Synthesis of a Water Soluble, Monosubstituted C_{60} Polymeric Derivative and Its Photoconductive Properties

Junwei Yang, Lang Li, and Changchun Wang*

Department of Macromolecular Science, Fudan University and Key Laboratory of Molecular Engineering of Polymers, Ministry of Education, Shanghai, 200433, P. R. China

Received December 4, 2002; Revised Manuscript Received May 19, 2003

ABSTRACT: Atom transfer radical polymerization (ATRP) catalyzed by *N,N′,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA)/CuBr was performed to synthesize poly(*tert*-butyl acrylate) with predictable molecular weight, low polydispersities, and well-defined bromine end groups. The bromine end groups have been substituted by azides. Then C_{60} end-capped poly(*tert*-butyl acrylate) was synthesized by the reaction of C_{60} with PtBA−N_3 in DMF. GPC measurement showed that C_{60} was chemically bonded to the end chain of poly(*tert*-butyl acrylate); i.e., the final products (PtBA−C_{60}) were monosubstituted. ^{1}H NMR, FTIR, and UV−vis measurements confirmed that the water-soluble, monosubstituted C_{60} derivatives of poly(acrylic acid) (PAA−C_{60}) have been obtained by hydrolysis of PtBA−C_{60}. The photoconductivities of PtBA−C_{60} and PAA−C_{60} were measured by photoinduced xerographic discharge technique. Experimental results showed that C_{60} bonded in the polymers is the headstream of the photoconductivity, and an increase of the C_{60} content in C_{60} polymeric derivatives could improve the photoconductivity dramatically. The microstructures of CGL are very important for the photoconductive properties, and perfect hole-transport channels in the CGL will improve the photoconductivity notably.

Introduction

Because of the wide range of interesting features of the C_{60} molecule, many C_{60} polymeric derivatives have been prepared in recent years.[1−3] The hydrophobic nature of C_{60} and its unique shape render this molecule very interesting for its potential use in superconductors, ferromagnets, lubricants, photoconductors, catalysts, medical materials, etc. But a wider application of fullerenes is heavily limited by their poor solubility in aqueous media, especially for biological applications. Now, several approaches have been explored for preparation of water-soluble C_{60} derivatives,[4−8] such as water-soluble fullerene carboxylic acid derivatives,[4,5] fullerene amino acid derivatives,[6,7] and peptide-functionalized C_{60} derivatives.[8] Bonding of C_{60} into water-soluble polymers is another important approach for preparation of water-soluble C_{60} derivatives.[2,9,10]

Preparation of soluble polymeric C_{60} derivatives usually failed due to C_{60} acting as a cross-linker. Therefore, many attempts have been conducted to prepare soluble polymeric C_{60} derivatives with well-defined structures. Samulski et al.[11] first reported the preparation of “flagellenes” by reacting C_{60} with polystyryllithium. Our group[12] reported that the addition of polystyryl radicals from TEMPOL-terminated polystyrene onto C_{60} can form monosubstituted C_{60} derivatives. Cloutet et al.[13] prepared hexafullerene stars via hexaazido star-shaped polystyrene synthesized by carbocationic polymerization. Until now, many polymeric C_{60} derivatives have been prepared. Recently, a new effective and attractive method of “living”/controlled radical polymerization, atom transfer radical polymerization (ATRP), was developed.[14,15] Coessens and Matyjaszewski[16] reported the end group transformation method of polymers prepared by ATRP. They found that bromine end functionalized polystyrene as well as polyacrylate could be efficiently converted to azide end functionalized polymer, and its yield almost approached 100%. Meanwhile, Hawker[17] reported a simple and versatile method to prepare polystyrene C_{60} derivatives by the cycloaddition reaction of azide end group functionalized polystyrene with C_{60}. Then it is reasonable that preparation of monosubstituted C_{60} polymeric derivatives from the reaction of azide end functionalized polymers with C_{60}.

In this paper, we prepared a new type of water-soluble monosubstituted C_{60} derivatives of poly(acrylic acid) based on ATRP. Bromine end group functionalized poly(*tert*-butyl acrylate) with narrow molecular weight distribution was synthesized by ATRP first. Then a nucleophilic substitution reaction was performed to substitute the bromine with azide group. Finally, the well-defined monosubstituted C_{60} derivatives of poly(*tert*-butyl acrylate) (PtBA−C_{60}) was prepared by the reaction of azide end group functionalized poly(*tert*-butyl acrylate) with C_{60}. PAA−C_{60} was obtained by hydrolysis of PtBA−C_{60} (Scheme 1). All these polymeric C_{60} derivatives can be used as biomedical materials and photoconductive materials. In this paper, photoconductive measurements of these monosubstituted C_{60} polymeric derivatives were carried out.

Experimental Section

Materials. The monomer, *tert*-butyl acrylate (tBA), was vacuum distilled and stored at −15 °C for use. CuBr from Shanghai Zhenxin Chemical Reagent Factory was purified as described elsewhere.[14] PMDETA (98%) and methyl 2-bromopropionate (2-MBP, 97%) were obtained from Fluka and used without further purification. C_{60} (99.9%) from Wuhan University (China) was used as received. Stearyl 2-bromopropionate (2-SBP) was prepared in our lab. Sodium azide (NaN_3) was recrystallized from ethanol. 1,2-Dichlorobenzene was distilled under reduced pressure. All other reagents were used as received.

Synthesis of PtBA—Br by ATRP. A typical procedure is as follows: A glass tube was charged with tBA (4.0 g, 31.2 mmol), CuBr (44.4 mg, 0.312 mmol), PMDETA (16.3 μL, 0.312 mmol), and 2-MBP (8.7 μL, 0.312 mmol). Sealed with a rubber septum, the tube was degassed with three freeze−vacuum−thaw cycles. The tube was placed in an 80 °C oil bath, and the reaction was continued for 12 h. Then the tube was

---

* To whom correspondence should be addressed.

10.1021/ma025909b CCC: \$25.00 © 2003 American Chemical Society
Published on Web 07/12/2003

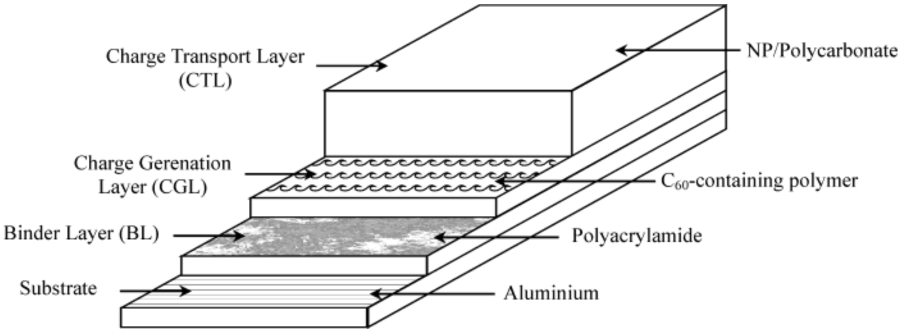

Figure 1. Scheme of dual-layer photoconductor.

Scheme 1. Synthesis Procedure of Monosubstituted C_{60} Derivatives of PAA

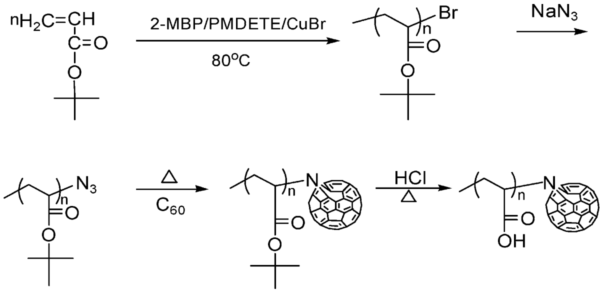

Table 1. Summarized Data of PtBA−Br Synthesized by ATRP and Its Fullerenation Products

precursor	M_n (M_w/M_n)	product	M_n (M_w/M_n)	C_{60} (wt %)[a]
PtBA−Br−1	10 600 (1.5)	PtBA−C_{60}−1	11 000 (1.4)	1.50
PtBA−Br−2[b]	13 200 (1.4)	PtBA−C_{60}−2	13 200 (1.5)	1.40
PtBA−Br−3	20 000 (1.3)	PtBA−C_{60}−3	22 100 (1.3)	0.38
PtBA−Br−4[b]	26 500 (1.3)	PtBA−C_{60}−4	26 500 (1.3)	0.54
PtBA−Br−5	45 500 (1.4)	PtBA−C_{60}−5	50 200 (1.3)	0.72

[a] All these calculations are based on the absorbance of C_{60} at 330 nm in UV−vis spectra. [b] These polymers were initiated by 2-SBP.

removed from the oil bath, and the reaction mixture was diluted with ethyl ether. The solution was filtered through a neutral alumina column to remove the catalyst. Ethyl ether was then removed by evaporation under reduced pressure. The product was dried in vacuo at 60 °C (yield 88%). ^{1}H NMR ($CDCl_3$): $\delta = 1.31-1.52$ ($-C(C\mathbf{H}_3)_3$), 1.83 ($-C\mathbf{H}_2-$), 2.22 ($-C\mathbf{H}(CO-)-$) ppm. FTIR (film): $\nu = 2900-3000$ ($-CH_3$ and $-CH_2-$), 1728 ($-CO-$) cm^{-1}.

Preparation of PtBA—N_3. A 0.066 mmol sample of PtBA−Br was weighed into a 25 mL round-bottom flask, and 42.8 mg (0.658 mmol) of NaN_3 was dissolved in 20 mL DMF and then added into the flask. The solution was stirred and allowed to react at 25 °C for 8 h. The product was precipitated in methanol/water (50 vol %/50 vol %), and the white precipitate was washed several times with water to remove the unreacted NaN_3, and then the product was dried under vacuum at 25 °C (yield 98%). ^{1}H NMR ($CDCl_3$): $\delta = 1.31-1.66$ ($-C(C\mathbf{H}_3)_3$), 1.83 ($-C\mathbf{H}_2-$), 2.22 ($-C\mathbf{H}(CO-)-$) ppm. FTIR (film): $\nu = 2900-3000$ ($-CH_3$ and $-CH_2-$), 2114 ($-N_3$), 1728 ($-CO-$) cm^{-1}.

Preparation of PtBA—C_{60}. A 1.50 g (0.033 mmol) sample of PtBA−N_3, 35.2 mg (0.049 mmol) of C_{60}, and 10 mL of 1,2-dichlorobenzene were charged into a round-bottom flask equipped with a spiral condenser. The flask was immersed in an oil bath at 130 °C. After refluxing for 48 h, the reaction solution was evaporated to remove 1,2-dichlorobenzene. After the product was dissolved with THF, excessive C_{60} was separated by centrifugation and supernatant was precipitated in hexane. The brown powder product was dried in vacuo at 60 °C (yield 95%). ^{1}H NMR ($CDCl_3$): $\delta = 1.31-1.60$ ($-C(C\mathbf{H}_3)_3$), 1.83 ($-C\mathbf{H}_2-$), 2.22 ($-C\mathbf{H}(CO-)-$) ppm. FTIR (film): $\nu = 2900-3000$ ($-CH_3$ and $-CH_2-$), 1728 ($-CO-$) cm^{-1}.

Preparation of PAA—C_{60}. A 1.0 g sample of PtBA−C_{60} and 10 mL of 1,4-dioxane were charged into a 25 mL round-bottom flask equipped with a spiral condenser. 3 mL concentrated hydrochloric acid was dropwise added slowly. Then the mixture was refluxed for 24 h, and the final product was precipitated in hexane. The dark brown product was dried under vacuum at 60 °C (yield 93%). ^{1}H NMR ($CDCl_3$): $\delta = 1.83$ ($-C\mathbf{H}_2-$), 2.22 ($-C\mathbf{H}(CO-)-$) ppm. FTIR (film): $\nu = 3000-3700$ ($-COOH$), 2900−3000 ($-CH_3$ and $-CH_2-$), 1728 ($-CO-$)cm^{-1}.

Characterization. GPC measurements were carried out using a HP series 1100 Chromatograph equipped with Zorbax HV1618 columns and RI/UV dual-mode detectors. The elution rate of THF was 1 mL/min, and the calibration was standard polystyrene. UV−vis spectra were taken on a Hitachi U-3000 spectrophotometer. ^{1}H NMR analysis was conducted on the Philips DMX500 spectrometer. FTIR spectra were obtained using the Magna 550 spectrophotometer. Dynamic light scattering (DLS) measurements were performed on a Malvern Autosizer 4700 spectrometer, and the applied laser wavelength (λ) in measurements was 514.5 nm.

Fabrication of Photoreceptor and Measurement of the Photoconductivity. The photoconductivity of monosubstituted C_{60} polymeric derivatives was studied in dual-layer photoreceptor. The photoreceptor was prepared by sequential coating an binder layer (BL) of polyacrylamide, a charge generation layer (CGL) of PtBA−C_{60} or PAA−C_{60}, and a charge transportation layer (CTL) of α-naphthalic hydrazone (NP)/polycarbonate (PC) blend onto an aluminum sheet (see Figure 1). Photoconductive measurements were carried out on a GDT II model photoconductive measuring device by the photoinduced xerographic discharge technique, which included charging, dark decaying, and illuminating steps. The intensity of exposure light (I) was tunable, where a halogen lamp (5 W, 24 V) was used as light source. In the measurement, the surface of the dual-layer photoreceptor was negatively charged in the dark with initial surface potential (V_0). As soon as the lamp was lit, charge carriers were generated in the CGL and injected into the CTL. The surface voltage decreased because of the recombination of photoinduced carriers with the surface charges. The photoinduced discharge curve was output by a computer, from which we can obtain V_0, residual potential (V_R), dark decaying rate (R_d), and the time from original surface potential to half under illumination ($t_{1/2}$). The photosensitivity could be characterized by $t_{1/2}$ and the half-decaying exposure energy ($E_{1/2}$), which is defined as the product of half-decaying time ($t_{1/2}$) and the intensity of exposure light (I), that is, $E_{1/2} = It_{1/2}$. A desired photoreceptor should have a large V_0 and a small V_R, R_d, and $t_{1/2}$. The smaller the $E_{1/2}$ is, the higher the photosensitivity of the photoreceptor is.

Results and Discussion

The typical atom transfer radical polymerization of *tert*-butyl acrylate (tBA) in acetone solution was reported by Matyjaszewski et al.[18] In this paper, bulk polymerization of tBA initiated by 2-MBP or 2-SBP under PMDETA/CuBr catalysis was conducted. The summarized data of PtBA−Br and PtBA−C_{60} are listed in Table 1. From Table 1, we can find that the molecular weights and polydispersities of PtBA−Br can be well

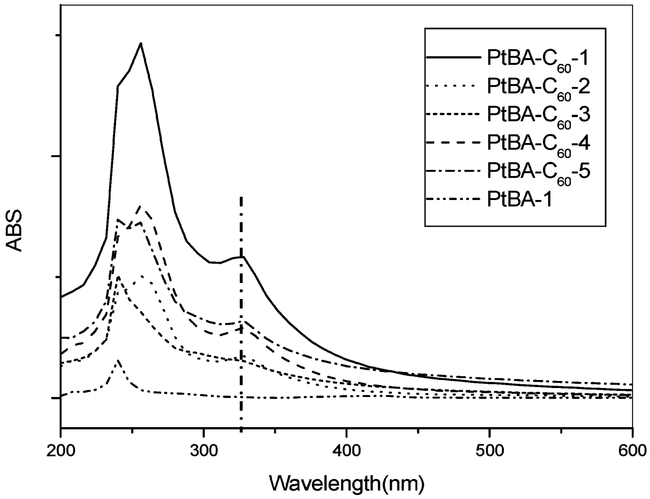

Figure 2. UV−vis spectra of PtBA−C$_{60}$−1 (8.9 × 10^{-4} g/mL), PtBA−C$_{60}$−2 (4.8 × 10^{-4} g/mL), PtBA−C$_{60}$−3 (8.2 × 10^{-4} g/mL), PtBA−C$_{60}$−4 (4.8 × 10^{-4} g/mL), PtBA−C$_{60}$−5 (7.8 × 10^{-4} g/mL), and PtBA−Br−1 (8.2 × 10^{-4} g/mL) in THF.

controlled. Bromine-terminated poly(*tert*-butyl acrylate) (PtBA−Br) reacted with excessive sodium azide in DMF at 25 °C to prepare the azide-terminated poly(*tert*-butyl acrylate) (PtBA−N$_3$). Because of the low concentration of terminal bromide atom, a high mole ratio of NaN$_3$/PtBA−Br(10/1) was supplied to expedite the reaction and to ensure the complete substitution of bromine with azide group. Because of the low concentration of terminated bromide atom in high molecular poly(*tert*-butyl acrylate), the methine proton signal of the −C**H**(COOR)−N$_3$ in the ^{1}H NMR spectra was too weak to be identified. Because a clear absorption band of azide group at 2114 cm^{-1} can be obtained even for the high molecular weight samples, we used FTIR spectra to monitor the process of the end group transformation.

Monosubstituted C$_{60}$ derivatives of polystyrene have been successfully prepared before.[19] Here, the same method was performed to prepare well-defined monosubstituted C$_{60}$ derivatives of poly(*tert*-butyl acrylate). The monosubstituted C$_{60}$ derivatives of poly(*tert*-butyl acrylate) is a brown powder and can be easily dissolved in various organic solvents such as CHCl$_3$, THF, DMF, etc., the summarized data are listed in Table 1. Because C$_{60}$ can dissolve in hexane, we can guarantee the unreacted C$_{60}$ can be separated by the process of precipitation. Figure 2 shows the UV−vis spectra of PtBA−C$_{60}$ and PtBA−Br in THF. PtBA−Br has only one absorption peak at 240 nm, while three absorption peaks of PtBA−C$_{60}$ are situated at 240, 256, and 330 nm. The difference of the adsorption peaks between PtBA−C$_{60}$ and PtBA−Br shows that the C$_{60}$ actually reacted with PtBA−N$_3$ and C$_{60}$ was covalently bonded to the poly(*tert*-butyl acrylate) chain. The C$_{60}$ contents in the PtBA−C$_{60}$ (Table 1) can be calculated based on the absorbance peak at 330 nm.[19] In comparison the C$_{60}$ content in PtBA with the theoretical data, we can find that the final polymer is a mixture of PtBA and PtBA−C$_{60}$, their miscibility is very good and it is hard to further separation.

To prove the chemical bonding between PtBA and C$_{60}$ further, gel permeation chromatography (GPC) measurements were carried out with RI and UV (330 nm) detector. Figure 3 shows the GPC curves of PtBA−Br−1 and PtBA−C$_{60}$−1. The precursor polymer (PtBA−Br−1) can only be detected by RID, while the PtBA−C$_{60}$−1 can be detected by RID and UVD at 330 nm. We also find that PtBA−Br−1 and PtBA−C$_{60}$−1 have very similar molecular weights. Because only the C$_{60}$ moiety bonded in the PtBA can be detected at the wavelength of 330 nm, the GPC trace of PtBA−C$_{60}$−1 detected at 330 nm strongly confirmed the covalent banding between C$_{60}$ and PtBA. Comparing the molecular weights of PtBA−C$_{60}$ with PtBA−Br in Table 1, we can conclude that the samples of PtBA−C$_{60}$ were monosubstituted.

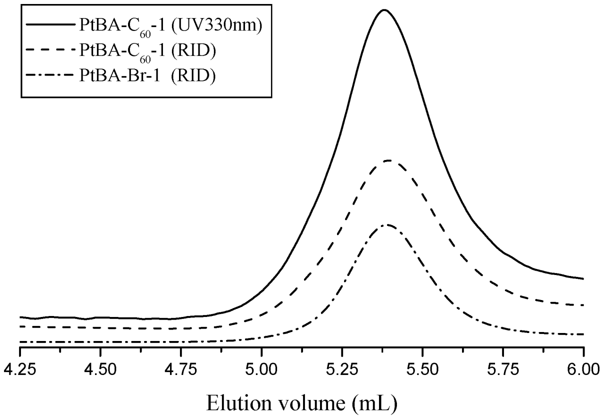

Figure 3. GPC elution curves of PtBA−Br−1 and PtBA−C$_{60}$−1 determined by RI and UV (330 nm) detectors, respectively.

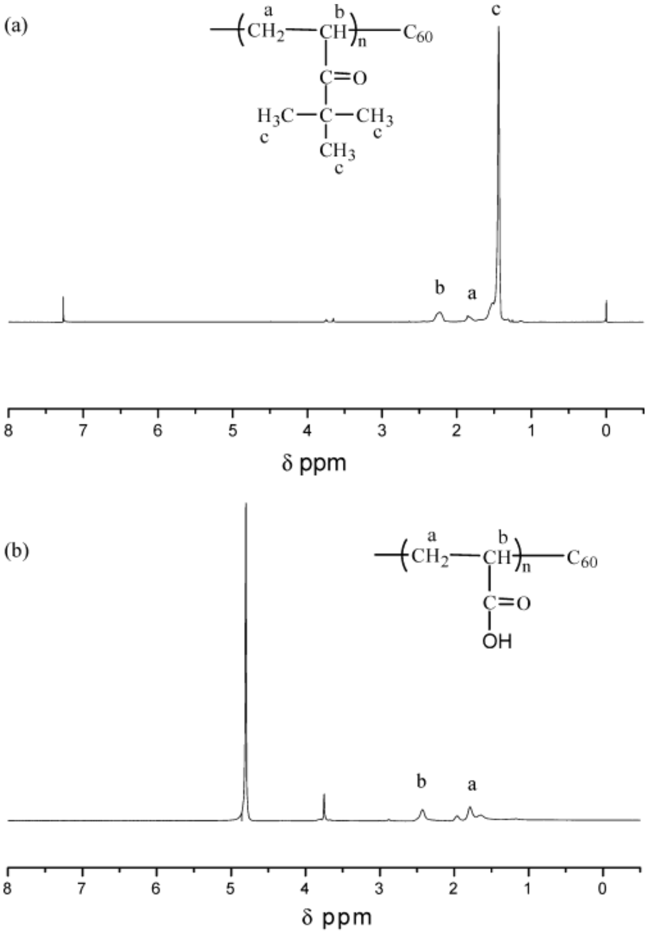

Figure 4. ^{1}H NMR spectra of (a) PtBA−C$_{60}$−1 in CDCl$_3$ and (b) PAA−C$_{60}$−1 in D$_2$O at 25 °C.

Through hydrolysis, three samples [PAA−C$_{60}$−1 (C$_{60}$ wt % = 2.75), PAA−C$_{60}$−2 (C$_{60}$ wt % = 2.43), PAA−C$_{60}$−4 (C$_{60}$ wt % = 0.95)] were obtained. Figure 4 is the ^{1}H NMR spectra of PAA−C$_{60}$−1 before and after hy-

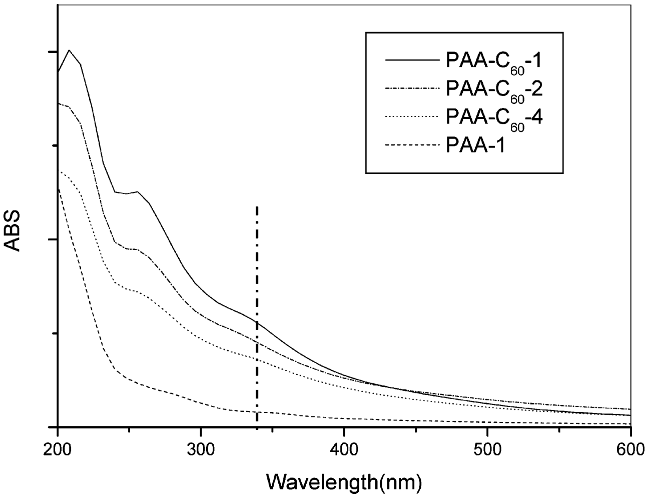

Figure 5. UV−vis spectra of PAA−1, PAA−C_{60}−1, PAA−C_{60}−2, and PAA−C_{60}−4 in H_2O.

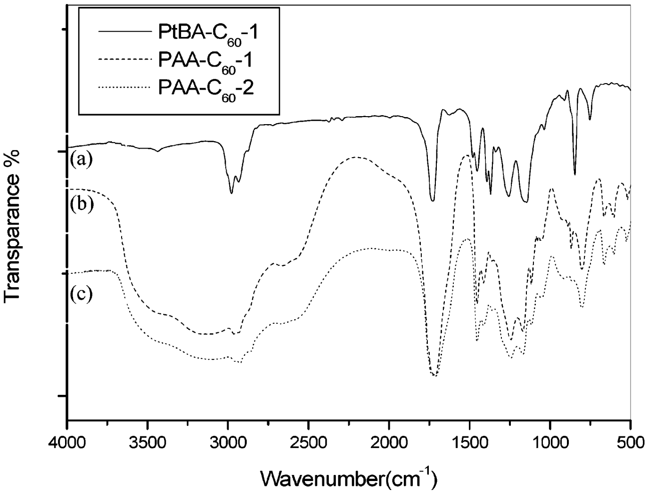

Figure 6. FTIR spectra of (a) PtBA−C_{60}−1, (b) PAA−C_{60}−1, and (c) PAA−C_{60}−2.

drolysis. From this figure, we can see that the proton signal $\delta = 1.44$ ppm of *tert*-butyl ($-C(C\mathbf{H}_3)_3$) completely disappeared after hydrolysis, and this result indicated that the hydrolysis is successful. The hydrolyzed polymeric products can be easily dissolved in water. The UV−vis spectra show that PAA−C_{60} possessed the typical characteristic absorption of polymeric C_{60} derivatives (Figure 5); i.e., the polymeric C_{60} derivatives have obvious absorption and no detail structure in the region 300−450 nm. FTIR spectra show that a strong absorption of the carboxyl group between 3000 and 3700 cm^{-1} is very clear (Figure 6). All of these results proved that the monosubstituted C_{60} derivatives of PAA were obtained.

Table 2. Photoconductive Data of PtBA−C_{60}−1, PAA−C_{60}−1 and PtBA−Br−1/C_{60}[a]

sample	C_{60} (wt %)	V_0 (V)	V_R (V)	$t_{1/2}$ (s)	$E_{1/2}$ (lx·s)	R_d (V/s)	ΔV (%)
PtBA−C_{60}−1	1.56	1130	148	0.79	190	31	54
PAA−C_{60}−1	2.66	1660	289	1.56	374	44	38
PtBA−Br−1/C_{60}[b]	1.50	1062	304	4.19	1006	14	19

[a] Note: exposure intensity of white light, 240 lx; CGL thickness, 1.0 μm; BL thickness, 1.0 μm, CTL thickness, 25 μm. [b] This sample is the blend of C_{60} and poly(*tert*-butyl acrylate).

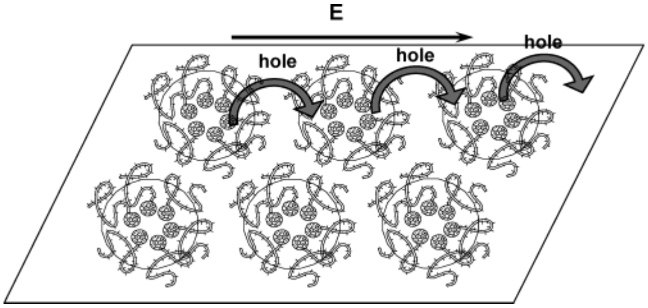

Figure 7. Cartoon of molecular packing of PAA−C_{60} in CGL film.

Table 2 shows the photoconductive data of PtBA−C_{60}−1, PAA−C_{60}−1, and the blend of PtBA−Br−1 and C_{60}. According to our previous work, poly(*tert*-butyl acrylate), as a nonconducting polymer, has no photoconductivity. After fullerenation, we can find that the polymeric C_{60} derivative possesses very good photoconductivity, its $t_{1/2}$ (the time from original surface potential to half under illumination) is about 0.79 s, which is much shorter than the $t_{1/2}$ (4.19 s) of the blend of PtBA−Br−1 and C_{60}. After hydrolysis, its photoconductivity decreased greatly; i.e., $t_{1/2}$ and $E_{1/2}$ (half-decaying exposure energy) increase a lot. What makes the big difference of photoconductivities before and after hydrolysis of PtBA−C_{60}? The difference of the microstructures in CGL might be the key factor. As a good photoconductor, CGL should generate more electron−hole pairs under light exposure, and then the holes could be transported to the photoconductor's surface quickly. PtBA−C_{60}, as a charge generation polymer, can form a homogeneous film, and the hole-transport channels can be well established in CGL. When this layer was exposed, holes will generate and transfer from one C_{60} molecule to another easily and furthermore go through CTL and finally arrive on the top surface of the photoconductor to neutralize the electrons on the surface. This whole process realizes the photoconductivity of this material. From Figure 1, we know that the BL (binder layer) is hydrophilic, and the CTL (charge transportation layer) is lipophilic. Between BL and CTL, it is CGL (charge generation layer), and the interface properties between CGL and CTL will change with the change of polarity of the CGL. When CGL is changed from lipophilic to hydrophilic, a new interface layer between CGL and CTL will form, and the holes must jump over the interface of CGL and CTL to finish the task of neutralization of the surface charges. This new interface layer will reduce the photoconductivity of PAA−C_{60}. At the same time, another more important factor must be considered, that is phase separation in CGL. The C_{60} moieties bonded in polymer chain will form microdomains, under the same electronic field (E), the transportation of holes will be hindered and retarded by the surrounding PAA layer (another new interface). If the holes want to finish the charge transportation, they must jump from one microdomain to another (see Figure 7), and the photoconductivity of PAA−C_{60} will decrease due to the hindrance. To prove the existence of the microdomains in CGL (Figure 7), the water solution of PAA−C_{60}−1 was measured by DLS. We found that the solution of PAA−C_{60}−1 is not a real solution, as the PAA−C_{60}−1 can form micelles in water, the hydrodynamic diameter is about 191 nm, and the polydispersity ($\mu_2/\langle\Gamma\rangle^2$) is 0.42 (Figure 8). This result hints that the hydrophobic moieties of C_{60} should form the core and the hydrophilic parts of PAA should form the shell in water solution. Can this core−shell

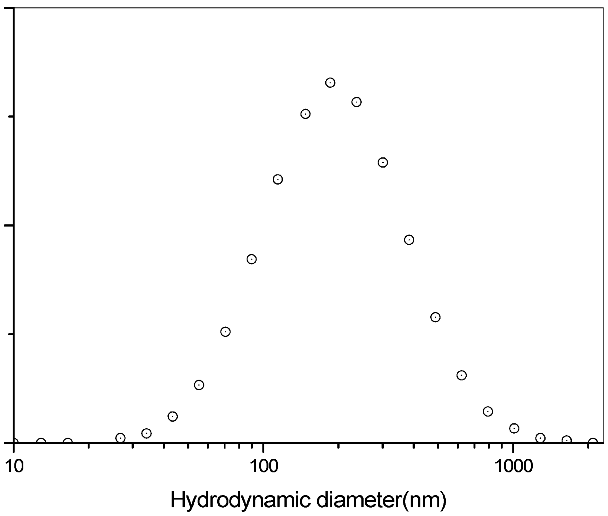

Figure 8. Hydrodynamic diameter curve of the PAA$-$C$_{60}$$-$1 in water.

structure of the PAA$-$C$_{60}$$-$1 in water be kept in the solid film? The TEM measurements answered this question. Figure 9 shows the TEM images of PAA$-$C$_{60}$$-$1 film. In these images, the microdomains of C$_{60}$ moieties bonded in PAA could be clearly identified, and the structures very like the illustration in Figure 7. Because C$_{60}$ and PAA are immiscible, when the film was cast from PAA$-$C$_{60}$$-$1 solution, the core$-$shell structure could be kept, C$_{60}$ moieties located in the center of the microdomains. When electronic field and light are supplied, the holes must overcome the hindrance of the PAA layer and jump to another microdomain of C$_{60}$ to realize the charge transportation. So, it is reasonable that the reduction of the photoconductivity of PAA$-$C$_{60}$ takes place.

From the above discussions, we can find that the good hydrophilic property is not suitable for our photoconductive system, so the detailed studies about photoconductivity were focused on PtBA$-$C$_{60}$. We prepared a new series of polymeric C$_{60}$ derivatives, the detailed information is listed in Table 3. From Table 3, we can see that the $t_{1/2}$ (the time from original surface potential to half under illumination) of the PtBA$-$C$_{60}$ under the same experimental conditions is in the following order, PtBA$-$C$_{60}$$-$I < tBA$-C_{60}$$-$II < PtBA$-C_{60}$$-$III < PtBA$-C_{60}$$-$IV. This order is in reverse proportion to the C$_{60}$ content bonded in polymer, and a linear relationship of $t_{1/2}{}^{-1}$ vs C$_{60}$ content can be obtained (Figure 10). The more C$_{60}$ bonded in the copolymers, the larger $t_{1/2}{}^{-1}$ and ΔV %, which indicate that the charge generation material possesses a higher efficiency of photogenerated carrier.

Table 3. Photoconductive Data of PtBA$-$C$_{60}$[a]

sample	C$_{60}$ (wt %)	V_0 (V)	V_R (V)	$t_{1/2}$ (s)	$E_{1/2}$ (lx·s)	R_d (V/s)	ΔV (%)
PtBA$-$C$_{60}$$-$I	0.82	835	113	0.6	144	13	58
PtBA$-$C$_{60}$$-$II	0.69	1260	156	0.75	180	39	55
PtBA$-$C$_{60}$$-$III	0.54	1260	179	1.0	240	26	50
PtBA$-$C$_{60}$$-$IV	0.48	1180	226	1.2	288	34	47

[a] Note: exposure intensity of white light, 240 lx; CGL thickness, 1.0 μm; BL thickness, 1.0 μm; CTL thickness, 15 μm.

From the above results, we can conclude that C$_{60}$ is the headstream of the photoconductiviy, and through covalent bonding of C$_{60}$ into the polymer chain, a new kind of good photoconductive material can be obtained.

Conclusion

Monosubstituted C$_{60}$ derivatives of poly(*tert*-butyl acrylate) were synthesized by reaction of C$_{60}$ with well-defined azide end functionalized poly*(tert*-butyl acrylate). Water-soluble C$_{60}$ derivatives of poly(acrylic acid) were prepared by hydrolysis of monosubstituted C$_{60}$ derivatives of poly(*tert*-butyl acrylate). GPC, ^{1}H NMR, FTIR, and UV$-$vis characterization indicated that the C$_{60}$ was chemically bonded to the end of poly(*tert*-butyl acrylate) and poly(acrylic acid); the polymeric C$_{60}$ derivatives were monosubstituted. The photoconductivities of PtBA$-$C$_{60}$ and PAA$-$C$_{60}$ were measured by the photoinduced xerographic discharge technique, and the photoconductivity of PtBA was dramatically enhanced

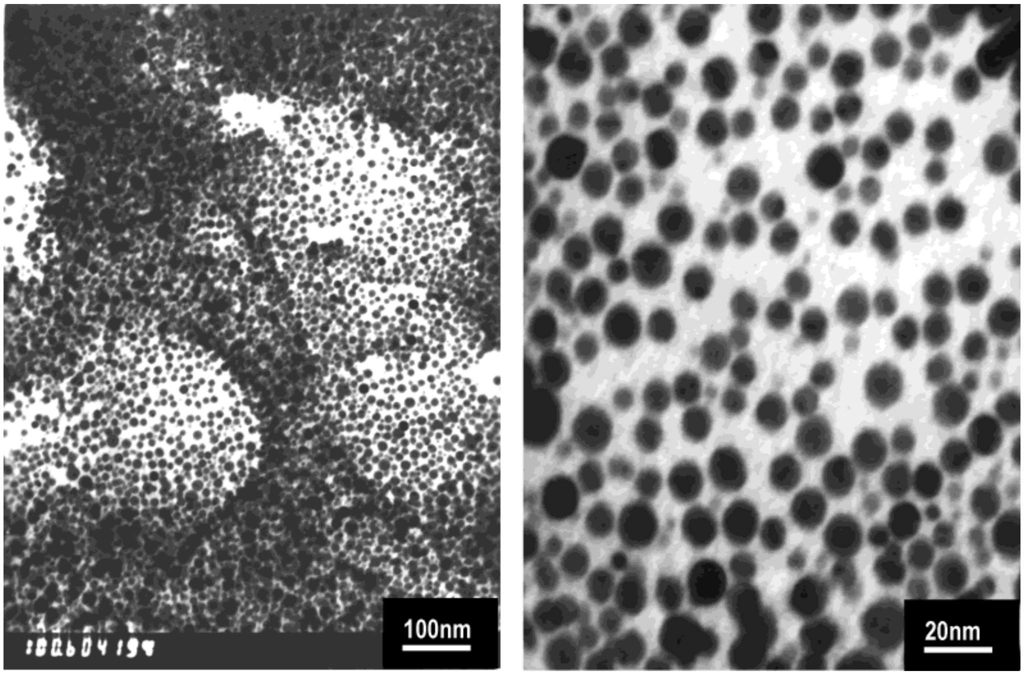

Figure 9. TEM images of PAA$-$C$_{60}$$-$1 film cast from water solution.

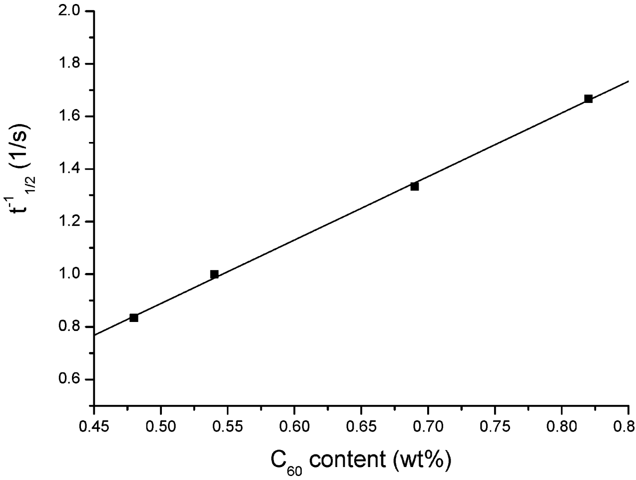

Figure 10. Plot of $t_{1/2}^{-1}$ (1/s) vs the C_{60} content in PtBA−C_{60}.

by combinations of C_{60}. The microstructures of CGL influenced the photoconductivity strongly. Perfect hole-transport channels in CGL will improve the photoconductivity notably. As a prediction, the water-soluble monosubstituted C_{60} derivatives of polymers will become a candidate of biomedical material, so related research work is underway in our lab.

Acknowledgment. This work was supported by National Science Foundation of China (Grant No. 50173005) and Foundation for University Key Teacher by Ministry of Education of China. Prof. M. Wang and Prof. H. Z. Chen are thanked for their help for the photoconductivity measurements.

References and Notes

(1) Mignard, E.; Hiorns, R. C.; Francois, B. *Macromolecules* **2002**, *35*, 6132−6141.
(2) Song, T.; Goh, S. H.; Lee, S. Y. *Macromolecules* **2002**, *35*, 4133−4137.
(3) Geckeler, K. E.; Samal, S. *Polym. Int.* **1999**, *48*, 743−757.
(4) Wang, N. X.; Sun, C. H.; Liu, W.; Zhang, L. X. *Chin. J. Org. Chem.* **2001**, *21*, 611−613.
(5) Cao, T. B.; Wei, F.; Yang, Y. L.; Huang, L.; Zhao, X. S.; Cao, W. X. *Langmuir* **2002**, *18*, 5186−5189.
(6) Bianco, A.; Da Ros, T.; Prato, M.; Toniolo, C. *J. Pept. Sci.* **2001**, *7*, 208−219.
(7) Andreev, S. M.; Babakhin, A. A.; Petrukhina, A. O.; Andreev, I. M.; Romanova, V. S.; Dubuske, L. M. *J Allergy Clin. Immun.* **2002**, *109*, S112−S113.
(8) Pantarotto, D.; Bianco, A.; Pellarini, F.; Tossi, A.; Giangaspero, A.; Zelezetsky, I.; Briand, J. P.; Prato, M. *J. Am. Chem. Soc.* **2002**, *124*, 12543−12549.
(9) Jiao, H.; Goh, S. H.; Valiyaveettil, S. *Macromolecules* **2002**, *35*, 1399−1402.
(10) Sun, Y. P.; Lawson, G. E.; Huang, W. J.; Wright, A. D.; Moton, D. K. *Macromolecules* **1999**, *32*, 8747−8752.
(11) Samulski, E. T.; Desimone, J. M.; Hunt, M. O.; Menceloglu, Y. Z.; Jarnagin, R. C.; York, G. A.; Labat, K. B.; Wang, H. *Chem. Mater.* **1992**, *4*, 1153−1157.
(12) Wang, C. C.; He, J. P.; Fu, S. K.; Jiang, K. J.; Cheng, H. Z.; Wang, M. *Polym. Bull. (Berlin)* **1996**, *37*, 305−311.
(13) Cloutet, E.; Fillaut, J. L.; Astruc, D.; Gnanou, Y. *Macromolecules* **1999**, *32*, 1043−1054.
(14) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614−5615.
(15) Matyjaszewski, K.; Patten, T. E.; Xia, J. H. *J. Am. Chem. Soc.* **1997**, *119*, 674−680.
(16) Coessens, V.; Matyjaszewski, K. *J. Macromol. Sci. Pure Appl. Chem.* **1999**, *A36*, 667−679.
(17) Hawker, C. J. *Macromolecules* **1994**, *27*, 4836−4837.
(18) Davis, K. A.; Matyjaszewski, K. *Macromolecules* **2000**, *33*, 4039−4047.
(19) Li, L.; Wang, C. C.; Long, Z. H.; Fu, S. K. *J. Polym. Sci. Pol. Chem.* **2000**, *38*, 4519−4523.
(20) Tao, Z. H.; Yang, W. L.; Wang, C. C.; Peng, C. J.; Fu, S. K. *Acta Polym. Sin.* **2000**, 584−589.

MA025909B