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Synthesis and characterization of the narrow polydispersity fullerene-end-capped polystyrene

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Summary

A living free radical polymerization process was adopted to synthesize a narrow polydispersity fullerene-end-capped polystyrene(NPFECPS). The UV-Vis, DSC, GPC demonstrated that fullerene(C_{60}) was chemically bonded to polystyrene successfully, and C_{60} was almost monosubstituted. The NPFECPS can be dissolved in a variety of solvents, such as THF, toluene, trichloromethane, and so on. The good photoconductivity is also found for NPFECPS.

Introduction

Polymeric fullerene derivatives have attracted much interested in view of the peculiar electrooptical properties of materials containing C_{60} homogeneously dispersed in the polymers[1]. Various methods to chemically modify the fullerene have been reported in the last few years. The preparation of polymeric fullerene derivative was generally complicated by multiple substitution, and usually obtained crosslinked products[2-4]. In order to improve its processability, it is desirable to obtain soluble polymeric C_{60} derivatives. Recently, several soluble polymeric C_{60} derivatives have been achieved, such as multisubstituted polystyrene-fullerene, which were designated 'flagellance" [5]. Frechet and co-workers have reported the synthesis of a dendrimer with a fullerene core[6,7]. Monosubstituted polymeric C_{60} derivatives have been also reported[8,9]. These C_{60} derivatives retain both the electronic properties of fullerene moiety and the solubility and processability of polystyrene. So far, the synthetic methods in the current literature are based on the reaction of functional polymers with C_{60}, for instance, amino-functional polymers[8], azido-substituted polystyrene[9], etc. Other approaches are based on polycondensation of monomers with attached fullerene[10,11], and so on.

In this paper, we give a method to synthesized the narrow polydispersity fullerene-end-capped polystyrene(NPFECPS). The synthesis is based on the reaction of TEMPOL(4-hydroxy-2,2,6,6-tetramethyl-piperidinyloxy)-terminated polystyrene with C_{60}, and also found that these NPFECPS have good photoconductivity.

Experimental part

Materials: Styrene, benzoyl peroxide(BPO) and toluene were purified according to

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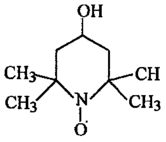
the usual procedures. TEMPOL used for polymerization was prepared by Zhang's method[12]. C_{60} (99.5%wt) was purchased from Beijing University. Other chemicals (research grade) were used as received.

Polymerization: The TEMPOL-terminated polystyrene were synthesized by living free radical polymerization. The process comprised heating a mixture of styrene, free radical initiator(BPO), and stable free radical(TEMPOL), which was carried out under nitrogen, at 95°C for 70h, yielded a TEMPOL-terminated polystyrene with a polydispersity of 1.16 (See table 1, III). In this paper, HPS denoted the sample III in table 1. The general synthetic route is shown in scheme I.



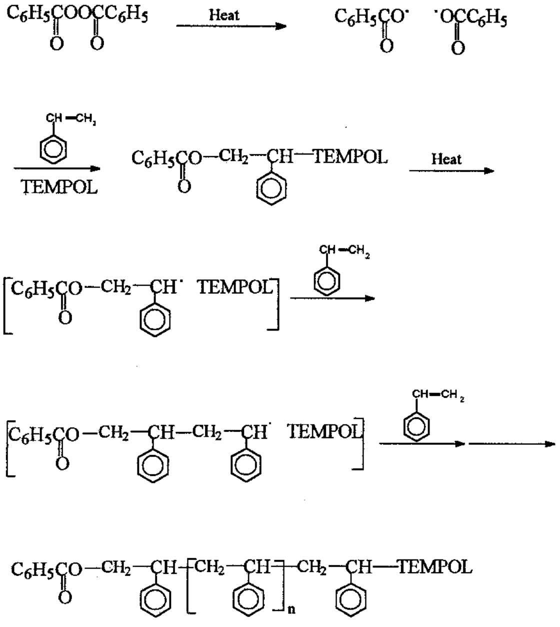
TEMPOL

Table 1. Polymerization of styrene(TEMPOL/BPO=1.1)

sample	reaction time (h)	conv.(%)	Mn(10^{-3})	Mw(10^{-3})	PD
I	2	22.0	7.7	11.0	1.42
II	20	26.5	10.9	14.4	1.32
III	70	31.1	12.2	14.9	1.16

The narrow polydispersity fullerene-end-capped polystyrene(NPFECPS) were

Scheme I

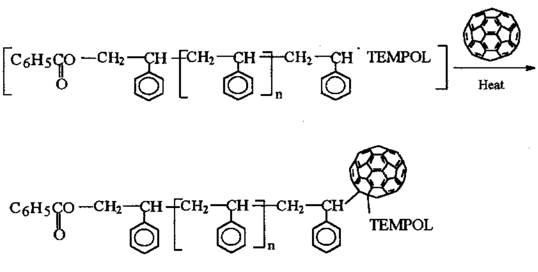


synthesized by the reaction of TEMPOL-terminated polystyrene with fullerene(C_{60}), which was performed under 95°C for 24 h. The data of the reaction were summarized in table 2, and the general synthetic route is shown in scheme II.

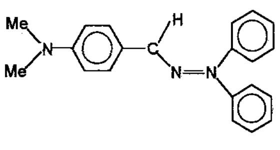
Table 2. Reaction of TEMPOL-terminated polystyrene(HPS) with C_{60}

sample	C_{60}(mg)	HPS(g)	yield(%)
HPSC_{60}-I	25	1.0	90
HPSC_{60}-II	60	1.0	86

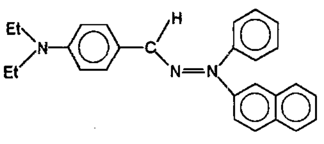
Scheme II



Preparation of Double-Layered Photoreceptor Device and Measurement of its Photoconductivity: The Double-layered photoreceptor device (P/R) was made by coating an interface layer(IFL) of polyamide(PA), a charge generation layer(CGL) of polymer which we have synthesized, and a charge transportation layer(CTL) of DMH-PC (1:1 by weight)or NP-PC (1:1 by weight)on an aluminium plate, in order. Here, the DMH and NP denote the hydrazone, and PC denotes the polycarbonate. The chemical structures of DMH and NP are shown below:



DMH



NP

A GDT-II model photoconductivity measuring device was used with a 5 W, 24 V visible lamp as light source to plot the photoinduced discharge curve(PIDC) of the P/R. In this measurement, the surface of the P/R was negatively charged, and hole charge carriers were generated in CGL and injected into the CTL under exposure. From PIDC, we obtained ΔV%, which is the percentage of potential discharge after 1 s of exposure, and $t_{1/2}$, which is the time from original potential to it's half value under exposure. The $t^{-1}_{1/2}$ can indicate photoconductivity. The bigger the $t^{-1}_{1/2}$, the higher the photoconductivity.

Results and discussion

All samples can be dissolved in THF easily. The THF solution of HPSC_{60}-I or

HPSC_{60}-II is golden brown. Figure 1 depicts the UV spectra of pure C_{60} (a), TEMPOL-terminated PS(b), and C_{60}-end-capped PS (c and d), The absorption of HPS occurs at 254 nm, while those of C_{60} and its derivatives are situated at 254, 296 and 330 nm. The spectra of C_{60} derivatives are obviously different with pure C_{60}. Because of destruction of the conjugation of C_{60}, the peaks at 330 nm of the derivatives are suppressed, and becomes a shoulder peak. Meanwhile, the peak at 296 nm becomes sharp. This result shows that it is true that C_{60} has reacted with TEMPOL-terminated polystyrene. The spectra of HPSC_{60}-I and HPSC_{60}-II (Fig.1 curve c and d) are similar to the mono-substituted samples[13], which suggests that the products here may be monosubstituted.

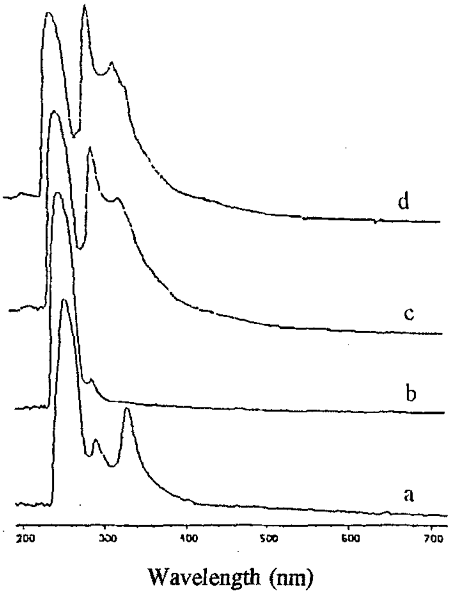


Figure 1. UV spectra of (a) C_{60}, (b) HPS, (c) HPSC_{60}-I and (d) HPSC_{60}-II

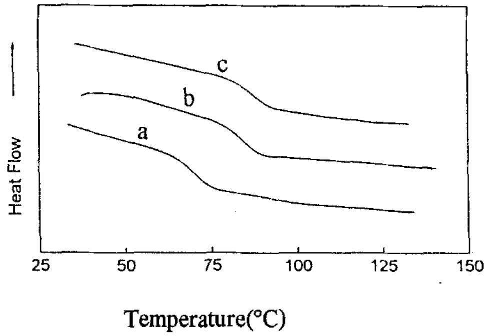


Figure 2. DSC curves of(a) HPS, (b) HPSC_{60}-I and (c) HPSC_{60}-II

Figure 2 shows the DSC curves of HPS, HPSC_{60}-I and HPSC_{60}-II. From this figure, we can see that, with the increasing of the content of C_{60} in the reaction, i.e., increasing of the content of C_{60}-bonded polystyrene in the final product, only one glass transition temperature was observed in each case, and Tg increased from 71.8°C (HPS) to 85.0°C (HPSC_{60}-I) and 88.4°C (HPSC_{60}-II). Of course, the Tg here may be referred to the miscible blend of HPS and C_{60}-bonded HPS, but this results also can demonstrate that C_{60} is chemically bonded into the polystyrene chain.

Gel permeation chromatography (GPC) measurements were performed on Shimadzu liquid chromatography LC-3A, using trichloromethane as eluent. GPC results are shown in figure 3. Curve a and a' are the GPC diagrams for HPS ($Mn=12.2\times10^3$, $Mw=14.9\times10^3$) at the detector wavelengths of 254 nm and 300nm, respectively. Pure polystyrene (HPS) can only be detected at 254 nm. HPSC_{60}-I and HPSC_{60}-II (curve b, b' and c, c') can be detected at 254nm and 300nm, and the molecular weights of HPS, HPSC$_{60}$-I and HPSC$_{60}$-II are very similar(See table 3), the polydispersity hardly have any changed. Because polystyrene can't be detected at the detactor wavelengths of 300nm, so the signal of HPSC$_{60}$-I and HPSC$_{60}$-II at 300nm is the signal of C$_{60}$ moiety. From above result, it can be concluded that the C$_{60}$ derivatives almost have only one type substituted products. The molecular weights of these products are summarized in table 3. The molecular weights of C$_{60}$-end-capped were just similar to the precursor HPS, which meant one TEMPOL-terminated polystyrene molecule reacted with one C$_{60}$ molecule and monosubstituted derivatives were formed.

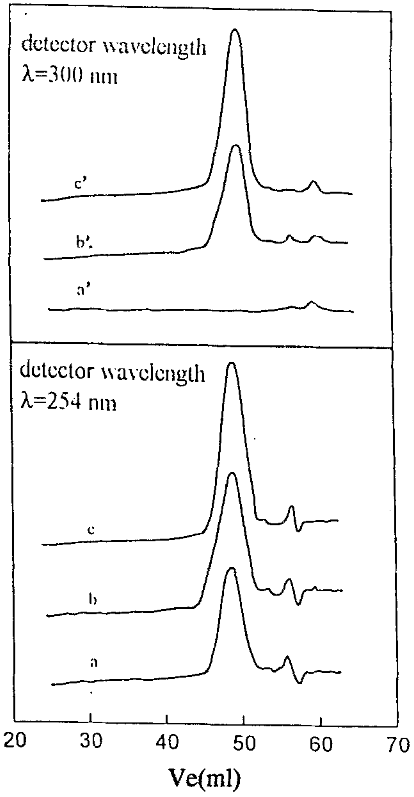


Figure 3. GPC curves of HPS(a, a'), HPSC$_{60}$-I(b, b'), and HPSC$_{60}$-II (c, c') with UV detector at 300nm or 254nm

Figure 4 is the photoinduced discharge curve (PIDC) of P/R from HPS, HPSC$_{60}$-I and HPSC$_{60}$-II. We can find that the pure HPS hardly have any photoconductivity, but the C$_{60}$-end-capped PS have good photoconductivity, their photoconductivity increases with increasing of the amount of bonded C$_{60}$. The data of the photoconductivity of the polymers are summarized in table 4. From table 4, we note that all polymers have a high charge acceptance (V_o=2000~3000V), when we used the NP as the CTL, the remain potential(V_R) is lower. The dark

Table 3. The results of molecular weights of HPS, HPSC$_{60}$-I and HPSC$_{60}$-II.

sample	wavelength (nm)	Mn (10^{-4})	Mw (10^{-4})	PD
HPS	254	1.22	1.41	1.16
	300	/	/	/
HPS-I-C$_{60}$	254	1.43	1.58	1.10
	300	1.26	1.44	1.14
HPS-II-C$_{60}$	254	1.45	1.62	1.12
	300	1.31	1.50	1.14

discharge is small (R_d=10~35V/s), while the rate of photodischarge is high(Rp= 750~ V/s).The more the bonded C_{60}, the higher the photoconductivity. meanwhile, the CTL influences the photoconductivity obviously, the NP-PC as the CTL is better than DMH-PC, the $t_{1/2}$ of HPSC$_{60}$-II by using NP as it's CTL is about 2.63s, and is about 8.33s by using DMH as it's CTL. The remain potential of HPSC$_{60}$-II by using DMH-PC (V_R =1549V) as it's CTL is higher than that by using NP-PC (V_R =90V). This result may relate to the matching of energy for CTL and CGL. Because of this study is just a preliminary result, more detailed work is needed on this study.

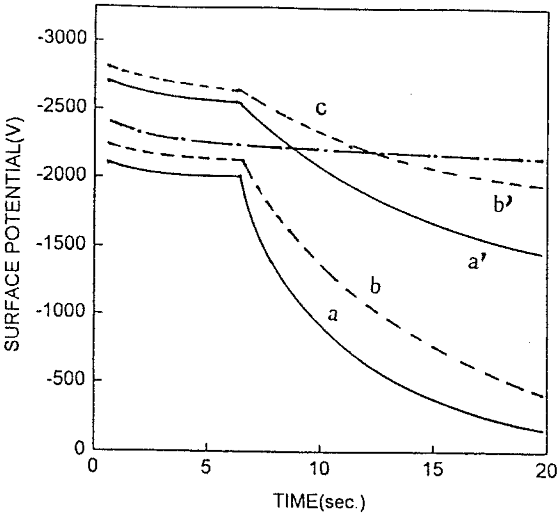


Figure 4. PIDC of P/R from:(—·—·—) HPS, (..........) HPSC$_{60}$-I, (———) HPSC$_{60}$-II.

curve a, b, c: the CTL is NP

curve a', b' : the CTL is DMH

Table 4. Photoconductivity of HPS, HPSC$_{60}$-I and HPSC$_{60}$-II.

CGL	CTL	V_o(V)	V_R(V)	R_d(V/s)	R_P(V/s)	ΔV(%)	$t_{1/2}$	$t^{-1}_{1/2}$
HPS	NP-PC	2363	2090	13.2	0	0.83	9.9	/
HPSC$_{60}$-I	NP-PC	2180	358	29.6	500	21.2	4.55	0.22
	DMH-PC	2773	1909	19.8	250	12.1	9.9	/
HPSC$_{60}$-II	NP-PC	2045	90.2	34.7	750	30.2	2.63	0.38
	DNH-PC	2681	1549	25.2	250	16.3	8.33	0.12

* The thickness of IFL is about 3.0 μm.

**The maximum value of $t_{1/2}$ in the device is 9.9.

In conclusion, C_{60}-end-capped polystyrene was successfully prepared by reaction of TEMPOL-terminated polystyrene with C_{60}, and in which C_{60} was almost monosubstituted. The polymeric C_{60} derivatives can be dissolved in a variety of solvents, such as THF, toluene, trichloromethane, and so on. Through the reaction of stable free radical terminated polymers with C_{60}, it is expected that C_{60} can be bonded into various polymer chains. Polystyrene C_{60} derivatives have good photoconductivity. The further study is continued in our laboratory.

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