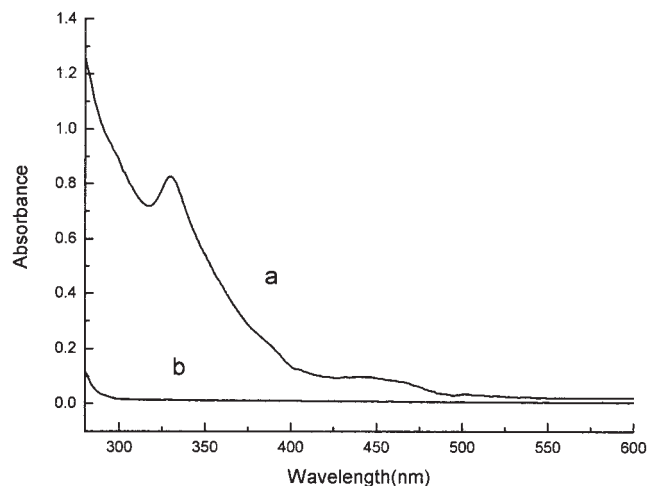


**Figure 1** GPC profiles of  $C_{60}$ -bonded polymer products and their bromo-terminated parent polymers, obtained by refractive index and UV dual detectors; the working wavelength for the UV detector was set at 330 nm.

compose completely at 450 and 405°C, respectively. The residue left could be considered as  $C_{60}$ . It can be seen in Table II that the content of  $C_{60}$  determined by TGA was close to the result of UV absorption. The content of  $C_{60}$  determined by both methods was roughly close to the theoretical value, further showing that each polymer was end-bonded with two  $C_{60}$  cores.

Unlike the UV-vis absorption spectra, the FT-IR spectra of the fullerene-bonded polymers show less useful information. Because of the relatively low  $C_{60}$  content and the overwhelming contributions of the

polymer chain in the polymer structure, the observed IR spectra shown in Figure 4 for  $C_{60}$ -bonded polymer products and their bromo-terminated parent polymers were basically similar; only a very weak band at about  $528\text{cm}^{-1}$  can be discovered, which was interpreted as being associated with the characteristic infrared absorption arising from functionalized  $C_{60}$  cages. The  $^1\text{H}$  NMR spectra results of the  $C_{60}$  end-capped products obtained in deuterated chloroform are not significantly different from the spectra of the parent bromo-ended polymers. The  $^{13}\text{C}$  NMR spectra of the products is more informative. In addition to signals due to

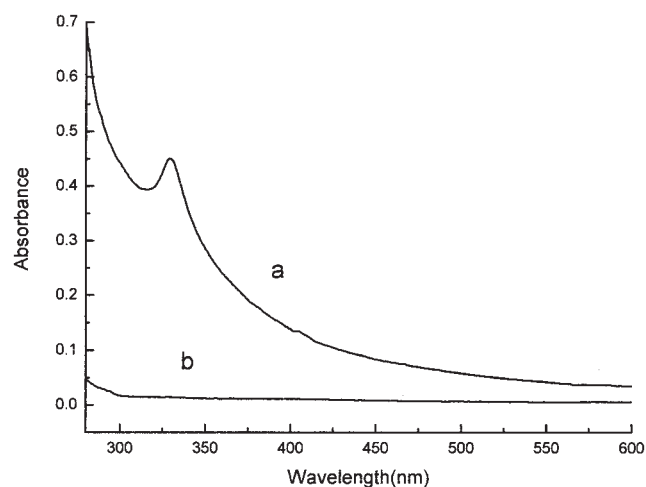


**Figure 2** UV-vis spectra of (a) Br-C<sub>60</sub>-PSt-C<sub>60</sub>-Br and (b) Br-PSt-Br in THF.

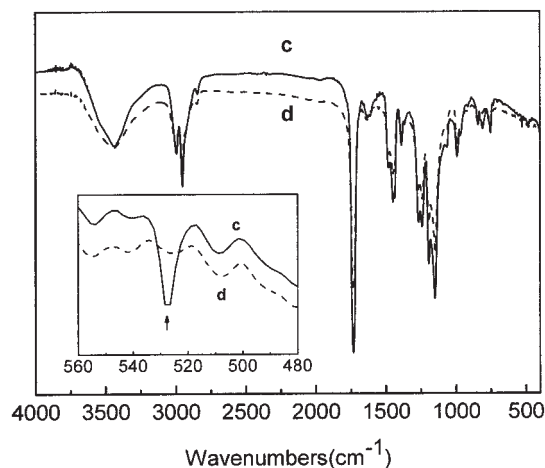
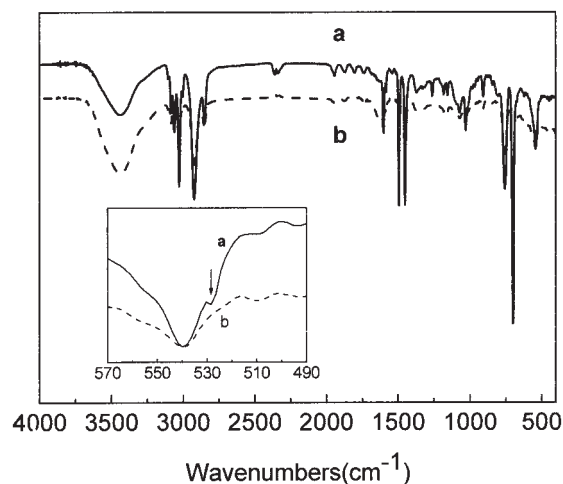
PMMA or PSt, there are some new weak peaks that located at the so-called fullerene region (128–160 ppm) and can be assigned to end-capped C<sub>60</sub> cages.

DSC measurements of glass transition temperatures ( $T_g$ ) of the polymers reported in Tables I and II demonstrate that all the samples had a single phase with distinct  $T_g$  values. The lower C<sub>60</sub> content has only a little effect on  $T_g$ , but higher C<sub>60</sub> content makes  $T_g$  increase significantly. DSC measurements show that the incorporation of C<sub>60</sub> would restrict the movement of polymer chain segments, thus increasing the  $T_g$  of the polymer. These results also demonstrated that C<sub>60</sub> is chemically bonded into the polymer chains.

The results of GPC, TGA, UV-vis, FT-IR, NMR, and DSC for telechelic C<sub>60</sub> end-capped polymers prepared under microwave irradiation are similar to the results for the conventional heating process, so it can be con-



**Figure 3** UV-vis spectra of (a) Br-C<sub>60</sub>-PMMA-C<sub>60</sub>-Br and (b) Br-PMMA-Br in THF.



**Figure 4** IR spectra of (a) Br-C<sub>60</sub>-PSt-C<sub>60</sub>-Br, (b) Br-PSt-Br, (c) Br-C<sub>60</sub>-PMMA-C<sub>60</sub>-Br, and (d) Br-PMMA-Br.

cluded that the physical properties and structure of the C<sub>60</sub> end-capped polymers are not modified by the use of microwaves.

## CONCLUSIONS

Bromo-Double-Terminated polymers with pre-designed molecular weights and narrow molecular weight distributions, synthesized by atom transfer radical polymerization (ATRP) initiated by DBX, were allowed to react with excess amounts of fullerene C<sub>60</sub> in the presence of a CuBr/bipy catalyst system under microwave irradiation to yield C<sub>60</sub> end-capped polymers. The resulting polymers can be dissolved in common solvents, such as THF, toluene, trichloromethane, and so forth. The GPC measurements equipped with UV and RI detectors showed that the molecular weight of products rose a little and the molecular weight distribution of polymers remained almost unchanged after reaction with C<sub>60</sub>. From the GPC data and the fullerene weight contents determined by TGA

and UV absorption, it can be confirmed that the products were telechelic C<sub>60</sub> end-capped polymers. FT-IR and <sup>13</sup>C NMR characterization further indicated that the C<sub>60</sub> was chemically bonded to the end of the polymers. Compared with the conventional heating process, it can be concluded that microwave irradiation could significantly increase the rate of the fullerenation reaction, and the physical properties and structure of the C<sub>60</sub> end-capped polymers are not modified by the use of microwaves.

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