New Synthetic Method for Soluble Starlike C_{60}-Bonding Polymers

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ABSTRACT: Novel starlike C_{60}-bonding polymers were synthesized by using the iniferter technique. The fullerene C_{60} with pendent *N,N*-diethyldithiocarbamate groups (C_{60}–SR) was used as polyfunctional photoiniferter. The effects of UV-irradiation time and ambient temperature on the molecular weight of polymer were investigated. The photopolymerization with C_{60}–SR proceeded via a living-radical mechanism, and gave soluble polyfunctional polymers (photoiniferters). Multiple polymer arms were attached to the C_{60} core and the polymers obtained by C_{60}–SR could also be used as excellent crosslinking agents. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1286–1290, 2001

Key words: fullerene; photoiniferter; living-radical polymerization; starlike polymer–bound C_{60}

INTRODUCTION

Buckminsterfullerene may well be the most intensively researched single molecule in modern science.[1] As a result, the buckyball has quickly proved to be not only a new carbon allotrope of esthetic structure but also a molecule of many talents, possessing a range of exotic properties such as superconductivity, ferromagnetism, optical nonlinearity, and anti-HIV bioactivity.[2] Utilization of such properties for practical applications, however, has been largely hampered by C_{60}'s poor tractability.[3] Synthesis of fullerene-based polymers has attracted a great deal of interest among polymer scientists and entrepreneurs because well-designed fullerene-based polymers are easily processable and exhibit novel properties, which are superior to those of the parent forms.

The starlike polymers and dendritic macromolecules are an area of increasing interest and their choice as the polymeric fragment is attributed to their globular three-dimensional structure, which may lead to greater encapsulation and the ability to prepare monofunctional, monodisperse materials of known molecular weight.[4,5] Although there have been many investigations concerning the polymeric modification of C_{60}, so far only a few of them reported the preparation of the starlike polymers and dendritic macromolecules containing C_{60}. The reaction of living polystyrene with C_{60} was previously reported,[6] in which a broad distribution of products was obtained, with the number of attached polymer chains ranging from 1 to 10. Hawker et al.[5] described the preparation of dendrimer-modified C_{60} by a controlled one-
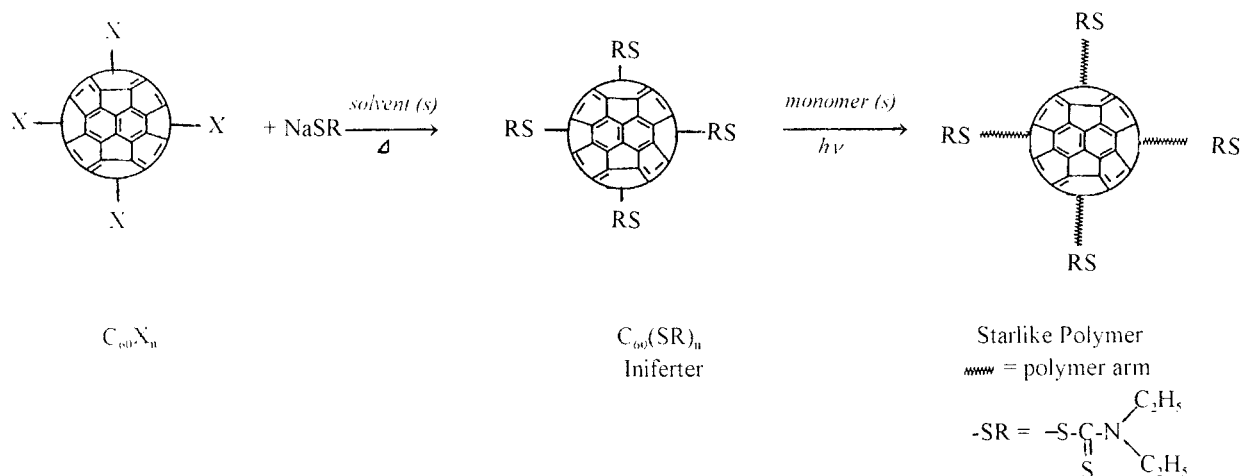
Scheme 1

step cycloadditional reaction of a dendritic azide with C_{60}. The formation of fullerene-bound dendrimers[7] was accomplished by reaction of each of the two phenolic groups located at surface of the functionalized fullerene with the single benzylic bromide group at the focal point of a fourth-generation dendrimer [G-4]–Br in the presence of K_2CO_3.

Very recently, by the use of fullerenol as a molecular core, urethane-connected polyether star polymers[8] were synthesized as a soluble material containing on average six chemically bonded polymer arms per C_{60}, with a narrow distribution of the number of arms per molecule and a polydispersity index of 1.45. Chiang et al.[9] reported the remarkable advantage of incorporating polyhydroxylated fullerenes in the synthesis of poly(urethane-ether) networks, giving high-performance elastomers with greatly enhanced tensile strength, elongation at break, and thermal mechanical stability, compared with that of their linear analogs or conventional polyurethane elastomers crosslinked by trihydroxylated reagents. Mono- and dipolystyrene-substituted C_{60} were synthesized via termination of living anionic polymerization of styrene in a heterogeneous medium.[10] This synthesis contains two significant variations: (1) the addition of 20% (v/v) tetrahydrofuran to the polystyryl carbanion solution and (2) the addition of tetrahydrofuran to the C_{60} solution and the cooling of the solution to $-78°C$ prior to termination.

In the search for fullerene-containing polymeric materials with novel structure and properties, we herein report a more convenient synthetic method of soluble starlike C_{60}-bonding polymers.

EXPERIMENTAL

Fullerene C_{60} was synthesized and purified by the usual method.[11,12] HPLC analysis showed that the C_{60} is 99.5% pure. The photoiniferter C_{60} with pendent N,N-diethyldithiocarbamate groups (C_{60}–SR) was prepared through the reaction of $C_{60}X_n$ with sodium N,N-diethyldithiocarbamate (NaSR, supplied by Shanghai Chemical Co., China). Methyl methacrylate (MMA), styrene (St), maleic anhydride (MA), and other reagents were used after ordinary purification. Photopolymerization was carried out in the presence of C_{60}–SR under irradiation by a high-pressure mercury lamp (250 W) from a distance of 18 cm at a given temperature and time, the content of the reactor (Pyrex glass tube) was then poured into a large amount of methanol to isolate the polymer. The reactions are shown in **Scheme 1**.

The polymers obtained from the reaction were extracted in a Soxhlet apparatus, and were fractionated by dissolution in acetone and precipitated in methanol (the volume ratio of solvent versus nonsolvent is about 1 : 5). After separation and filtration, the products were dried in a vacuum drying oven at room temperature.

Molecular weights were evaluated with gel permeation chromatography (GPC) and Ubbelohde viscometer, using in the latter case, the Mark–Houwink relationship:

$$[\eta] = 4.8 \times 10^{-5} \, M_v^{0.8} \qquad (1)$$

in chloroform for the poly(methyl methacrylate)-bound C_{60} at $25 \pm 0.1°C$;

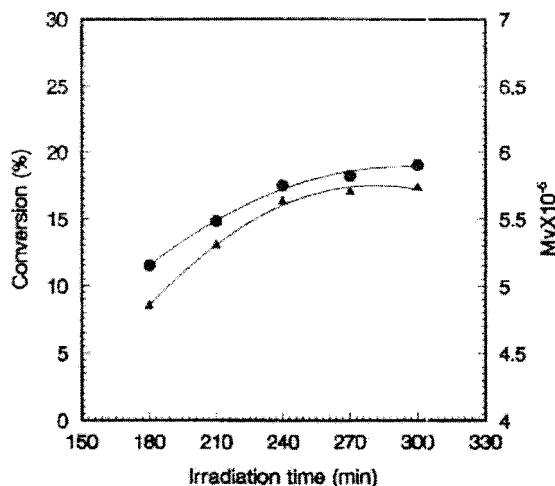$$[\eta] = 4.9 \times 10^{-4} \, M_n^{0.794} \qquad (2)$$

Figure 1 The effects of UV-irradiation time on conversion and M_v in photopolymerization of MMA with C_{60}–SR in benzene at 30°C: [MMA] = 2.6 mol L^{-1}; [C_{60}–SR] = 3.5×10^{-5} mol L^{-1}. –▲–, time–conversion relation; –●–, time–M_v relation.

in chloroform for the polystyrene-bound C_{60} at 30 ± 0.1°C;

$$[\eta] = 12.4 \times 10^{-5} M_v^{0.69} \qquad (3)$$

in acetone for the MMA–MA copolymer-bound C_{60} at 30 ± 0.1°C; and

$$[\eta] = 0.77 \times 10^{-4} M_v^{0.725} \qquad (4)$$

in tetrahydrofuran for the St–MA copolymer-bound C_{60} at 30 ± 0.1°C.

RESULTS AND DISCUSSION

Living-Radical Polymerization of MMA and St with C_{60}–SR Photoiniferter

Figure 1 and Figure 3 show the UV-irradiation time versus conversion and UV-irradiation time versus molecular weight M relations in the photopolymerization of MMA and St with C_{60}–SR as the polyfunctional photoiniferter. It can be seen from Figures 1 and 3 that the irradiation time versus conversion and irradiation time versus M relations observed by MMA and St are similar to one another, indicating that all of the pendent N,N-diethyldithiocarbamate groups on C_{60}–SR show similar reactivity for the radical polymerization of MMA and St. Furthermore, the irradiation time versus conversion curve obtained by St has a better linearity than that of MMA. This
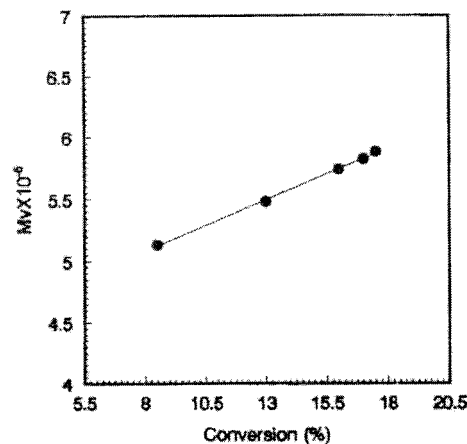

Figure 2 Conversion–M_v relation in photopolymerization of MMA with C_{60}–SR. The conditions are the same as those in Figure 1.

result seems to have originated from the different characters of photopolymerizations between MMA and St. The M values of the polymers obtained by MMA and St were also observed to be increased as a function of irradiation time and/or conversion (see Figs. 1–4), indicating that the polymerization proceeded via an ideal living-radical mechanism.[13]

Synthesis of MMA–MA and St–MA Copolymers

MA is a unique monomer because it does not readily undergo homopolymerization, but rather forms copolymers without difficulty. It is also
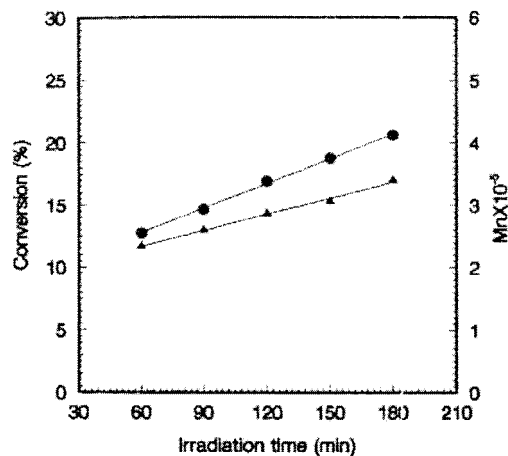

Figure 3 The effects of UV-irradiation time on conversion and M_n in photopolymerization of St with C_{60}–SR in benzene at 30°C: [St] = 2.5 mol L^{-1}; [C_{60}–SR] = 3.5×10^{-5} mol L^{-1}. –▲–, time–conversion relation; –●–, time–M_v relation.

Figure 4 Conversion–M_n relation in photopolymerization of St with C$_{60}$–SR. The conditions are the same as those in Figure 3.
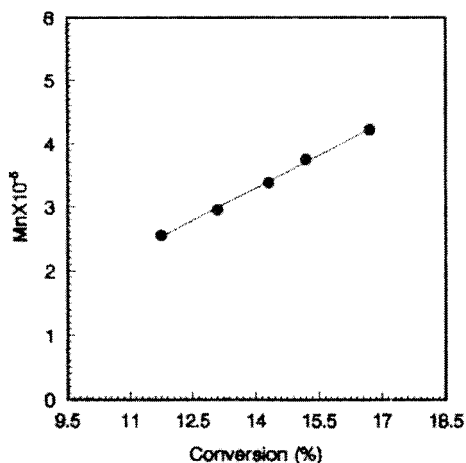

Figure 6 Conversion–M_v relation in photopolymerization of MMA–MA with C$_{60}$–SR. The conditions are the same as those in Figure 5.

unique in that the copolymers formed in the presence of radical initiators are in a 1 : 1 ratio and in an alternating sequence. Moreover, MA copolymers exhibit many and various biological activities, and generate direct antitumor effects.[14] So, C$_{60}$–SR was also applied to synthesize MMA–MA and St–MA copolymers.

Figure 5 and Figure 7 show the irradiation time versus conversion and irradiation time versus M relations in photopolymerization of MMA–MA and St–MA with C$_{60}$–SR as photoiniferter. Like the photopolymerization of MMA and St, MMA–MA and St–MA could also be polymerized easily when
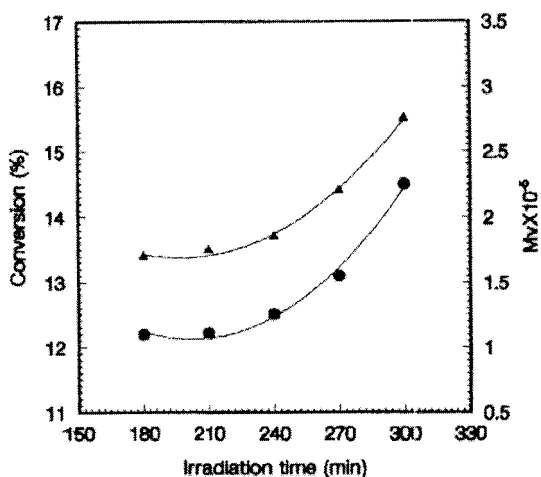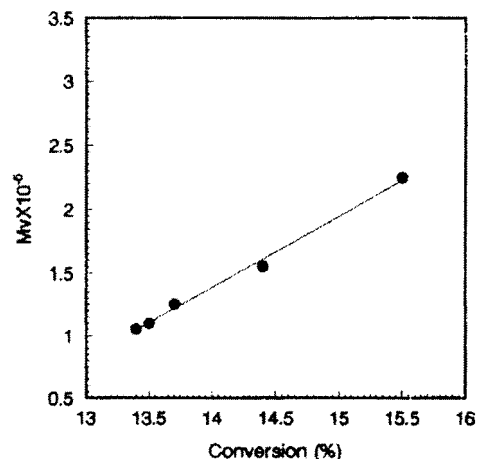
C$_{60}$–SR was used as photoiniferter. From Figures 5–8, the M values of the copolymers obtained by MMA–MA and St–MA are increased as a function of time and/or conversion as well. This result indicates that the copolymerizations of MMA–MA and St–MA by C$_{60}$–SR proceed through a living-radical mechanism, and the reaction of MMA–MA is in a manner consistent with the ideal living multiple-radical mechanism.

CONCLUSION

We report a more convenient new method to synthesize soluble starlike C$_{60}$-bonding polymers.
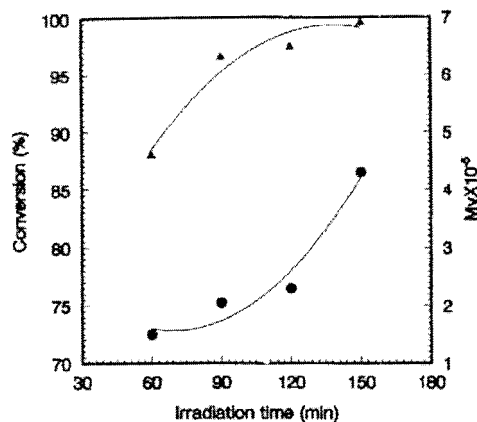

Figure 5 The effects of UV-irradiation time on conversion and M_v in photopolymerization of MMA–MA with C$_{60}$–SR in benzene at 30°C: [MMA] = [MA] = 1.4 mol L^{-1}; [C$_{60}$–SR] = 3.5 × 10^{-5} mol L^{-1}. –▲–, time–conversion relation; –●–, time–M_v relation.

Figure 7 The effects of UV-irradiation time on conversion and M_v in photopolymerization of St–MA with C$_{60}$–SR in benzene at 30°C: [St] = [MA] = 1.25 mol L^{-1}; [C$_{60}$–SR] = 8.4 × 10^{-5} mol L^{-1}. –▲–, time–conversion relation; –●–, time–M_v relation.
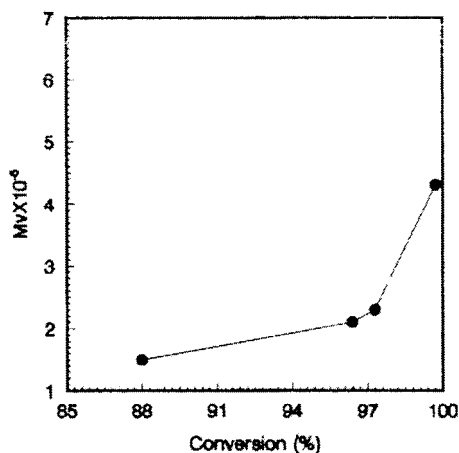
Figure 8   Conversion–M_v relation in photopolymerization of St–MA with C_{60}–SR. The conditions are the same as those in Figure 7.

The polymerization of MMA and St with C_{60}–SR as photoiniferter proceeded with a living-radical mechanism. The synthesis of MMA–MA and St–MA copolymers using C_{60}–SR also followed the living-radical mechanism.

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