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Synthesis and characterization of polystyrene-substituted [70]fullerene

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Abstract

Polystyrene-substituted [70]fullerene was synthesized via the reaction of C_{70} with living polystyrene anions in the THF–C_6H_6 mixed solvents. The covalent graftings of the polystyrene arms onto the C_{70} core result in the enhancement of the absorption degree at longer wavelengths, and in the decrease of the thermal stability and the glass transition temperature of the parent polymer. The other characterization results are also described. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: C_{70}; Polystyrene; Polystyrene-substituted C_{70}

1. Introduction

Over the past seven years investigations into the covalent [60]fullerene chemistry have made enormous progress and led to a rich variety of tailor-made building blocks for many technological applications [1–4]. In comparison, much less work has been done on [70]fullerene chemistry due to its high cost, lower symmetry and lower abundance. Unlike C_{60}, the prolate spheroidal fullerene D_{5h}-C_{70} [5], which consists of 12 pentagonal faces fused to 25 hexagonal faces, has a lower electron-withdrawing character than C_{60} [6], and exhibits a striking variety of structural features with five types of non-equivalent carbon atoms, eight distinct types of carbon–carbon bonds, two types of five-membered rings, and three types of six-membered rings in which the bond distance alternation is marked in type I rings, moderate in type II rings, and non-existent in the equatorial type III rings [7]. Theoretical and experimental methods show that C_{70} is a closed shell system with a HOMO–LUMO gap of 1.76 eV (to be compared to 1.68 eV in C_{60}) which accounts for the stability of this cluster [8,9]. Its lower symmetry relaxes the forbiddenness of some absorption and emission processes [10], resulting in the visible absorption of C_{70} being markedly stronger than that of C_{60}, and giving rise to a more complicated pattern of isomeric structures than for C_{60} upon functionalization of the fullerene core [11]. The chemistry of C_{70} is thus more complicated than that of C_{60} due to differences in reactivity between the various double bonds. This difference can be estimated by considering π bond orders or the local spheroid curvature, which is expressed as pyramidalization angles of the corresponding carbon atoms and is greatest at the poles [12]. Like C_{60}, C_{70} has also been functionalized in many ways and its possible organic reactions mainly include: (1) hydrogenation [13]; (2) oxidation reactions [14,15]; (3) halogenations [16,17]; (4) organometallic reactions [7,18,19]; (5) cycloadditions [20–26]; (6) the addition of nucleophiles [27,28]; and (7) the addition of radicals [29]. Noteworthy is the general tendency for additions at 6–6 bonds in areas of highest local curvature near the poles of C_{70}, and for bis-additions at 6–6 bonds in apposite hemispheres [12]. Compared to C_{60}, C_{70} shows a higher selectivity in multiple nucleophilic additions and a somewhat lower affinity for radicals. In recent years, there are already some papers concerning the functionalization of C_{70}, however, only a few of them reported the polymeric modification of [70]fullerene. Cao and Webber [30] described simply a method for incorporation of C_{70} into polystyrene (PS) by direct free radical copolymerization under routine conditions. Although a great deal remains to be done to characterize fullerenes as comonomers in free radical polymerization, this method may be of interest to a wide range of researchers working in the area of fullerene chemistry. Cai and coworkers reported the synthesis of photoconductive C_{70} chemically modified poly(*N*-vinycarbazole) via the reaction of C_{70} with the carbanion intermediates of polymer [31]. This novel polymer is highly soluble in some common organic solvents, and has significantly different spectroscopic properties from both poly(*N*-vinycarbazole) and C_{70}. Here, we report the covalent attachment of "living" PS carbanions pregenerated onto the C_{70} core and describe the effect of

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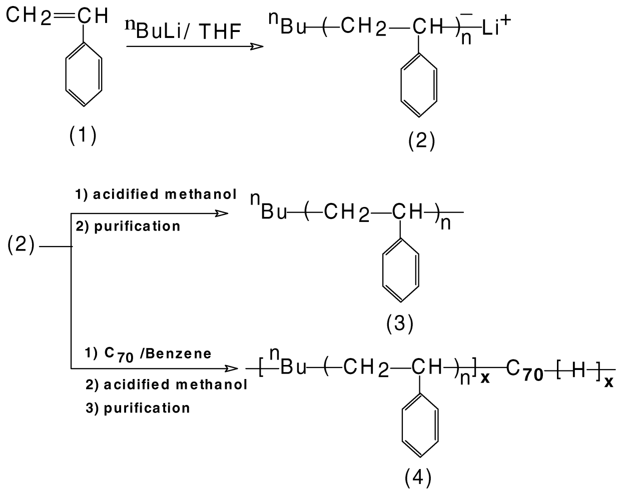

Scheme 1.

C_{70} chemical modification on the physical and chemical properties of PS.

2. Experimental

All the operations for synthesis prior to the termination reaction were carried out under purified dry argon by use of standard *schlenk* tubes. Into a stirring solution of styrene (6 ml) in THF (80 ml) at 0°C under argon was added 0.31 M *n*-butyllithium (4 ml) via a syringe. The color of the solution changed rapidly from colorless to red-orange which is characteristic of styryl carbanions in THF. After stirring for 40 min, the "living " PS solution was divided into two equal parts. The first part of solution was directly terminated by acidified methanol. The molecular weight average (M_w) and molecular number average (M_n) of pure PS obtained are 7.7×10^3, 4.5×10^3, respectively. Then, a diluted solution of C_{70} (100 mg, 0.119 mmol, purity $>$99%) in dry, degassed benzene (100 ml) was added dropwise to the another part of solution within 1 h, followed by stirring for 1 week. The resultant polymer was precipitated with acidified methanol, redissolved in THF, filtered to remove any insoluble impurity (if any) and reprecipitated with methanol to give a brownish yellow solid (this procedure was repeated twice). Solvent residues were removed by freeze drying under vacuum for several hours. Gel permeation chromatography of this product gave $M_n = 2.49 \times 10^4$ and $M_w/M_n = 1.3$. The synthetic route of polystyrene-substituted [70]fullerene is shown in Scheme 1.

3. Results and discussion

Recently, studies on the preparation and structural characterization of styrene-based polymeric C_{60} derivatives have increased rapidly. The results show that the fullerene molecule may be incorporated covalently into the PS backbone by use of [32–37]: (1) radical-initiated polymerization reactions; (2) sodium naphthalene-initiated anionic copolymerization reactions; (3) cycloaddition reaction of azido-substituted polystyrenes with fullerene; (4) Friedel–Crafts type reactions; (5) amine addition reactions; and (6) reaction of polymeric living carbanions with fullerene. Of all polymerization methods, the addition of living anionic polymers pre-generated onto the C_{60} core could offer an unique opportunity to control both the number of chains grafted onto the fullerene and the molar mass and polymolecularity of the grafts [37]. The maximum number of grafted chain depends on the reactivity of the carbanion borne by the chain. Although the chemistry of C_{70} is more complicated than that of C_{60}, their mode of addition reaction are very similar and differ only in their rates of reaction with certain species. The living PS carbanions thus also could add to the carbon–carbon bonds of [70]fullerene. This idea is confirmed by our experimental results. By assuming that the *n*-butyllithium added is completely used to initiate anionic polymerization of styrene monomer and in the addition reaction C_{70} is also completely consumed, the degree of polymerization and average molecular weight of pure PS obtained may be roughly calculated as 42 and 4377, respectively. The average number of grafted chains and average molecular weight of polystyrene-substituted [70]fullerene (i.e. C_{70}-PS copolymer) are about 5 and 2.36×10^4, respectively. These calculated values are comparatively in agreement with the experimental values.

The UV–VIS absorption spectra of C_{70}, PS and C_{70}-PS copolymer indicated that the main absorption bands of C_{70} in *n*-hexane (C_{70} is not soluble in any polar solvents) are located at 210, 231, 245, 312, 327, 354, 373 and 468 nm, respectively. Unlike C_{60}, the visible absorption of C_{70} is markedly stronger than that of C_{60}, probably because its lower symmetry relaxes the forbiddenness of the longest wavelength transition [10]. For polystyrene-substituted [70]fullerene, in the UV-region, the strong absorption bands at 242, 248, 254, 262 and 268 nm corresponding to the copolymer are in general agreement with those of pure PS, but their relatively peak intensities are different. The covalent graftings of multiple PS chains onto the C_{70} core apparently result in the enhancement of the absorption degree at longer wavelengths. Further, it is found that, polystyrene-substituted [70]fullerene polymer loses specific bands of C_{70}. Similar to the UV–VIS spectrum exhibited by C_{60}–styrene copolymer prepared in sodium naphthalene-initiated anionic polymerization reactions [32], the somewhat structured absorption band of free C_{70} is also replaced by a steadily decreasing curve, typical for substituted C_{70}.

^{13}C NMR results of the C_{70}–PS copolymer and pure PS obtained in deuterated chloroform showed that, in the pure *n*-butyl-terminated PS, the resonant signals of aliphatic carbons locate at $\delta = 40.6$, 42.8, 43.6, 44.0, 14.0, and 22.5 ppm, respectively. Among these peaks, the final two peaks are attributed to the *n*-butyl-terminated groups, the peak at 40.6 ppm may be ascribable to α-C, the other three peaks correspond to the triad splitting β-C. The six

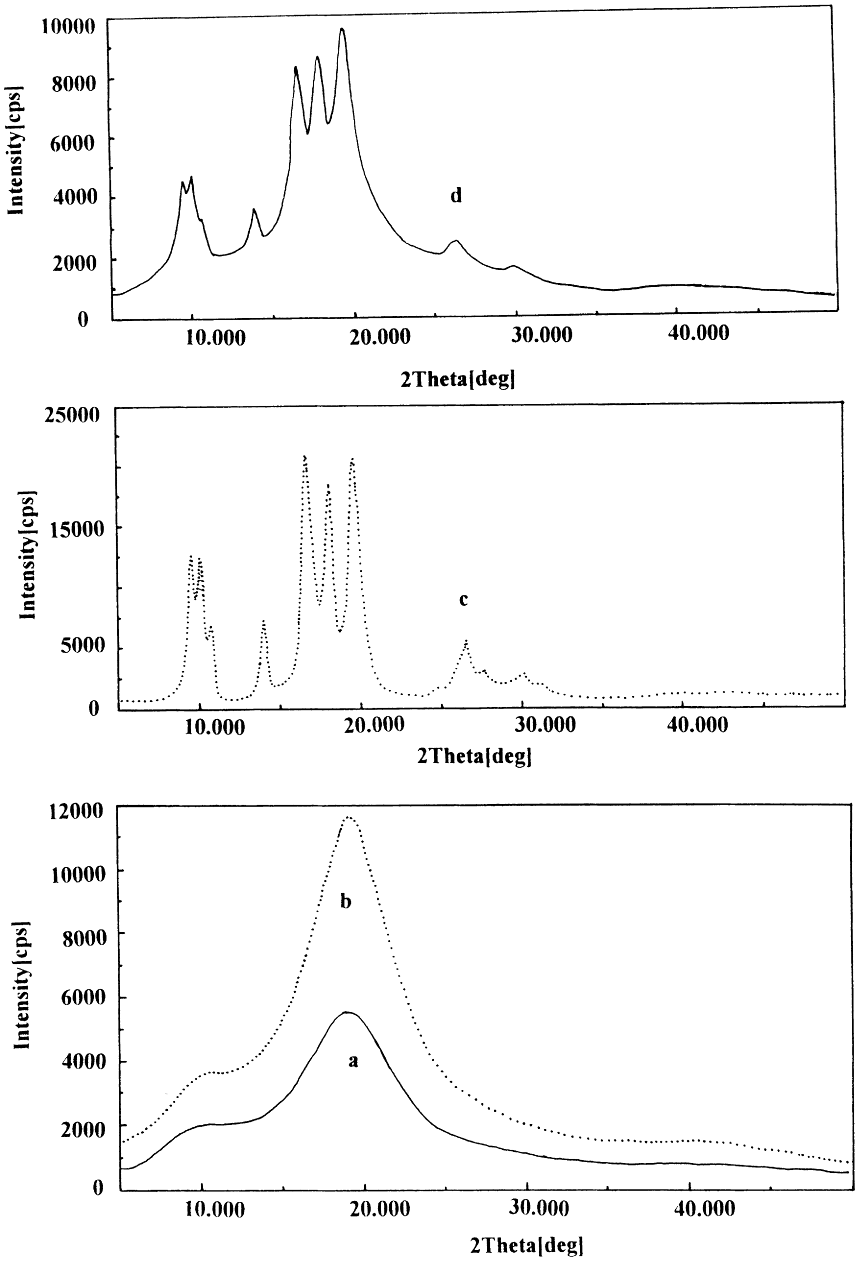

Fig. 1. X-ray powder diffraction diagrams from: (a) PS; (b) C_{70}–PS copolymer; (c) C_{70}; and (d) C_{70}-doped PS.

carbon signals at 125.4, 126.0, 127.7,129.2, 145.7, and 145.3 ppm in the aromatic region may be assigned to C-4 (125.4, 125.9 ppm), C-3, C-5 (127.7 ppm), C-2, C-6(129.2 ppm) and C-1 (145.7, 145.3 ppm) on phenyl rings of PS, respectively. For the copolymer, the observed ^{13}C NMR spectrum is essentially the same as that of pure PS and gave a little structural information due to the relatively lower content in the copolymer of [70]fullerene with large relaxation time. In the aliphatic region of ^{13}C NMR spectrum of copolymer, four new peaks located at 25.6, 29.7, 30.2, and 68.0 ppm were detected. The chemical shift at $\delta = 68.0$ ppm is attributed to the sp^3 hybridized carbons of substituted C_{70} cages [26]. Due to the effect of stronger electron affinity of C_{70} on the aliphatic carbons of PS backbone, the chemical shifts of partial α-C and β-C on the adjacent PS chain segments attached directly to the C_{70} cores shift to the up-field considerably, and appear at 25.6 ppm for α-C, 29.7 and 30.2 ppm for β-C, respectively. Similarly, because of the overwhelming contributions of multiple PS chains, which may lead to a great encapsulation to C_{70} core, in the polymer structure, the structure changes can hardly be observed by the IR spectrum.

Differential scanning calorimetric measurements of the glass transition temperatures of polymers show that like PS, the C_{60}–PS copolymer has also a single glass transition temperature (53.9°C as against 83.4°C for PS), implying a single-phase system. However, covalent graftings of living PS arms onto the C_{70} core result in the decrease of the glass transition temperature of the parent polymer. Perhaps a better rationalization might run as follows. In contrast to [60]fullerene with high symmetry, additions at 6–6 bonds of olivary [70]fullerene often occurred in areas of highest local curvature near the poles, while further multiple additions at 6–6 bonds occurred in apposite hemispheres [12]. In this case, the relatively lower steric hindrance effect from inter-chains of polymer in copolymer leads to the increase of the flexibility of polymer chains, and consequently results in the decrease of the glass transition temperature of the parent polymer. Likewise, the thermal stability of the parent polymer is also decreased due to the chemical modification with C_{70}, and distinct stages of weight loss on the pure PS and PS substituted [70]fullerene: 320–480°C and 200–550°C, respectively, are observed.

The X-ray powder diffraction scan for the C_{60}-PS copolymer is shown compared with those from pure PS and C_{70}-doped PS in Fig. 1. The eight relatively stronger sharp diffraction peaks of C_{70} centered at 2θ 16.74° ($I/I_0 = 100$), 19.68° ($I/I_0 = 99$), 18.12° ($I/I_0 = 87$), 9.62° ($I/I_0 = 60$), 10.18° ($I/I_0 = 60$), 14.04° ($I/I_0 = 35$), 10.82° ($I/I_0 = 32$) and 26.54° ($I/I_0 = 26$). The XRD pattern from C_{70}-PS copolymer was very similar to that of pure PS. After multiple PS arms were attached onto the C_{70} core, two main diffraction peaks at $2\theta = 10.10°$ and 19.04° still keep unchanged, indicating that the periodicity of the main arrangement of atoms or atomic groups in the copolymer remains unchanged on the incorporation of C_{70} cage into the polymer. However, it is seen that the diffracted intensities of the peaks at $2\theta = 10.10°$ and 19.04°, especially at 19.04° 2θ, were increased and consequently the peak form narrowed. The XRD spectrum of C_{70}-doped PS seems to be only a simple superposition of two spectra corresponding to C_{70} and pure PS, further indicating that in copolymer C_{70} the molecule has indeed incorporated covalently into the PS backbone.

In summary, we have demonstrated the synthesis of polystyrene-substituted [70]fullerene in the heterogeneous medium and described the initial results of the structural characterization. Further characterization and study of the properties of this material are currently being investigated.

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