

Synthesis of C₆₀-Bonded Polystyrene Initiated with C₆₀Cl_n/Ni(naph)₂/P(Ph)₃

Jing Hua,¹ Haiqiang Yang,¹ Zhixin Guo,² Ling Xu,¹ Dianbao Chen¹

¹Key Laboratory of Rubber-Plastics, Ministry of Education, Qingdao University of Science and Technology, Qingdao 266042, China

²Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

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ABSTRACT: A linear-shaped polystyrene with C₆₀ core was prepared with a novel initiator system, C₆₀Cl_n (*n* average value is 20)/Ni(naph)₂/P(Ph)₃, and *T*_p was 130 °C. The results of gel-permeation chromatography detected by UV detector and fluorescence spectrum of C₆₀-PSt demonstrated that C₆₀ was chemically bonded to polystyrene. The linear increasing of molecular weights (*M*_{n,GPC}) with conversion indicated that this novel initiator system had some charac-

ters of living polymerization. A bathochromic shift was found in the UV-vis spectra curves with increasing concentration of C₆₀-PSt in THF solution. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1215–1218, 2005

Key words: fullerenes; polystyrene; living polymerization; ATRP; optical property

INTRODUCTION

As a new form of carbon, fullerenes and their organic or polymeric derivatives possess the richness of unusual and uniquely attractive properties such as superconductivity, ferromagnetism, inhibition of HIV protease, anti-Lou Gehrig's disease, free radical scavenging bioactivity, photoconductivity, and nonlinear optical and optical limited properties, thus attracting considerable interest in the fields of physics, chemistry, material science, and the life sciences.

However, the ability to fabricate devices based on C₆₀ has been limited due to its poor processability and its complex nature due to multiaddition of the organic group onto the cage. There have been considerable reports on the macromolecular modification of C₆₀ aiming at the materialization of C₆₀ for practical purposes. It is obvious that C₆₀-bonded polymers obtained by introducing C₆₀ to the polymer lead to improvement in the solubility and processability of C₆₀. Various methods to synthesis polymeric C₆₀ derivatives have been reported in the past few years, such as ordinary radical polymerization^{1–3}, living anionic polymerization^{4,5}, coordinational polymerization,^{6,7} cationic polymerization,⁸ and reacting C₆₀ with an end-functionalized polymer^{9–11}.

Recently, some efforts have been devoted to the synthesis of well-defined polymeric C₆₀ derivatives by living radical polymerization. Wang et al.¹² reported on the preparation of C₆₀-containing PSt (polystyrene) with narrow molecular weight distribution by reaction of C₆₀ with PSt-TEMPO (polystyrene adducts with 2,2,6,6-tetramethylpiperidinyl-1-oxy). By using C₆₀ as monomer in atom transfer radical polymerization (ATRP), Zhou et al.¹³ synthesized C₆₀-end-capped well-defined polystyrene using the ATRP technique. The C₆₀-end-capped polystyrene was synthesized by reacting C₆₀ with predesigned molecular weight and narrow polydispersity azide end functional PSt (PStN₃), which was prepared by ATRP¹⁴.

Ordinary ATRP was initiated with a variety of alkyl halides, *R*-X (*X* = Cl or Br) and a transition metal species complexed by suitable ligand as the catalyst. A novel initiator, C₆₀Cl_n (a chlorided derivative of fullerene), instead of alkyl halide in ATRP and CuCl/Bpy as the catalyst has been used to initiate polymerization of styrene in our laboratory¹⁵. Under this condition, a star-shape polystyrene with a C₆₀ core has been produced. A few Ni complexes can also be used as ATRP catalyst^{16–19}. Compared with other nickel catalyst systems in ATRP, Ni(naph)₂ (nickel naphthenate) can be easily soluble in oil phase. Ni(naph)₂/P(Ph)₃ (triphenyl phosphor) as a novel catalyst system and C₆₀Cl_n as initiator have been used to initiate polymerization of styrene in this paper. This polymerization system has some characteristics of living polymerization. The light transmittance (*T*%) of C₆₀-PSt in THF solution can be adjusted easily by increased con-

Correspondence to: J. Hua (huajing72@263.net).

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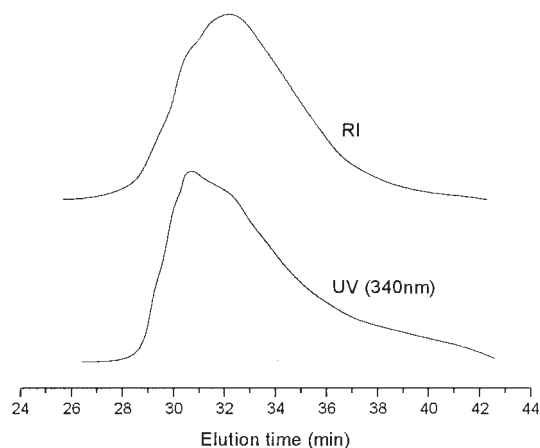


Figure 1 GPC traces of PSt- C_{60} by UV (340 nm) and RI detector.

centration of the solution. Herein we will report the preliminary results of this polymerization system.

EXPERIMENTAL

Materials

Styrene and methylmethacrylate were distilled under reduced pressure from calcium hydride power before use. Toluene was purified by refluxing over metal sodium in nitrogen atmosphere. Carbon tetrachloride was purchased and distilled under reduced pressure before use; PPh_3 was recrystallized twice from ethanol at 40 °C, vacuum-dried, and stored *in vacuo* in the dark. $C_{60}Cl_n$ was synthesized according to Ref.²⁰ by our own lab. The value of n was decided by elementary analysis and weight method. In the MALDI-TOD mass spectrum by fast atom bombardment of $C_{60}Cl_n$, we can only find the peak of C_{60} (in $m/z = 720$). Due to the loss of chloride in this condition, the peak of $C_{60}Cl_n$ cannot be detected.

Polymerization

Polymerization was carried out in a 10-mL flask sealed with a rubber septum in an ampule and degassed on a vacuum line. The flask was filled with stoichiometric quantities of initiator, catalyst, and ligand and then degassed to remove oxygen. Degassed monomer and toluene were added using a syringe. The polymerization was carried out in an oil bath at 130 °C. The polymer was recovered by precipitation in methanol and pumped overnight in a vacuum oven. The yields were calculated from the weight of polymers. Before detecting the UV-vis spectrum, PSt and PMMA catalyst by $Ni(naph)_2$ were extracted by hydronated gasoline after 12 h to remove Ni complex. Polystyrene was then recovered by precipitation in methanol.

Analysis

The $M_{n,GPC}$ of polystyrenes was measured by gel permeation chromatography (GPC) with a Shimadzu system composed of a set of KF-1, KF-2, KF-3, KF-4, KF-6 microstyrigel columns and a dual detector system (UV detector and refractometer) in tetrahydrofuran with polystyrene standard calibration. The UV-vis detector was set at 340 nm, at which the polystyrene used in this work was not detected, and only C_{60} and its derivatives were absorbed.

UV-vis spectra were obtained in THF using a Shimadzu spectrophotometer.

The fluorescence spectrum was obtained in methylene dichloride using a Spex Fluorolog-3 photoncounting emission spectrometer fluorescence.

RESULTS AND DISCUSSION

The Ni(II) complex can be used as ATRP catalyst, so $Ni(naph)_2/P(Ph)_3$ was chosen as a novel catalyst system and $C_{60}Cl_n$ as initiator. Styrene was polymerized with the novel initiator system. The molar ratio of styrene/ $C_{60}Cl_n/Ni(naph)_2/P(Ph)_3$ was 100/0.05/1/2 and T_p was 120 °C. The conversion of the monomer exceeded 98% after polymerizing for 20 h. The color of the product was reddish-brown.

Figure 1 shows GPC profiles obtained by UV and RI dual detectors of this product. The UV detector was set at 340 nm where the polystyrene could not be detected and only C_{60} and its derivative can be recorded. The molecular weight distribution obtained by RI detector was a little broader than that obtained by the UV detector. But the two curves were almost superpositioned, thus confirming the covalent attachment of PSt onto C_{60} .

Figure 2 shows the fluorescence spectrum of C_{60} -PSt

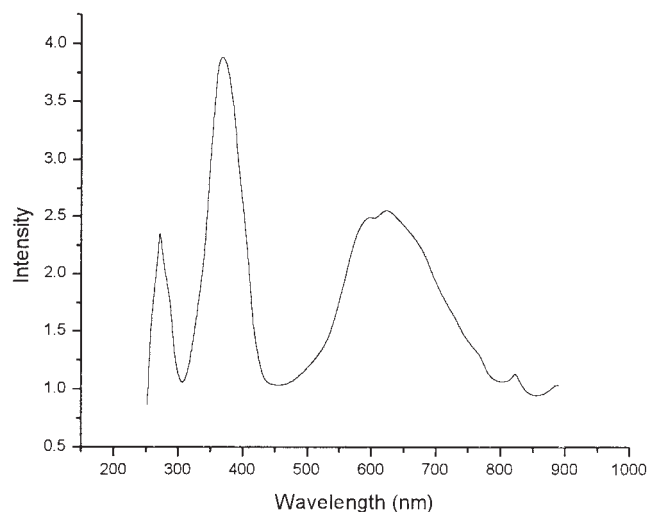


Figure 2 Fluorescence spectra of C_{60} -PSt in dichloromethane at room temperature. $\lambda_{ex} = 248$ nm.

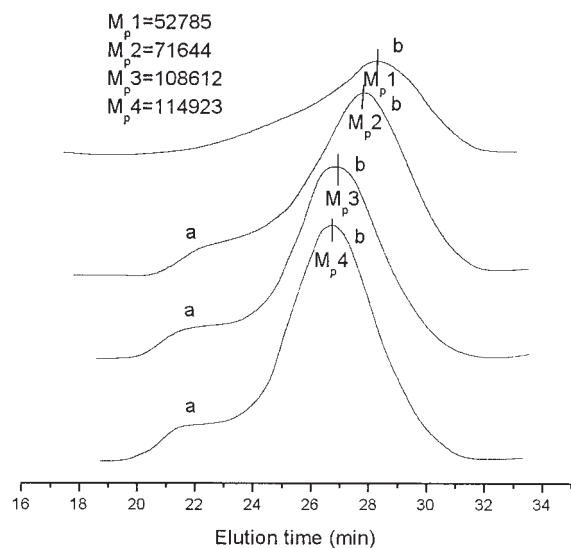


Figure 3 The GPC curves of PSt in different conversions (21, 33, 73, and 81%).

in dichloromethane at room temperature; λ_{ex} was 248 nm. The peak around 650 nm was the fluorescence emission peak of C₆₀ and its derivatives. The peak at 395 nm should be ascribed to the energy transfer by benzene rings of PSt to the C₆₀-CH₂-CH- moiety¹³. This also indicates that C₆₀ was chemically bonded on the PSt.

Figure 3 shows the GPC curves of PSt under different conversion. There are two peaks in the GPC curves: the first peak (a) was almost unchanged during the increase of conversion, and the molecular weights of this part were higher than the others; this part of the polymer may be the product of therm polymerization. On the other hand, the molecular weights of the second peak (b) increased linearly with conversion as shown in Figure 4. The DP_n were about 1.7, broader than that of the product of ordinary ATRP. But it almost retained consistency. By adding methylmethacrylate after the styrene polymerizes completely, the copolymer of polystyrene-*block*-poly-

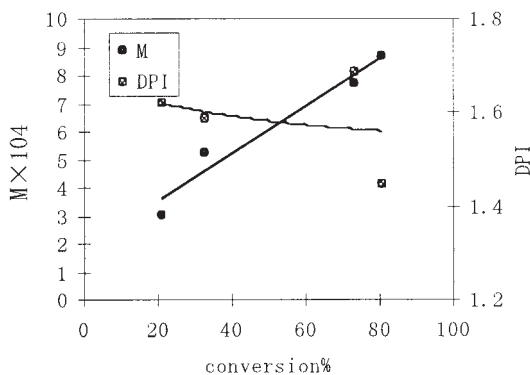


Figure 4 The relation of conversion (%) and M_n and DP_n.

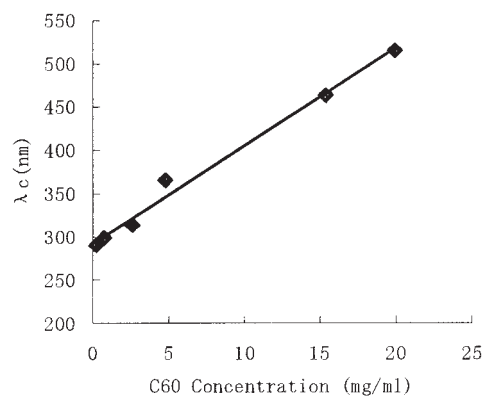


Figure 5 The C₆₀ concentration of C₆₀-PSt THF solution with cutoff wavelength (λ_c).

methylmethacrylate can also be compounded. All of these indicate a “living” nature of this polymerization system. C₆₀Cl_n can be used as initiator and Ni(naph)₂/P(Ph)₃ as the catalyst in this ATRP system.

Given the living nature of this polymerization system, we can roughly calculate that the arm number of this C₆₀-bonded polystyrene is about 2, by the formula of $M_{n,GPC} = ([M]C\%/ [I])W_M$. So linear-shape polystyrene with a C₆₀ core may be obtained by ATRP initiated with C₆₀Cl_n/Ni(naph)₂/P(Ph)₃.

A bathochromic shift was found in the UV-vis spectra curves with increasing concentration of C₆₀-PSt in THF solution. That is, with the increase of concentration of C₆₀ polymer solution, the light transmittance ($T\%$) shifted to the longer wavelength, which suggested a strong association among the molecules of C₆₀Cl_n and the formation of a cluster compound of C₆₀Cl_n. The cutoff wavelength λ_c of the C₆₀-PSt THF solution moves from 290 to 515 nm when C₆₀ concentration increases from 0.24 to 19.90 mg/mL as shown in Figure 5. So, the light transmittance ($T\%$) of the polymer solution can be adjusted easily by an increase in the concentration of the C₆₀-PSt solution. The special optical property of the C₆₀-PSt has a broad application foreground.

CONCLUSIONS

In conclusion, the controlled molecular weight and linear-shape polystyrene with a C₆₀ core was synthesized with a novel initiator system, C₆₀Cl_n/Ni(naph)₂/P(Ph)₃. The molar ratio of styrene/C₆₀Cl_n/Ni(naph)₂/P(Ph)₃ was 100/0.05/1/2 and T_p was 120 °C. The result of gel-permeation chromatography demonstrated that therm polymerization partly existed in this polymerization. GPC detected by UV detector and fluorescence spectrum of the polymer demonstrated that C₆₀ was chemically bonded to polystyrene. The linear increasing of molecular weights ($M_{n,GPC}$) with conversion indicated that this novel

initiator system has some characteristics of living polymerization. A bathochromic shift was found in the UV-vis spectra curves with increasing concentration of C₆₀-PSt in THF solution. The cutoff wavelength λ_c of C₆₀-PSt polymer THF solution moved from 290 to 515 nm when the C₆₀ concentration increased from 0.24 to 19.90 mg/mL.

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