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Covalent incorporation of [70]fullerene into poly(*p*-methylstyrene) by anionic copolymerization

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Abstract

A soluble non-crosslinked C_{70}-*p*-methylstyrene (C_{70}-PMS) copolymer was prepared in sodium naphthalene-initiated anionic polymerization reaction. This copolymer exhibits the lower intrinsic viscosity and higher absolute molecular weight compared with linear polystyrene at equal retention time, suggesting that the copolymer possess star-shaped structure. The covalent graftings of multiple poly(*p*-methylstyrene) (PPMS) chains onto the C_{70} core result in the marked enhancement of the absorption degree at longer wavelengths, and in the increase of glass transition temperature. Like pure PPMS, C_{70}-PMS copolymer also exhibits the higher solvency in common solvents. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: [70]Fullerene; Poly(*p*-methylstyrene); Anionic copolymerization

1. Introduction

Over the past several years, the systematic development of synthetic methodologies for the functionalization of [60]fullerene has paved the way for the preparation of novel organic or polymeric compounds of interest in the search of new materials with marvelous photophysical, electric and magnetic properties as well as biological activities [1–4]. In comparison, however, much less work has been done on the [70]fullerene chemistry due to its highest 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 [7–9]. Its lower symmetry relaxes the forbiddingness of some absorption and emission processes [10], this results in that the visible absorption of C_{70} is markedly stronger than that of C_{60}, and gives 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 [12]. Like C_{60}, C_{70} has also been functionalized in many ways, 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]. In recent years, there are some papers already concerning the functionalization of C_{70}, however, only a few of them reported the polymeric modification of [70]fullerene [30–32]. Here, we report the covalent attachment of [70]fullerene into poly(*p*-methylstyrene) and describe the effect of C_{70} chemical modification on the physical and chemical properties of poly(*p*-methylstyrene) (PPMS).

2. Experimental

2.1. Reagents and instrumentation

C_{70} (purity $> 99.99\%$) was obtained from Fullerene Institute of Wuhan University of China. The *p*-methylstyrene (PMS) monomer used was first dried by calcium hydride and then distilled in the vacuum system from calcium hydride. A middle cut, bp45°C, collected and stored under purified argon was used for subsequent experiments. Sodium naphthalene was prepared by the conventional method under a purified argon atmosphere, and its molar concentration in THF was about 0.44 M. Both of benzene and tetrahydrofuran (THF) were dried, deoxygenated and distilled before use. Unless noted otherwise, other analytically pure reagents, for example, methanol, hydrochloric acid, etc. were used as received.

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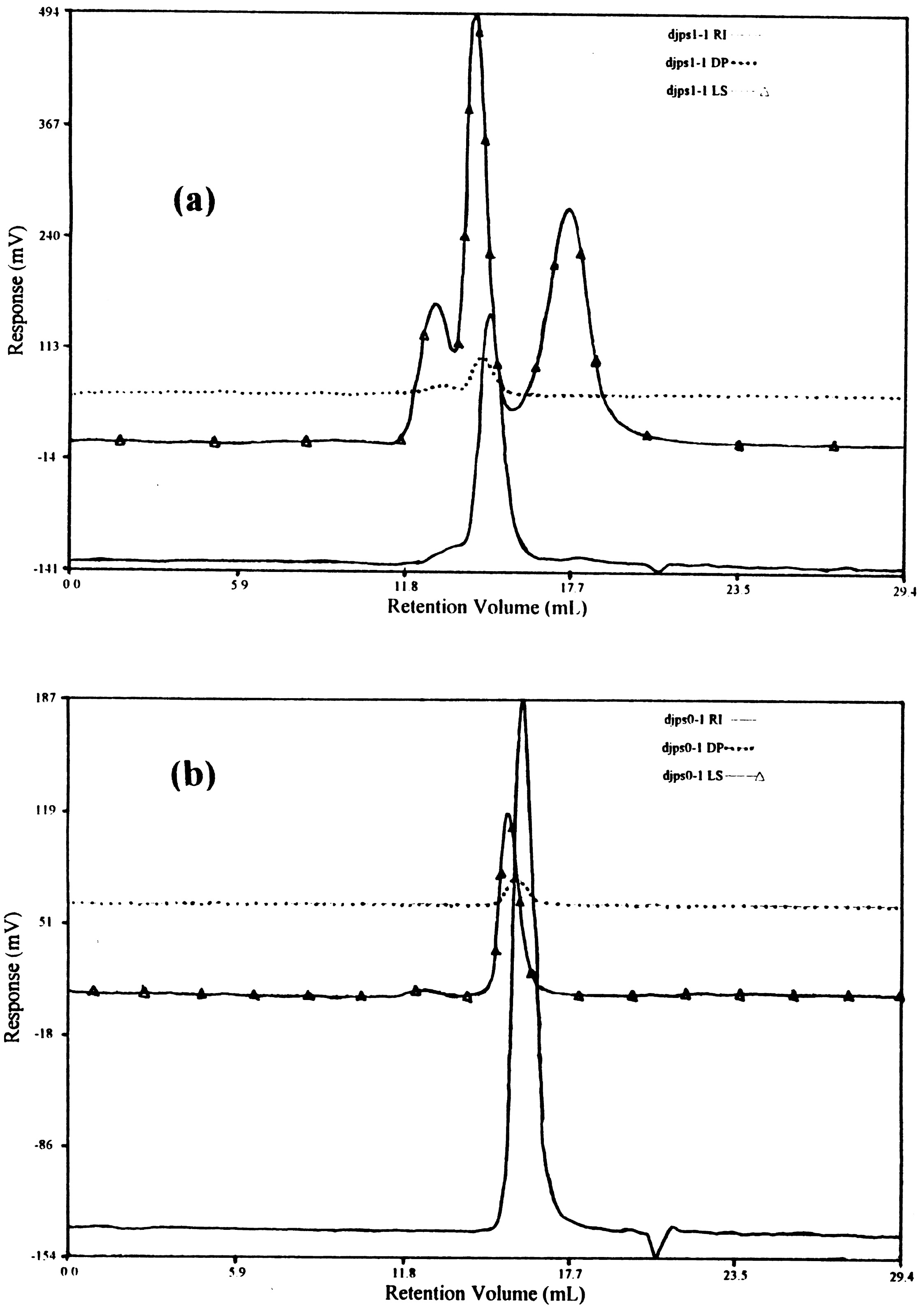

Fig. 1. SEC/RI/RALLS/DV chromatograms of: (a) C_{70}-PMS copolymer and (b) PPMS.

Table 1
SEC analyses of C_{70}-PMS copolymer and PPMS polymer

Sample	Molecular weight ($\times 10^{-4}$)			M_w/M_n	$[\eta]_n$	$[\eta]_w$	Rg_n	Rg_w
	M_n	M_w	M_p		(dl/g)	(dl/g)	(nm)	(nm)
$PPMS_0$	1.13	1.23	1.25	1.008	0.103	0.106	3.49	3.57
$PPMS_1$	42.8	49.60	40.30	1.158	0.0487	0.0866	10.08	10.24

The operations for synthesis prior to the termination reaction were carried out under purified dry argon by use of standard schlenk tubes. The molecular weight of the polymer was analyzed by Waters 410 Size Exclusion Chromatograph (SEC) in THF solutions with linear polystyrene standards. This SEC system was equipped with a refractive index (RI) detector (External RI), a Viscosity detector (Viscotek Model T60) and a light scattering (LS) detector (Viscotek Model T60). UV–VIS absorption spectra in THF were measured on a UV-240 spectrophotometer. FTIR spectra were recorded on a Nicolet FTIR-5DX spectrophotometer using KBr pellets. ^{13}C NMR spectra in $CDCl_3$ were run on a Bruker MSL-300 NMR spectrometer. The chemical shifts are reported in parts per million (δ ppm) downfield from tetramethylsilane, which had been used as an internal standard. Thermal properties of the samples were measured using a Dupont 2000 thermogravimetric analyzer.

2.2. Synthesis of poly(p-methylstyrene) ($PPMS_0$)

To a stirring solution of *p*-methylstyrene (5 ml, 43.49 mmol) in THF(20 ml) and benzene (10 ml) at −70°C under dry argon was added 0.44 M sodium naphthalene in THF (2 ml) via syringe. The solution color changes rapidly from colorless to blackish red. This reaction mixture was stirred for 40 min at the same temperature. The polymer was precipitated with methanol/H_2O (v/v, 90:10) solution, washed with acetone (20 ml) to remove naphthalene, redissolved in THF, filtered to remove any insoluble impurity, reprecipitated with methanol to give a colorless solid (this procedure was repeated twice). Solvent residues were removed by freeze-drying under vacuum for several hours.

2.3. Synthesis of C_{70}-PMS copolymer ($PPMS_1$)

Into a stirring reddish brown solution of C_{70} (160 mg) in PMS (5 ml, 43.49 mmol) and benzene (150 ml) at 25°C under dry argon 160 ml of THF was added. The mixed solution was cooled from 25 to −70°C. After stirring for 30 min, 2 ml of sodium naphthalene in THF was added to the above solution via syringe and then continued to stir for 5 h at −70°C, followed by reaction for 50 h under argon at ambient temperature. The reaction mixture was hydrolyzed with HCl (2 N)–MeOH–H_2O (volume ratio: 10:90:10) mixed solvents in air. The organic phase (red oily liquids) was concentrated to dryness under vacuum at 50°C, followed by a wash with acetone (20 ml, removal of residual naphthalene) and air drying. The crude product obtained was redissolved in THF, filtered to remove any insoluble impurities. Only a mere trace of black–brown or yellow–brown insoluble material was observed on the filter paper. Since the FTIR spectrum of this insoluble material is very similar to that of the fullerol $C_{70}(OH)_x$, it should mainly be a hydrolysis product of Na_xC_{70} produced by the side reaction of C_{70} with sodium naphthalene. The above result implied that in polymerization process crosslinking reaction might be negligible. To the transparent red filtrate was added HCl/H_2O (1:1) solution to give a layer of red oily liquids. This organic phase was concentrated to dryness, washed with acetone, freeze-dried and then exposed to slightly higher vacuum (removal of solvent residues) for several hours. The purification procedure was repeated twice. Like PPMS prepared under the same conditions in the absence of C_{70}, the C_{70}-PMS copolymer (yield 80%) also exhibited high solvency in many common organic solvents, which suggests that this copolymer is a soluble non-crosslinked polymer. The content of C_{70} moieties in the copolymer may be calculated roughly by the feed molar ratio of C_{70}/PMS. Its value is about 4%. Of course, as reported by many researchers, the actual amount of fullerene incorporated in the polymer is usually much less than that in the feed.

3. Results and discussion

In recent years, a great quantity of research achievements on the polymeric modification of fullerenes, particularly the most abundant [60]fullerene, have shown that polymers containing fullerenes can offer opportunities for the production of new optical and electroactive materials that can be processed into shaped objects and thin films [3,4,33–36]. [60]Fullerene has been incorporated covalently into polymers by a variety of reactions as part of the main chain, at the ends of side chains, as end groups, as branch points of stars, and as junctions of networks [4,34]. Although 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. In our previous article [37], we reported a new synthetic method of incorporation of [60]fullerene into polystyrene using the classical sodium naphthalene ($C_{10}H_8Na$) method of initiation of anionic polymerization. Similarly, C_{70} can also be incorporated into the PPMS covalently by using the same synthetic method.

Fig. 1 and Table 1 give SEC chromatograms of C_{70}-PMS copolymer and pure PPMS polymer, and the related

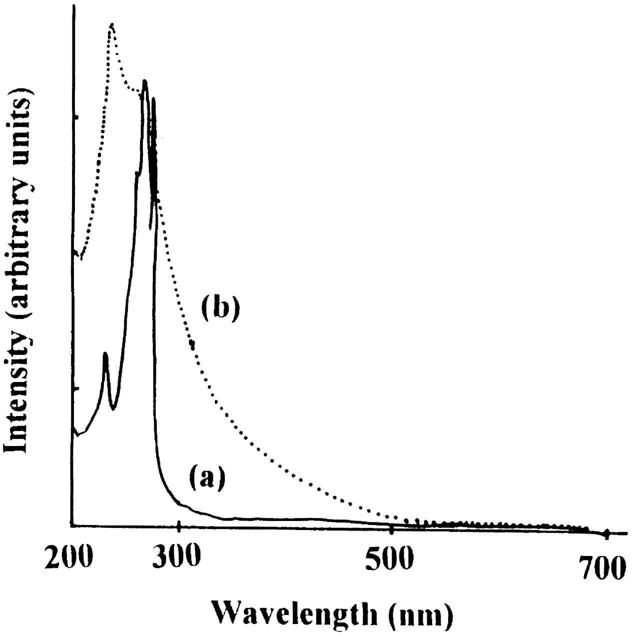

Fig. 2. UV–VIS absorption spectra in THF of: (a)PPMS and (b) C_{70}-PMS copolymer.

experimental data, respectively. It is found that, this copolymer exhibits a lower intrinsic viscosity and a higher absolute molecular weight compared with linear polystyrene at equal retention time, suggesting that the copolymer possess star-shaped structure [35,38]. The fullerene-containing polymer has a major RI peak at smaller retention volume than the parent polymer, which must be due to PMS adducts of C_{70}. Also, this copolymer has a smaller peak at still smaller retention volume similar to ones Ford and his coworkers found from addition of TEMPO-ended PS to C_{60} and they have attributed to either 2–3 PS chains per C_{60} or $(PS)_n(C_{60})_2$ [39,40]. This peak appears from all three detectors in our experiment and must be a higher molar mass component that differs from the major peak by integral multiple(s) of the major component. The peak of the copolymer at larger retention volume is a minor fraction of the mass according to the RI detector, and gives strong intensity in the LS detector. Its hydrodynamic volume is very small, and therefore this strong LS signal with no DV signal should not be assigned to a polymer. And then, what is it? We cannot distinguish whether it is due to a fullerene cluster [35] or to emission from a low-molar mass impurity in the sample. If it is a fullerene cluster, it is much smaller than the clusters Ford found from radical polymerizations, because their clusters appear at small retention volume and contain PS as well as fullerene units. Our C_{70}-PMS chromatogram shows similar result with even more of the large retention volume peak that is strong from the LS detector and much weaker from the RI detector. However, it is worthy to note that any information on the fullerenated polymeric materials from light scattering is untrustworthy if they contain fluorescent materials. For the fullerenes themselves (C_{60} and C_{70}) have no fluorescence and phosphorescence at the room temperature because fullerenes shift quickly to an excited triplet state; only in the very low temperature (about 5 K), people can observe very weak fluorescence excitation of fullerenes. The triple states have lifetimes in the 1–100 μs range, and if they emit as well as decay by radiationless processes, they would interfere with light scattering detection in a SEC experiment. Although some polymers, for example, poly(*N*-vinylcarbazole), polystyrene, poly(*p*-methylstyrene), poly(α-methylstyrene), etc. exhibit very strong fluorescence excitation, their fluorescence quantum yields would be decreased considerably, even down to zero completely by the chemical modification of fullerene on these parent polymers. This can be attributed to quenching through intramolecular excited-state energy transfers [41,42]. The fullerene-containing sites may act as energy traps. The observation from the fluorescence spectra of the fullerene-containing polymer shows no fluorescence excitation exhibited by the C_{70}-PMS copolymer. As it is so, the strong LS peak with no DV signal at the large retention volume (17.61 ml) cannot be assigned as unreacted C_{70} or poly-C_{70} with covalent fullerene–fullerene bonds [43]. In our previous article [37], we have found that in the sodium naphthalene-initiated anionic polymerization reaction of C_{60} with styrene, an important side-reaction, i.e. reaction of C_{60} with sodium naphthalene would occur simultaneously, whereas crosslinking reaction may be negligible. The by-product, which has an average composition $C_{60}(OH)_{24.5}$, from quenching with HCl–MeOH–H_2O

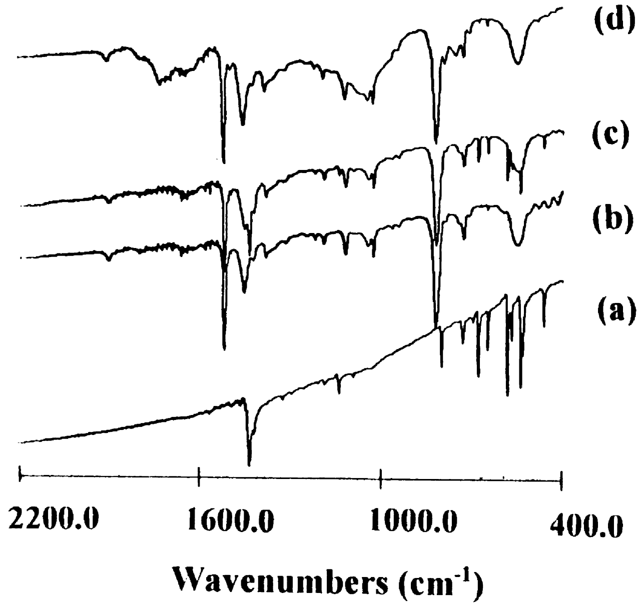

Fig. 3. FTIR spectra of the samples: (a) C_{70}; (b) PPMS; (c) C_{70}-doped PPMS; and (d) C_{70}-PMS copolymer.

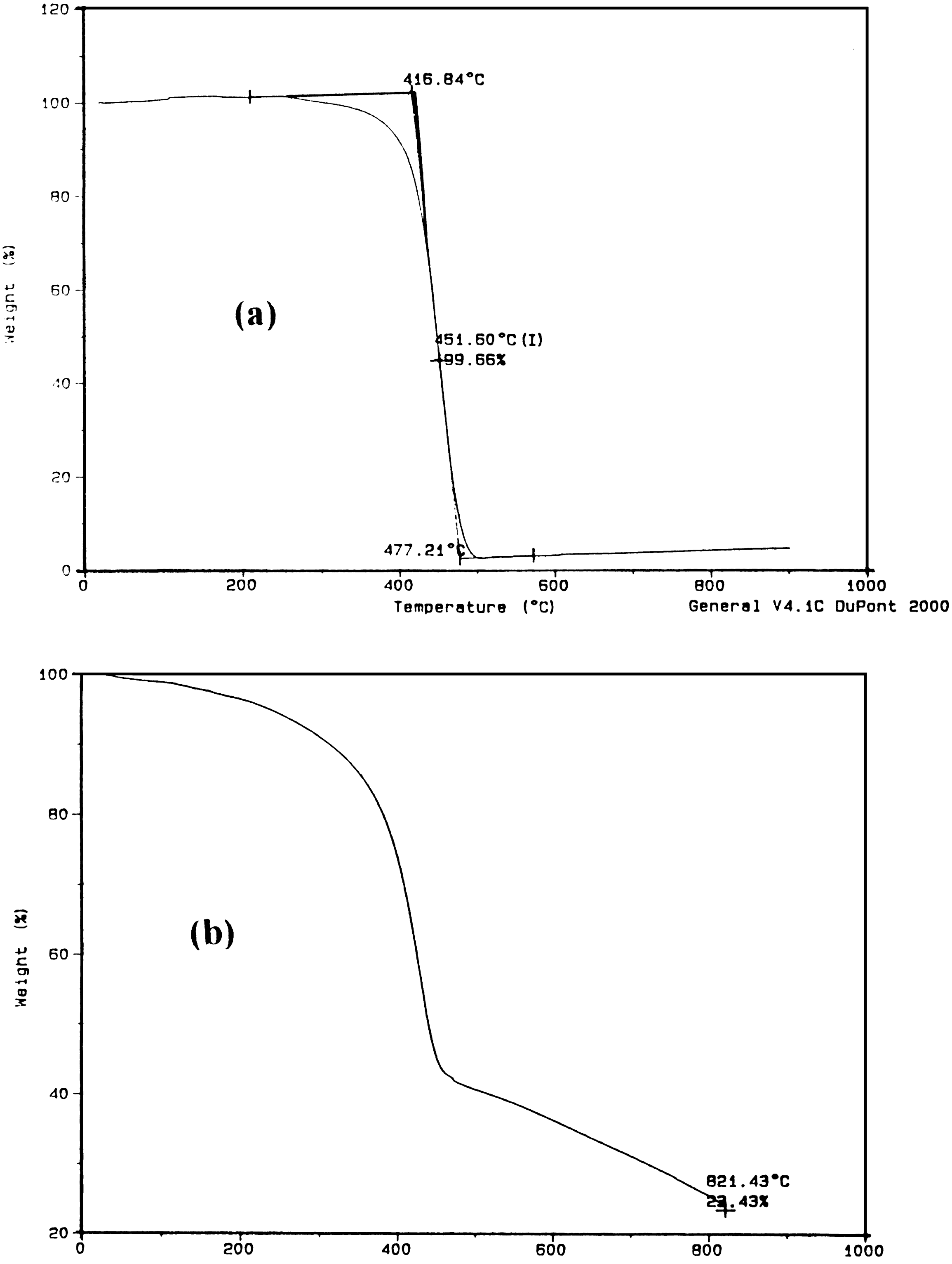

Fig. 4. TG curves at 20°C min^{-1} of the samples: (a) PPMS and (b) C_{70}-PMS copolymer.

mixed solvents of Na_xC_{60} obtained by the reaction of C_{60} with sodium naphthalene under exposed air is hardly soluble in any common organic solvents and could thus readily be removed from the resultant polymers by filtration. Thus, this unknown strong LS peak at 17.61 ml (ret. vol.) may be due to fullerols with just enough of some initiator fragment or monomer attached to make it soluble in THF.

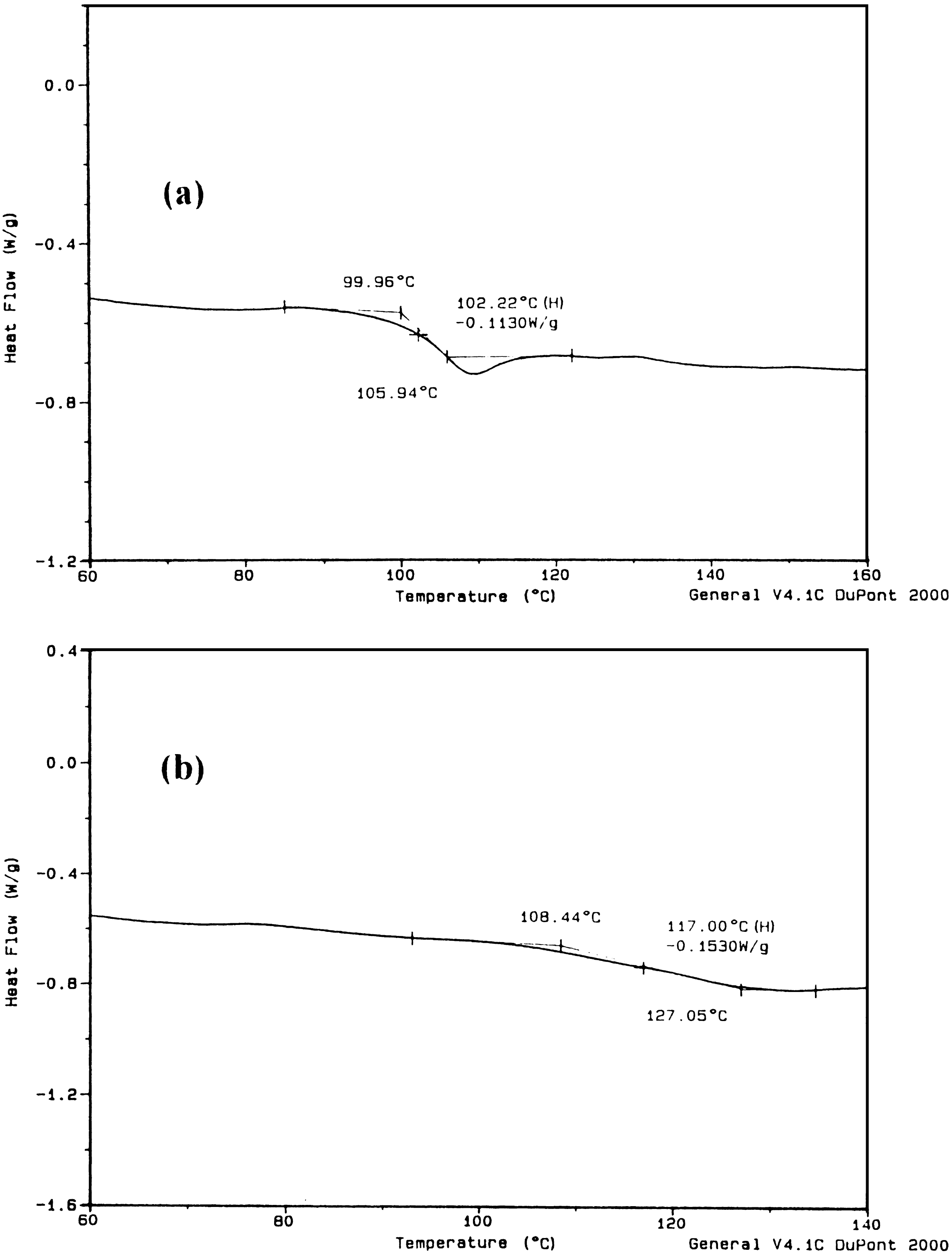

Fig. 5. DSC spectra of: (a) PPMS and (b) C_{70}-PMS copolymer.

Fig. 2 shows UV–VIS absorption spectra in THF of pure PPMS and C_{70}-PMS copolymer in room temperature. In the UV region, the strong absorption bands at 235, 256, 262 and 270 nm corresponding to the copolymer are in general agreement with those of the PPMS reference (230, 257, 262, and 270 nm), but their relative intensities are very different. After PPMS chains are attached covalently onto the [70]fullerene core, the first two peaks corresponding to the parent polymer move slightly to the higher wavelengths, and their signal intensities, especially signal at 257 nm, are apparently larger than those of the last two peaks. Furthermore, the covalent graftings of multiple PPMS chains onto the C_{70} core result in the marked enhancement of the absorption degree at longer wavelengths, probably because lower symmetry of [70]fullerene grafted onto the PPMS backbone relaxes the forbiddingness of the longest wavelength transition [10].

The FTIR spectra of the C_{70}-PMS copolymer, PPMS, C_{70} and C_{70}-doped PPMS polymer were shown in Fig. 3. Because of the overwhelming contributions of multiple PPMS chains in the polymer structure, which may lead to a great encapsulation to C_{70} core, the observed IR spectrum of copolymer is very similar to that of pure PPMS and gives no any information concerning polymer structure. Comparison of the spectrum of the copolymer with that of C_{70}-doped PPMS polymer containing the same fullerene content shows that, the latter one seems to be a simple superposition of two spectra corresponding to C_{60} and pure PPMS, demonstrating that C_{70} molecules have indeed incorporated covalently into the PPMS backbone. Similarly, ^{13}C NMR results of the C_{70}-PMS copolymer gives no useful information concerning structure. As we discussed in the section of FTIR spectrum of copolymer, the multiple unsubstituted PPMS chains in the copolymer structure are the overwhelming contributions due to the steric restrictions. Thus, the relative intensities of the ^{13}C NMR signals of functionalized [70]fullerene cages should be too low to separate from the background noises in the ^{13}C NMR spectrum. On the other hand, the locations of ^{13}C NMR peaks of [70]fullerene attached into the PPMS backbone are mainly in the aromatic region (130–160 ppm) in which the strong ^{13}C signals of the *p*-methylstyl groups appear. It is thus comprehensible that the structure changes of this copolymer with lower [70]fullerene content cannot be observed.

As shown in Fig. 4, after the parent polymer was bonded onto the [70]fullerene core, its thermal stability decreased apparently. This result differs greatly from that of the star-shaped C_{70}-substituted polystyrene [32] or, that of [60]fullerene-containing polymer prepared by the same synthetic method [37]. DSC analysis (see Fig. 5) indicated that C_{70}-PPM has a single high glass transition temperature (117.0 versus 108.4°C for pure PPMS polymer), this being congruent with its chemically modified structure. The bulky C_{70} cage incorporated covalently to the PPMS polymer should hinder the linear PPMS segments to fold properly and result in an increase in the glass transition temperature.

4. Conclusions

The C_{70}-PMS copolymer was prepared in sodium naphthalene-initiated anionic polymerization reaction. This copolymer exhibits the lower intrinsic viscosity and higher absolute molecular weight compared with linear polystyrene at equal retention time, suggesting that the copolymer possess star-shaped structure. The covalent graftings of multiple polystyrene chains onto the C_{70} core result in the marked enhancement of the absorption degree at longer wavelengths, and in the increase of glass transition temperature. Due to the overwhelming contributions of multiple PPMS chains in the polymer structure, which may lead to a great encapsulation to C_{70} core, both the IR spectrum and ^{13}C NMR spectrum of copolymer give no useful information concerning polymer structure. Further characterization and study of the properties of this material are currently being investigated.

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