Synthesis and Photoconducting Properties of C_{60}-Bonded Polystyrene Initiated with $C_{60}Cl_n$

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ABSTRACT: C_{60}-bonded polystyrene was produced with a novel initiator system, $C_{60}Cl_n$/CuCl/2,2'-bipyridine (where the average value of n is 20). The molar ratio of styrene/$C_{60}Cl_n$/CuCl/bpy was 100:1/20:1:2, and the polymerization temperature was 130°C. Gel permeation chromatography detected with an ultraviolet detector demonstrated that C_{60} was chemically bonded to polystyrene. The linear increase in the number-average molecular weight (by gel permeation chromatography) with the conversion indicated that this novel initiator system had some characteristics of living polymerization. A possible polymerization mechanism was examined. The photoconducting properties of C_{60}-bonded polystyrene were better than those of polystyrene initiated with CCl_4. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3001–3004, 2002

Key words: fullerenes; polystyrene; living polymerization

INTRODUCTION

Because fullerenes and their derivatives possess uniquely attractive properties in physics, photophysics, photochemistry, biochemistry, and so on,[1,2] there have been many studies on the macromolecular modification of C_{60} aiming at the materialization of C_{60} for practical purposes.[3,4] It is obvious that C_{60}-bonded polymers obtained by the introduction of C_{60} to the polymers leads to an improvement in the solubility and processability of C_{60}. Various methods for synthesizing polymeric C_{60} derivatives have been reported in the last few years, such as ordinary radical polymerization,[5–7] living anionic polymerization,[8] coordination polymerization,[9,10] cationic polymerization,[11] and the reaction of C_{60} with an end-functionalized polymer.[12–14]

Recently, living radical polymerization has been intensively studied because it can be applied to a wide variety of vinyl monomers to produce predictable average molecular weights [e.g., number-average molecular weight (M_n)], narrow polydispersity indices (PDIs), and controlled geometry/topology polymers. At the same time, it can be performed according to the ordinary free-radical polymerization procedure and, therefore, can avoid the stringent polymerization conditions that living anionic polymerization, for exam-

ple, needs. Some research[15] has been devoted to the preparation of well-defined C_{60}-bonded polymers by living radical polymerization. By using C_{60} as a monomer in atom transfer radical polymerization (ATRP), Zhou et al.[16] synthesized well-defined, C_{60}-end-capped polystyrene.

Ordinary ATRP[17] is initiated with a variety of alkyl halides, R—X (X = Cl or Br), and a transition-metal species complexed by a suitable ligand, with CuX/2,2'-bipyridine (bpy) as a catalyst. The novel initiator $C_{60}Cl_n$ (a chloride derivative of fullerene) was used to initiate the polymerization of styrene (St),[18] instead of an alkyl halide, as an ATRP initiator in our laboratory. Under these conditions, every polymeric chain was bonded by C_{60}, and star-shaped polymers were produced because of multiple chlorine atoms in one initiator molecule ($C_{60}Cl_n$). This may be a new and promising way to produce a star-shaped polystyrene with a C_{60} core. This polymerization system has some characteristics of living polymerization as well. Here we report the preliminary results for this initiation system.

EXPERIMENTAL

St was distilled under reduced pressure from a calcium hydride powder before use. Carbon tetrachloride was purified by distillation, and copper(I) chloride was purified through washing with acetic acid, acetone, and methanol and then drying in vacuo. bpy was used as received. Toluene was purified via refluxing over Na in a nitrogen atmosphere. $C_{60}Cl_n$ was synthesized according to ref. 19 by our own labora-
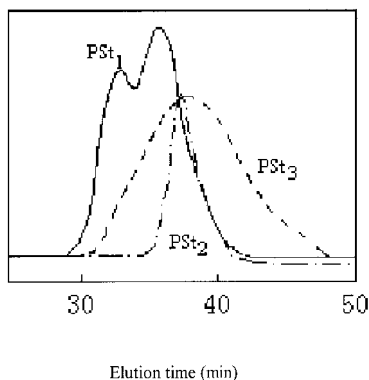
Figure 1 GPC profiles of PSt_1 (polystyrene initiated by $C_{60}Cl_n$/CuCl/bpy), PSt_2 (polystyrene initiated by CCl_4/CuCl/bpy) and PSt_3 (polymerization with only $C_{60}Cl_n$).

Figure 2 Dependence of the conversion on the polymerization time.

tory. The value of n was determined by elementary analysis and a weight method. The absolute value of n could not be decided by mass spectra by fast atom bombardment because even under these mild ionization conditions, $C_{60}Cl_n$ lost chlorine; only a peak due to C_{60} was observed.

St 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 $C_{60}Cl_n$, bpy, and CuCl and degassed for the removal of oxygen. Degassed St and toluene were added with a syringe. The polymerization was carried out in an oil bath at 130°C.The reaction mixture was cooled to room temperature and diluted with tetrahydrofuran (THF). The solution was then passed over alumina for the removal of the Cu complex, and polystyrene was recovered by precipitation in methanol and was pumped overnight in a vacuum oven. The yields were calculated from the weights of the recovered polymers.

$M_{n,GPC}$'s of polystyrenes were measured by gel permeation chromatography (GPC) with a Shimadzu (Tokyo) system consisting of a set of KF-1, KF-2, KF-3, KF-4, and KF-6 microstyragel columns and a dual-detector system (ultraviolet detector and refractometer) in THF with polystyrene standard calibration. The ultraviolet–visible detector was set at 350 nm, at which point the polystyrenes used in this work were not detected and only C_{60} and its derivatives absorbed.
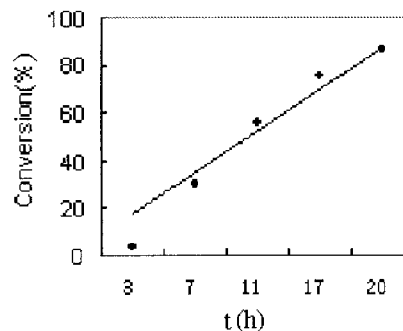
The photoconductivity was measured according to ref. 20.

RESULTS AND DISCUSSION

St was polymerized at 130°C in toluene with 1/20:1:2 $C_{60}Cl_n$/CuCl/bpy and 100:1 St/initiator. The conversion of the monomer exceeded 95% after polymerization for 20 h. The catalyst system had better state dispersion than ordinary ATRP catalysts (CCl_4/CuCl/ bpy = 1:1:2) as well. The GPC curves of polystyrenes PSt_1, PSt_2, and PSt_3 are shown as Figure 1. Their PDIs and M_n's (determined by GPC, which was calibrated with monodisperse polystyrene) are summarized in Table I. As St polymerized under 130°C, C_{60} could act as a terminator.[21] M_n of PSt_3 was much smaller than that of PSt_1 (see Table I). There were two peaks in the GPC curve of PSt_1. M_n of the first peak was about 7.80 × 10⁴, and that of the second peak was about 1.95 × 10⁴. Because there was a distribution of the numbers of chloride atoms in $C_{60}Cl_n$, there were several kinds of active centers in this polymerization system, which caused the DPI of PSt_1 to be rather broader. With multiple chlorine atoms in one $C_{60}Cl_n$ molecule, there were several radical active centers in one initiator molecule, and we speculated that there was star-shaped polystyrene in PSt_1.

GPC profiles of PSt_1 obtained by ultraviolet and refractive-index dual detectors were almost similar, indicating that $C_{60}Cl_n$ existed in the PSt_1 polymeric chains. As the ultraviolet detector was set at 350 nm, the polystyrene could not be detected, and only C_{60} and its derivative could be recorded. At the same time, PSt_1 had good solubility and could be dissolved in a variety of solvents, such as THF, toluene, and trichloromethane.

TABLE I
Polymerization of St with Different Initiator Systems

Initiator system	$C_{60}Cl_n$/CuCl/bpy (PSt_1)	CCl_4/CuCl/bpy(PSt_2)	$C_{60}Cl_n$ (PSt_3)
Conversion (%)	98.1	96.2	97.2
DPI	2.71	1.25	2.64
$M_n \times 10^4$	2.15	1.24	0.81

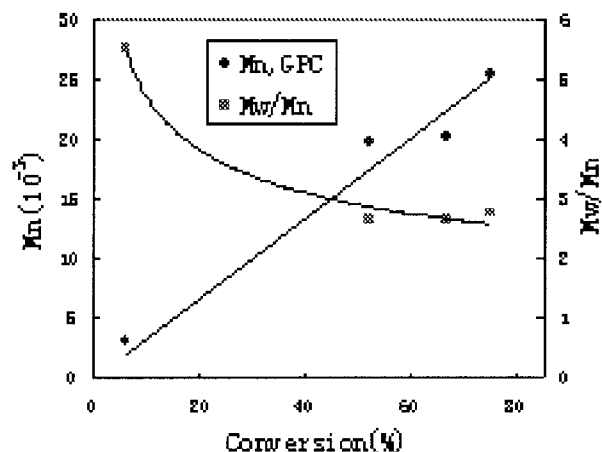[St] = 6.46×10^{-6} mol L⁻¹, solvent-toluene. Temperature = 130°C, time = 20 h.

Figure 3 Dependence of the molecular weight ($M_{n,GPC}$) and polydispersity [weight-average molecular weight/ number-average molecular weight (M_w/M_n)] on the monomer conversion.

Figure 4 Photoconductivity of the PSt$_2$ and C$_{60}$-bonded PSt$_1$.

A linear plot of the conversion of the monomer versus the polymerization time is shown in Figure 2. At the same time, the linear increase in the molecular weights ($M_{n,GPC}$) with the conversion, as shown in Figure 3, indicates the living nature of the polymerization. The polydispersities of the resulting polymers were broad because of the multiple active centers. After St polymerized completely, by the addition of methyl methacrylate, the copolymer polystyrene-*block*-poly(methyl methacrylate) could also be compounded. This also verified the living nature of the polymerization.

Because the value of *n* in C$_{60}$Cl$_n$ was uncertain, the existing structure of PSt$_1$ was difficult to determine. With the living nature of this polymerization system, we can roug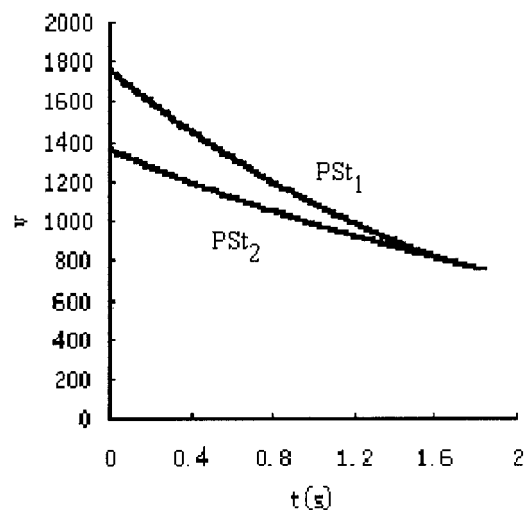hly calculate the arm number of this C$_{60}$-bonded polystyrene to be 2–6, using the following formula: $M_{n,GPC} = ([M]C\%/[I])W_M$. We have also considered the formation of a multiarm structure that is more compact (having a smaller hydrodynamic volume) than its linear counterpart with the same molecular weight. The arm number of C$_{60}$-bonded polystyrene is identical to the results of Ederle and Mathis[22] and Audouin et al.[23] Therefore, star-shaped polystyrene with a C$_{60}$ core may be obtained in this polymerization system.

The mechanism of the preparation of the C$_{60}$-bonded polystyrene might be deduced tentatively as shown in Scheme 1.

Figure 4 shows the photoinduced discharge curve of P/R from PSt$_2$ and PSt$_1$. C$_{60}$-bonded polystyrene (PSt$_1$) exhibited a higher charge acceptance ($V_0 = 1720$) than
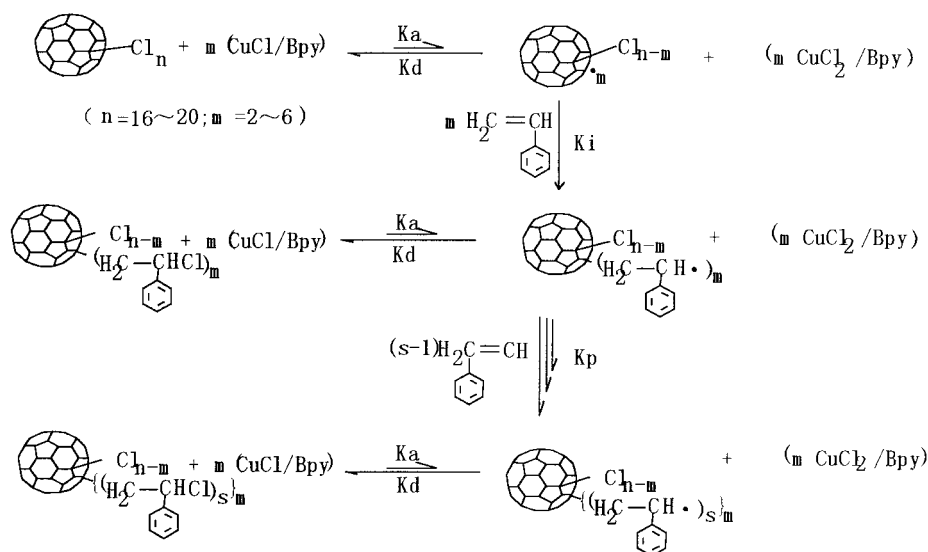
Scheme 1 Mechanism of the preparation of the C$_{60}$-bonded polystyrene initiated with C$_{60}$Cl$_n$.

PSt$_2$ (V_0 = 1320), and PSt$_1$ has a shorter $t_{1/2}$ (0.81 s) than PSt$_2$ (0.92 s). Therefore, C$_{60}$-bonded polystyrene exhibited better photoconductivity than PSt$_2$. However, this article only presents preliminary results; more detailed work is needed.

In conclusion, C$_{60}$-bonded polystyrene was synthesized with the novel initiator system C$_{60}$Cl$_n$/CuCl/bpy. Its structure might be star-shaped with a C$_{60}$ core. This initiator system showed some characteristics of living polymerization. A possible polymerization mechanism was proposed. The photoconducting properties of C$_{60}$-bonded polystyrene were better than those of polystyrene initiated with CCl$_4$.

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