Synthesis of C_{60} End-Capped Polymers from Azide Functional Polystyrene via Atom Transfer Radical Polymerization

LANG LI, CHANGCHUN WANG, ZHAOHUI LONG, SHOUKUAN FU

Department of Macromolecular Science and Key Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai, 200433, People's Republic of China

Received 25 July 2000; accepted 19 September 2000

ABSTRACT: Atom transfer radical polymerization (ATRP) was performed to prepare azide end-functional polystyrene (PSt-N_3) with predesigned molecular weight and narrow polydispersity. Then C_{60} end-capped polystyrene was synthesized by reacting C_{60} with PSt-N_3. The UV-VIS, DSC, GPC characterizations indicated that C_{60} was chemically bonded to the end of polystyrene chain, and the brown powder products, which can be dissolved in THF, $CHCl_3$, DMF, and so forth, were monoadditional and diadditional according to C_{60}. © 2000 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 38: 4519–4523, 2000

Keywords: atom transfer polymerization; azide; C_{60}; end-capped polymers

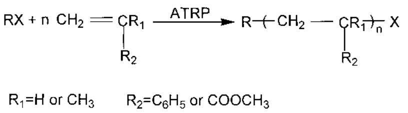
INTRODUCTION

C_{60}-containing polymers have attracted much attention due to the unique properties of the C_{60} as well as the processability of polymers. Various methods for chemical modification of the C_{60} have been reported in recent years. The polymeric C_{60} derivatives, however, were multiadditional or crosslinked according to general methods. Therefore, many attempts have been made for the preparation of C_{60} end-capped polymers to obtain a well-defined structure: Samulski et al.[1] first reported the preparation of "flagellenes" by reacting C_{60} with polystyryllithium. Our group[2] and Fukuda et al.[3] reported the addition of C_{60} onto TEMPOL (4-hydroxy-2,2,6,6-tetramethyl-piperidinyloxy)-terminated polystyrene obtaining monosubstituted and disubstituted C_{60}, respectively. Gnanou and coworkers[4] also prepared hexafullerene stars via hexaazido star-shaped polystyrene synthesized by carbocationic polymerization. It is obvious that living/controlled polymerization were involved in these methods to prepare polymer precursors and then polymeric C_{60} derivatives with well-defined structures were synthesized.

Recently, a new effective and attractive method of living/controlled radical polymerization, atom-transfer radical polymerization (ATRP), was developed rapidly.[5,6] With the dynamic equilibrium of the halogen atom transfer between dormant polymer chains and ligands, the polymerization of styrene and (meth)acrylate based monomers could be well controlled when ATRP method was used. Based on the mechanism of ATRP (Scheme 1), various end-functional polymers were prepared for different applications.[7–11] Coessens and Matyjaszewski[12] reported the transformation of the end group of polymers prepared by ATRP from bromine to azide at an amiable reaction condition. Since Hawker[13] reported a simple and versatile method to prepare C_{60}-styrene copolymers by the cycloaddition reaction of azide polystyrene with C_{60}, it is possible to prepare C_{60}

Correspondence to: C. Wang (E-mail: ccwang@online.sh.cn)

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 38, 4519–4523 (2000)



Scheme 1

end-capped polymers from azide end functional polymers synthesized by ATRP.

In this article, we give a method to prepare C_{60} end-capped polystyrene (Scheme 2). Predesigned molecular weight and narrow polydispersity bromine-ended polystyrenes were synthesized by ATRP. Then a simple organic reaction was carried to substitute the bromine end group by azide with reacting azide sodium to bromine ended polystyrene. The azide-ended polystyrene was applied to react with C_{60} to prepare well-defined C_{60} end-capped polystyrene.

EXPERIMENTAL

Materials

St was vacuum distilled and stored at −15 °C. CuBr from Shanghai Zhenxin Chemical Reagent Factory was purified according to the published procedure.[14] *N,N′,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA, 98%) and methyl 2-bromopropionate (2-MBP, 97%) were obtained from Fluka and used without further purification.C_{60} (99.9%)from Wuhan University, China, was used as received. Sodium azide (NaN_3) was recrystallized from ethanol. All other reagents were used as received.

Synthesis of Bromine-Terminated Polystyrene (PSt-Br) by ATRP

The polymerization was carried out in the bulk of St. A glass tube was charged with St 1 mL (8.70 mmol), CuBr 25.0 mg (0.174 mmol), PMDETA 36.4 μL (0.174 mmol) and 2-MBP 19.4 μL (0.174 mmol). The tube was sealed with a rubber septum and three freeze–vacuum–thaw cycles were performed. Then the tube was placed in an oil bath 110 °C.After a definite time, the tube was removed from the oil bath and the reaction mixture diluted with THF. The solution was filtered through a neutral alumina column to remove the catalyst. Then it was precipitated in methanol and dried under vacuum.

Synthesis of Azide End-Functional Polystyrene (Pst-N_3)

A 1.5-g (0.197 mmol) sample of PSt-Br was weighted into a 25-mL round-bottom flask, 25.7 mg (0.394 mmol) NaN_3 was dissolved in 10 mL DMF and then added into the flask. The solution was stirred and allowed to react at 25 °C for 8 h. The product was precipitated in methanol and the white precipitate was washed with deionize water three times to remove the unreacted NaN_3, then it was dried under vacuum at 25 °C.

Synthesis of C_{60} End-Capped Polystyrene

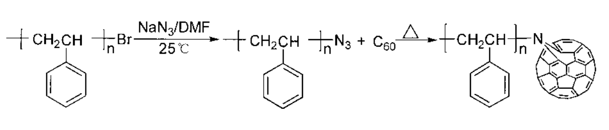
A round-bottom flask equipped with a spiral condenser was charged with PSt-N_3 1.00 g (0.131 mmol), C_{60} 113.2 mg (0.157 mmol) and then chlorobenzene was added. The flask was immersed in an oil bath at 130 °C.After refluxing for 48 h, the reaction mixture was evaporated and was purified by reprecipitation with a toluene (solvent)/*n*-hexane (nonsolvent) system. The final product was brown powder and was dried under vacuum.

CHARACTERIZATION

UV-VIS spectra were taken on a HITACHI U-3000 Spectrophotometer. GPC measurements were carried out using a HP series 1100 Chromatograph equipped with Zorbax columns and RI/UV dual-mode detectors. The elution rate of THF was 1 mL/min and standard PSt was used for calibration. A Bruker MSL300 NMR Spectrometer was used for ^{1}H NMR analysis with $CDCl_3$ as the solvent. FTIR spectra were obtained using a Magne 550 spectrophotometer. Glass-transition temperatures were measured on a Netzsch DSC 204 differential scanning calorimeter at a heating rate 10 °C/min.

RESULTS AND DISCUSSION

The typical catalyst system used in ATRP was Rbr/CuBr/2,2-bipyridine. When the bipy system



Scheme 2

Table I. Results of the PSt by ATRP and the C_{60} End-Capped PSt

Precursor[a]	M_n (M_w/M_n)	Product	M_n (M_w/M_n)	M_p[b]	C_{60} Content[c] (wt %)
PSt-Br-1	2,400 (1.14)	PSt-C_{60}-1	2,800 (1.42)	2,100/5,800	2.34
PSt-Br-2	7,400 (1.13)	PSt-C_{60}-2	10,300 (1.25)	8,900/16,600	2.20
PSt-Br-3	12,900 (1.11)	PSt-C_{60}-3	16,400 (1.21)	14,500/28,600	1.24
PSt-Br-4	24,000 (1.11)	PSt-C_{60}-4	26,000 (1.36)	25,100/56,800	0.38

[a] The bulk ATRP of St was performed at 110 °C with 2-MBP/CuBr/PMDETA = 1/1/1.
[b] Molecular weight values at the peaks of the GPC traces.
[c] Calculated on the basis of the absorbance at 330 nm.

was performed in the bulk polymerization of St by ATRP, the living polymer can be achieved successfully with predetermined molecular weight and narrow polydispersity. The polymerization rate, however, was relatively slow. In this work, we applied PMDETA, an inexpensive simple amine, as the ligand for CuBr, instead of 2,2-bipydine, in the synthesis of PSt-Br to accelerate the polymerization.[15] Table I shows a series of PSt-Br with different molecular weights that were prepared using the catalyst system 2-MBP/CuBr/PMDETA with a constant mol ratio of 1/1/1. After 8 h polymerization, conversions of monomer St were up to 90% and quite low polydispersities (M_w/M_n = 1.1–1.2) of these PSt-Br indicate the polymerization reactions were well controlled on the simple amine ligand system for ATRP.

Bromine-terminated polystyrene (PSt-Br) was reacted with excessive sodium azide in DMF at 25 °C to prepare the azide-terminated polystyrene (PSt-N3). When the complete substitution of the bromine end group by the azide was observed, the product was precipitated in methanol and washed with a large quantity of deionize water to remove the unreacted NaN_3. The ^1H NMR spectra show the methine proton of the —C***H*** (Ph)—Br (σ = 4.4ppm) had completely disappeared and that of the —C***H***(Ph)—N_3 (σ = 3.9 ppm) appeared clearly. The strong band at 2094 cm^{-1} for the azide group give another evidence of the successively replace of the N_3 at the end of the polystyrene. The white powder of PSt-N_3 products was dried under vacuum at 25 °C to avoid the crosslinking reaction.

Wudl[16] first reported the addition of azide group to C_{60}, which provided an excellent method for the preparation of C_{60} derivatives. Hawker applied this cycloaddition reaction to synthesize *on-chain* polymeric C_{60} derivatives. Here we perform the method for preparation C_{60} end-capped polystyrene with definite structure. The PSt-N_3 and C_{60} were dissolved in chlorobenzene and refluxing at 130 °C for 48 h. The final products purified with a toluene/hexane reprepitation system are brown-colored powder, and can be easily dissolved in various organic solvents such as $CHCl_3$, THF, DMF, etc. Figure 1 shows the UV-VIS spectra of PSt-C_{60} in comparison to those of PSt-Br and C_{60} in CH_2Cl_2. The PSt-Br has only one absorption at 256 nm, while the absorption peaks of C_{60} situated at 228, 257, and 330 nm.[17] Different from the PSt-Br precursor, the spectra of PSt-C_{60} are similar to that of C_{60}, which shows that the C_{60} actually reacted with PSt-N_3, and was covalent bonded into the polystyrene. The C_{60} contents in the PSt-C_{60} can be calculated based on the absorbance of the peak at 330 nm.[18] The results listed in Table I indicate that the C_{60} contents in PSt-C_{60} increase with decreasing the M_n of the PSt-Br, and it is the way we expected to control the contents of C_{60} in Pst-C_{60}.

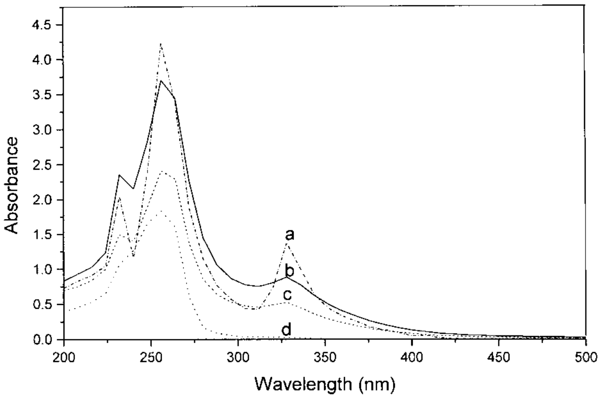


Figure 1. UV-VIS spectra of (a) C_{60} (1.4 × 10^{-5} g/mL), (b) PSt-C_{60}-2 (4.04 × 10^{-4}g/mL), (c) PSt-C_{60}-3 (4.28 × 10^{-4} g/mL), and (d) PSt-Br-2 (6.04 × 10^{-4} g/mL) in CH_2Cl_2.

Figure 2 shows the DSC curves of the PSt-C_{60} and their precursors PSt-Br. According to the curves, only on glass-transition temperature was observed in each case of PSt-C_{60} and T_g of increased from 76.9 to 83.4 °C, from 92.4 to 102.7 °C, and from 102.2 to 103.2 °C, respectively. This result can also demonstrate that C_{60} is chemically bonded into the polystyrene chain.

Gel Permeation Chromatography (GPC) measurements were carried out with IR and UV (254 and 330 nm) detector. The M_n of the PSt-C_{60} products raised slightly, compared with their PSt-Br precursors and the polydispersities are also broader (Table I). The GPC traces of PSt-Br-2 and PSt-C_{60}-2 were shown in Figure 3, respectively. The PSt-Br-2 precursor can only be detected at 254 nm, while the PSt-C_{60}-2 can be detected at 254 and 330 nm. The GPC trace of PSt-C_{60}-2 detected at 330 nm strongly confirms the covalent-banded C_{60} to the polystyrene because only the C_{60} moiety in the PSt-C_{60} can be detected at this detector wavelength. Both GPC traces of PSt-C_{60}-2 at 254 and 330 nm have two peaks (M_p = 8900 and M_p = 16,600), compared with the monopeak in the PSt-Br-2 trace at 254 nm, indicating the C_{60} end-capped polystyrene are monoadditional and diadditional products, which is constant to our earlier results and the suggestion of Goh et al.[19]

CONCLUSION

C_{60} end-capped polystyrene was successfully prepared by reaction of C_{60} with predesigned azide end-functional polystyrene prepared based on ATRP. The polymeric C_{60} derivatives can be dissolved in organic solvents, such as THF, $CHCl_3$, DMF, etc. With this method, it is expected that C_{60} can be bonded onto the terminals of a variety of polymer chains. Photoconductivity and other properties of C_{60} end-capped polystyrene are under investigating in our laboratory and the further studies such as the synthesis and characterization of water-soluble C_{60} end-capped polymers are also going on.

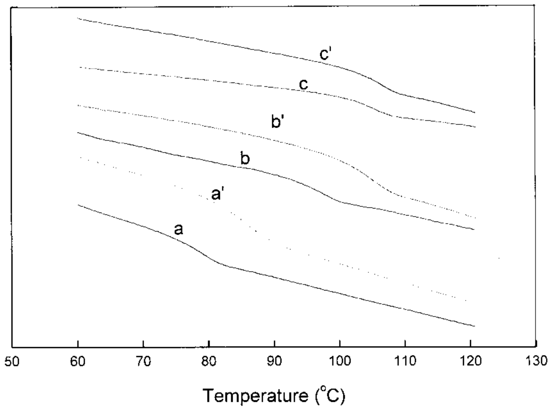


Figure 2. DSC curves of (a) PSt-Br-1, (a′) PSt-C_{60}-1, (b) PSt-Br-2, (b′) PSt-C_{60}-2, (c) PSt-Br-4, (c′) Pst-C_{60}-4.

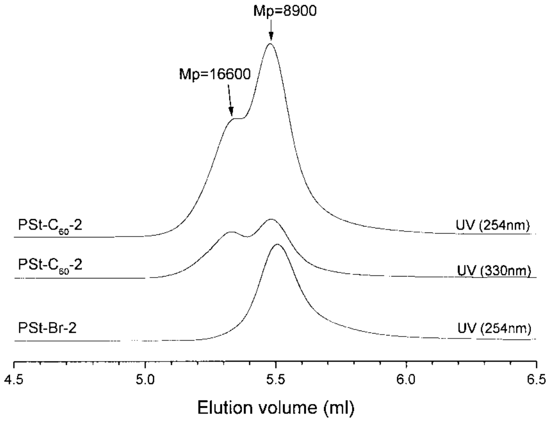


Figure 3. GPC traces of PSt-C_{60}-2 by UV (254 and 330 nm) compared with the trace of PSt-Br-2 by UV (254 nm).

This work was supported by National Science Foundation of China (Grant No. 59703004) and Foundation for University Key Teacher by Ministry of Education of China.

REFERENCES AND NOTES

1. Samulski, E. Y.; DeSimone, J. W.; Hunt, M. G., Jr.; Mencelogu, Y. Z.; Jarhagin, R. C.; York, G. A.; Labet, K. B.; Wang, H. Chem Mater 1992, 114, 9665.
2. Wang, C. C.; He, J. P.; Fu, S. K.; Jiang, K. J.; Cheng, H. Z.; Wang, M. Polym Bull 1996, 37, 305.
3. Okamura, H.; Terauchi, T.; Minoda, M.; Fukuda, T.; Komatsu, K. Macromolecules 1997, 30, 5279.
4. Cloutet, E.; Fillaut, J. L.; Astruc, D.; Gnanou, Y. Macromolecules 1999, 32, 1043.
5. Wang, J. S.; Matyjaszewski, K. J Am Chem Soc 1995, 117, 5614.
6. Matyjaszewski, M.; Patten, T. E.; Xia, J. H. J Am Chem Soc 1997, 119, 674.
7. Matyjaszewski, M.; Nakagawa, Y. Polym J 1998, 30, 138.
8. Malz, H.; Komber, H.; Voigt, D.; Hopfe, I.; Pionteck, J. Macromol Chem Phys 1999, 200, 642.

9. Baumert, M.; Zimmerman, J.; Scherble, J.; Mulhaupt, R. Macromolecules 1999, 32, 2503.
10. Coessens, V.; Matyjaszewski, M. J Macromol Sci Pure Applied Chem 1999, A36, 811.
11. Coessens, V.; Matyjaszewski, M. J Macromol Sci Pure Applied Chem 1999, A36, 653.
12. Coessens, V.; Matyjaszewski, M. J Macromol Sci Pure Applied Chem 1999, A36, 667.
13. Hawker, C. J. Macromolecules 1994, 27, 4836.
14. Keller, R. N.; Wycoff, H. D. Inorg Synth 1946, 2, 1.
15. Matyjaszewski, M.; Xia, J. H. Macromolecules 1997, 30,7697.
16. Prato, M.; Li, Q. C.; Wudl, F. J Am Chem Soc 1993, 113, 1148.
17. Wang, C. C.; Shu, C.; Fu, S. K. Chem J Chin Univ 1996, 17, 1634.
18. Tao, Z. H.; Yang, W. L.; Wang, C. C.; Fu, S. K. Acta Polym Sinica 2000, 5, 565.
19. Zheng, J. W.; Goh, S. H.; Lee, S. Y. Polym Bull 1997, 39, 79.