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Synthesis and Characterization of [60]Fullerene-poly(3-azidomethyl-3-methyl oxetane) and Its Thermal Decomposition

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A new functionalized fullerene derivative [60]fullerene poly(3-azidomethyl-3-methyl oxetane) (C_{60}-PAMMO) was synthesized for the first time using a modified Bingel reaction of [60]fullerene (C_{60}) and bromomalonic acid poly(3-azidomethyl-3-methyl oxetane) ester (BM-PAMMO). The product was characterized by Fourier transform infrared (FTIR), ultraviolet-visible (UV-vis), and nuclear magnetic resonance (NMR) spectroscopy analyses. Results confirmed the successful preparation of C_{60}-PAMMO. Moreover, the thermal decomposition of C_{60}-PAMMO was analyzed by differential scanning calorimetry (DSC), thermogravimetric analysis coupled with infrared spectroscopy (TG-IR), and in situ FTIR. C_{60}-PAMMO decomposition showed a three-step thermal process. The first step at approximately 150 °C was related to the cycloaddition of azido groups ($-N_3$) with [60]fullerene. The second step was ascribed to the remainder decomposition of the PAMMO main chain at approximately 230 °C. The final step was attributed to the burning decomposition of amorphous carbon, the main chain, N-heterocyclic and carbon cage at around 510 °C.

Introduction

Given the attractive chemical and physical properties of C_{60}, studies on its application are extensive since its macroscale synthesis,[1] which shows promising applications in medicine and material science. As C_{60} has good features such as thermal stability, antioxidation, etching resistance, good compatibility with propellant components, and beneficial for preventing aging.[2-5] Thus, C_{60} can replace carbon black as the solid rocket fuel additive that can increase the burning rate and combustion catalytic efficiency and decrease the amount of NO_x in the exhaust gas.[6-11] If some energetic groups, such as nitro group ($-NO_2$) and azido group ($-N_3$), were incorporated in the [60]fullerene cage, then a better fuel additive may be obtained.[12-26]

Usually, azide energetic material has higher thermal stability[27-33] and the thermal decomposition of azido group was ahead of the main chain and independent, which can help increase the energy and accelerate the decomposition of the propellant. Poly(3-azidomethyl-3-methyl oxetane) (PAMMO), a azido polymer, has attracted researchers' attention and has been used as energetic binder in propellant and explosive formulations because of its higher positive heat of formation, higher density, higher nitrogen content, and lower mechanical sensitivity.[34-39] Moreover, the terminal hydroxyl group of PAMMO can be easily modified through various reactions, such as esterification, acetalization, etherification, etc.[40,41] In this paper,

PAMMO was further functionalized *via* esterification with malonyl dichloride and subsequent brominate reaction to afford bromomalonic acid PAMMO ester (BM-PAMMO). BM-PAMMO easily reacts with C_{60} through a modified Bingel reaction[42] to afford an energetic fullerene derivative C_{60}-PAMMO. The thermal decomposition performance and decomposition mechanism of C_{60}-PAMMO were also examined in detail.

Experimental section

Chemicals and Apparatus

[60]fullerene was purchased from Henan Tianan Company. HMMO was purchased from Xiya Reagent. The 300-400 mesh silica gel was purchased from Qingdao Hailang. All the other chemicals were purchased from Chengdu Kelong Chemical Reagents Company. Dichloromethane was dried on P_2O_5 and redistilled under vacuum before use. N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were dried on anhydrous $MgSO_4$ and distilled under vacuum.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance DRX 400-MHz instrument with $CDCl_3$ as the solvent and tetramethylsilane as the internal reference. FTIR spectra were obtained on a Nicolet 6700 FT-IR spectrometer with a resolution of 4 cm^{-1} from 400 cm^{−1} to 4000 cm^{−1}. UV-vis spectra were recorded on UNICON UV-2102 PCS spectrometer with CH_2Cl_2 as the solvent. Differential scanning calorimetry (DSC) curves were

recorded on a SDT Q600 TGA-DSC instrument in flowing air at a heating rate of 10 °C/min. Thermogravimetry with infrared spectrometry (TG-IR) was performed using a Q500 thermogravimetric analysis (TGA) instrument in air at a heating rate of 10 °C/min. The molecular weights and the polydispersity index were obtained with gel permeation chromatography (GPC; LC-20A, Shimadzu) and the mobile phase was tetrahydrofuran (1.0 mL/min). The hydroxyl value (OHV) of PAMMO was determined by the acetic anhydride acetylation method.[43]

Synthesis

[60]Fullerene-poly(3-azidomethyl-3-methyl oxetane) (C_{60}-PAMMO) was synthesized in six steps, as shown in Scheme 1. First, Ts protected 3-hydroxymethyl-3-methyl oxetane (TMMO) was obtained *via* the reaction of 3-hydroxymethyl-3-methyl oxetane and tosyl chloride. With the use of $BF_3 \cdot OEt_2$ as catalyst and ethanol as initiator, TMMO was polymerized to produce monoethyl-terminated PTMMO. The azide substitution of PTMMO resulted to afford the monoethyl-terminated PAMMO. BM-PAMMO was synthesized by esterifying and then brominating of PAMMO and malonyl dichloride. Finally, BM-PAMMO was allowed to react with C_{60} through a modified Bingel reaction to get C_{60}-PAMMO.
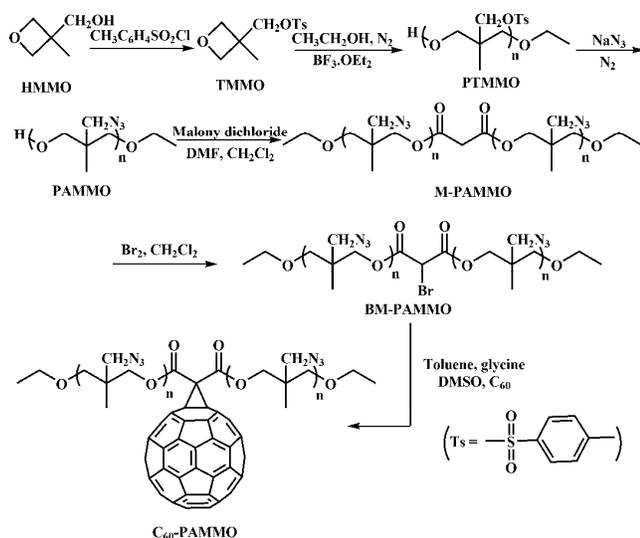
Scheme 1. Synthesis route of C_{60}-PAMMO.

Synthesis of TMMO.

20.97 g Tosyl chloride (0.11 mol) dissolved in 40 mL pyridine was added slowly into a flask containing 10.20 g 3-hydroxymethyl-3-methyl oxetane (0.10 mol). The mixture was reacted at -5 °C for 0.5 h under nitrogen atmosphere and then reacted at room temperature for 12 h. The mixture was filtered and the filtrate was added slowly into a vigorously stirred mixture of deionized water (200 mL) and crushed ice, which was maintained under stirring for another 2 h. A white precipitate appeared and was collected, washed with cold water thrice, and dried under vacuum to obtain a white powder of product (18.20 g, corresponding to a yield of 71.1%). Elemental analysis (EA): Found/%: C, 58.54; H, 5.85; S, 12.48. Calculated/%: C, 58.47; H, 5.88; S, 12.54. UV-vis (CH_2Cl_2) λ/nm: 205, 211, 237, 262, 273. IR (KBr) v/cm^{-1}: 2875 (v_s CH_2), 1598 (v_{as} C-

C aromatic ring), 1463 (δ CH_2), 1360 (v_{as} S(=O)_2), 1180 (v_s S(=O)_2), 1096 (δ_s C-H aromatic ring), 977 (v_{as} C-O-C oxetane, v_{as} S-O-C), 837 (v_s S-O-C), 665 (ω C-H aromatic ring). ^{1}H-NMR (CDCl_3, 400 MHz) δ/ppm: 7.83-7.38 (4H, m, aromatic ring), 4.39-4.35 (4H, dd, J = 16.9, 6.2 Hz, CH_2O oxetanic ring), 4.12 (2H, s, CH_2OTs), 2.47 (3H, s, CH_3 aromatic ring), 1.32 (3H, s, CH_3).

Synthesis of PTMMO.

1.85 g $BF_3 \cdot OEt_2$ (13.02 mmol), 1.20 g absolute ethyl alcohol (26.00 mmol) and 25 mL dry methylene chloride were introduced into a 100 mL three-neck flask equipped with a mechanical stirrer and thermometer. This mixture was stirred for 0.5 h under argon at (0–5) °C. A solution of 10 g TMMO (0.04 mol) in 20 mL methylene chloride was added dropwise to this reaction mixture. The reaction mixture was stirred at (0–5) °C for 18 h, and then the mixture was allowed to reach 35 °C and maintained for 25 h. Thereafter, the reaction was completed by adding 100 mL of saturated NaCl solution. The organic layer was washed with water (200 mL×3) and the mixture of water/methanol, dried over Na_2SO_4, and filtered and evaporated in vacuum to produce 9.70 g of PTMMO, with a yield of 87%. UV-vis (CH_2Cl_2) λ/nm: 236, 262, 273. IR (KBr) v/cm^{-1}: 2878 (v_s CH_2), 1598 (v_{as} C-C aromatic ring), 1460 (δ CH_2), 1358 (v_{as} S(=O)_2), 1176 (v_s S(=O)_2), 1098 (δ_s C-H aromatic ring), 966 (v_{as} C-O-C, v_{as} S-O-C), 833 (v_s S-O-C), 666 (ω C-H aromatic ring). ^{1}H NMR (CDCl_3, 400 MHz) δ/ppm: 7.76–7.34 (4H, dd, J = 12.8, 7.8 Hz, aromatic ring), 3.79 (2H, s, CH_2OTs), 3.43-3.11 (2H, q, J = 10.0, 6.3Hz, CH_2 ethyl), 3.07 (2H, s, CH_2O main chain), 2.43 (3H, s, CH_3 aromatic ring), 1.09-1.06 (3H, t, J = 4.8 Hz, CH_3 ethyl), 0.75 (3H, s, CH_3). Molecular Weight (by GPC): M_w=1534, M_n=1225, M_w/M_n=1.25.

Synthesis of PAMMO.

6.0 g NaN_3, 18.0 g PTMMO and 30 mL DMSO were introduced into a 100 mL three-neck flask equipped with a mechanical stirrer and thermometer. The reaction mixture was stirred under 100 °C for 120 h. Thereafter, the reaction solution was poured into 200 mL distilled water and extracted with dichloromethane (50 mL×3). The organic layer was washed with distilled water (200 mL×3), dried over Na_2SO_4, and filtered and evaporated in vacuum to produce 6.6 g of PAMMO, with a yield of 83%. UV-vis (CH_2Cl_2) λ/nm: 236, 284. IR (KBr) v/cm^{-1}: 2972 (v_{as} CH_2), 2876 (v_s CH_2), 2102 (v_{as} N_3), 1282 (v_s N_3), 1455 (v CH_2), 1378 (δ_s CH_3), 1355 (v CH_2), 1111 (v_{as} C-O-C). ^{1}H-NMR (CDCl_3, 400 MHz) δ/ppm: 0.94 (3H, s, CH_3 side chain), 1.14-1.22 (3H, t, J = 7.0 Hz, CH_3 ethyl), 3.21 (4H, m, CH_2O), 3.26 (2H, s, CH_2N_3), 3.69-3.33 (2H, q, J = 18.1 Hz, CH_2 ethyl). ^{13}C-NMR (CDCl_3, 100 MHz) δ/ppm: 75.68 (-CH_2O-), 68.36 (HOCH), 67.07 (-CH_2CH_3), 55.53 (N_3CH_2CCH_3), 40.80 (N_3CH_2CCH_3), 18.06 (-CH_2N_3), 14.99 (-CH_3). Molecular weight (by GPC): M_w=1027, M_n=718, M_w/M_n=1.43. The hydroxyl equivalent weight was 80.07 mg/g.

Synthesis of M-PAMMO.

0.25 mL of malonyl chloride (2.63 mmol) in 10 mL of dry CH_2Cl_2 was added dropwise to a stirred solution of 2.80 g of PAMMO (4.0 mmol hydroxyl group) and 0.60 mL DMF (7.78 mmol) in 25 mL dry CH_2Cl_2 under Ar atmosphere in an ice bath, and the duration of this

process was more than 30 min. The reaction mixture was stirred at room temperature for 11 h and washed repeatedly with deionized water to neuter. The organic layer was dried with anhydrous $MgSO_4$, filtered, and evaporated in vacuum to afford 2.0 g of brown M-PAMMO, with a yield of 66%. UV-vis (CH_2Cl_2) λ/nm: 235, 335. IR (KBr) v/cm^{-1}: 2974 (v_{as} CH_2), 2877 (v_s CH_2), 2102 (v_{as} N_3), 1740 (v C=O), 1279 (v_s N_3), 1456 (v CH_2), 1377 (δ_s CH_3), 1353 (v CH_2), 1112 (v_{as} C-O-C). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ/ppm: 0.94 (3H, s, CH_3 side chain), 1.14-1.22 (3H, t, J = 7.0 Hz, CH_3 ethyl), 3.21 (4H, m, CH_2O), 3.26 (2H, s, CH_2N_3), 3.69-3.33 (2H, q, J = 5.3 Hz, CH_2 ethyl), 3.33 (2H, s, $COCH_2CO$). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ/ppm: 166.17 (-CH_2COCH_2-), 76.03 (HOCH-), 68.85 (-CCH_2CH_2-), 66.82 (-CH_2CH_3), 55.56 (-CH_2N_3), 41.58 ($N_3CH_2CCH_3$), 41.44 (-$COCH_2CO$-), 21.62 (-CCH_3), 15.01 (-CH_3). Molecular weight (by GPC): M_w=2082, M_n=1520, M_w/M_n=1.37.

Synthesis of BM-PAMMO.

0.13 mL of Br_2 (2.54 mmol) in 10 mL of dry CH_2Cl_2 was added dropwise to a stirred solution of 3.1 g of M-PAMMO in 45 mL dry CH_2Cl_2 at room temperature. Then the reaction mixture was stirred at room temperature for 6 h. The reaction was terminated by adding saturated NaBr solution. The mixture was washed with water until the pH was neutral to obtain 2.9 g of BM-PAMMO, with a yield of 85%. UV-vis (CH_2Cl_2) λ/nm (log ε): 235 (4.89), 339 (3.98). IR (KBr) v/cm^{-1}: 2973 (v_{as} CH_2), 2877 (v_s CH_2), 2102 (v_{as} N_3), 1740 (v C=O), 1279 (v_s N_3), 1455 (v CH_2), 1377 (δ_s CH_3), 1112 (v_{as} C-O-C), 604 (v C-Br). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ/ppm: 0.94 (3H, s, CH_3 side chain), 1.14-1.22 (3H, t, J = 7.0 Hz, CH_3 ethyl), 3.21 (4H, m, CH_2O), 3.26 (2H, s, CH_2N_3), 3.61-3.33 (2H, q, J = 6.4 Hz, CH_2 ethyl), 5.54 (1H, s, CHBr). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ/ppm: 166.17 (-CH_2COCH_2-), 76.03 (HOCH-), 68.85 (-CCH_2CH_2-), 66.82 (-CH_2CH_3), 55.56 (-CH_2N_3), 41.83 (-$COCHBrCO$-), 41.58 ($N_3CH_2CCH_3$), 21.62 (-CCH_3), 15.01 (-CH_3). Molecular weight (by GPC): M_w=2157, M_n=1586, M_w/M_n=1.36.

Synthesis of C$_{60}$-PAMMO.

0.89 g C_{60} (1.24 mmol) and 0.556 g glycine (7.41 mmol) were dissolved in 250 mL of chlorobenzene and 100 mL of DMSO by using ultrasonic irradiation method. Thereafter, 1.21 g of BM-PAMMO was added to the above solution. The mixture was stirred at room temperature for 12 h, and then the resulting solution was repeatedly washed with distilled water to remove DMSO and glycine. Chlorobenzene was then removed under vacuum. The residue was separated on a silica gel column through carbon disulfide and CH_2Cl_2/ethyl acetate (1:2) as the eluent to obtain 44.30 mg unreacted C_{60} and 1.58 g of C_{60}-PAMMO, with a yield of 87% (based on the consumption of C_{60}). UV-vis (CH_2Cl_2) λ/nm (log ε): 235 (4.85), 258 (4.86), 330 (4.35), 435 (3.22). IR (KBr) v/cm^{-1}: 2965 (v_{as} CH_2), 2856 (v_s CH_2), 2096 (v_{as} N_3), 1736 (v C=O), 1262 (v_s N_3), 1456 (v CH_2), 1384 (δ_s CH_3), 1171 (C_{60} specific absorbing peak), 1103 (v_{as} C-O-C), 526 (C_{60} specific absorbing peak). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ/ppm: 0.87 (3H, s, CH_3 side chain), 1.16-1.08 (3H, t, CH_3 ethyl), 3.15 (4H, m, CH_2O), 3.19 (2H, s, CH_2N_3), 3.61-3.33 (2H, q, CH_2 ethyl). Molecular weight (by GPC): M_w=3255, M_n=2276, M_w/M_n=1.43.

Results and discussion

Characterization of C$_{60}$-PAMMO.

The structure of C_{60}-PAMMO was confirmed by FT-IR, UV-vis, ^{1}H NMR, and ^{13}C NMR spectral analyses. The UV-vis spectra of BM-PAMMO and C_{60}-PAMMO are presented in Figure 1. As shown in Figure 1, the UV-vis spectrum of BM-PAMMO shows an absorption peak at 235 nm, which is ascribed to the $\pi\rightarrow\pi^*$ transition of the –N_3 group. The UV-vis spectrum of C_{60}-PAMMO also shows a sharp absorption peak at approximately 235 nm, which implies the presence of –N_3 group in C_{60}-PAMMO. Moreover, compared with BM-PAMMO, three new absorption peaks at 258, 330 and 435 nm are observed in the UV-vis spectrum of C_{60}-PAMMO. The peaks at 258 and 330 nm are the characteristic absorption of the skeleton structure of C_{60}, and the weak absorption band at 435 nm is typical of monoadducts at the closed 6,6-junction of C_{60}.[44,45]
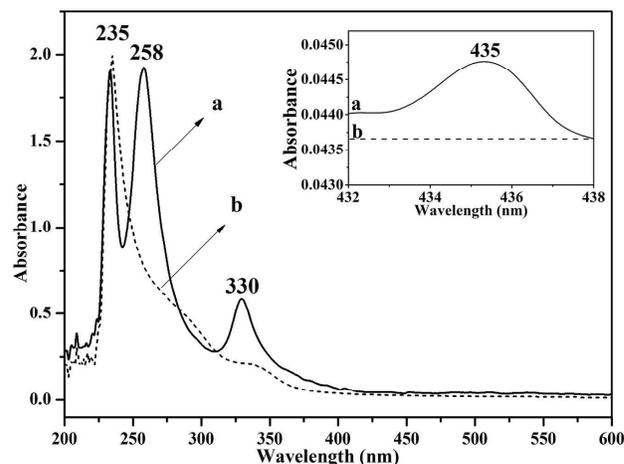
Figure 1. UV-vis absorption spectrum of BM-PAMMO and C_{60}-PAMMO. (a) C_{60}-PAMMO and (b) BM-PAMMO

Figure 2 shows the FTIR spectra of BM-PAMMO and C_{60}-PAMMO. As shown in Figure 2(b), in the FTIR spectra of BM-PAMMO, the peak at 1740 cm^{-1} can be assigned to the C=O stretching vibration, and the peaks at 1112 cm^{-1} and 1279 cm^{-1} correspond to the C–O–C symmetric and antisymmetric stretching vibrations. The strong absorption peak at 2102 cm^{-1} corresponds to the -N_3 group of PAMMO, and the peaks at 2973, 2934 and 2877 cm^{-1} are ascribed to the C-H symmetric and antisymmetric stretching vibrations of PAMMO respectively. [39] The peak at 604 cm^{-1} is due to the C-Br stretching vibration. Compared with BM-PAMMO (Figure 2(b)), the C-Br stretching vibration peak disappeared in Figure 2(a). In addition, the new peaks in Figure 2(a) at 526 cm^{-1} and 1171 cm^{-1} are the characteristic absorption peaks of C_{60} cage. [46]
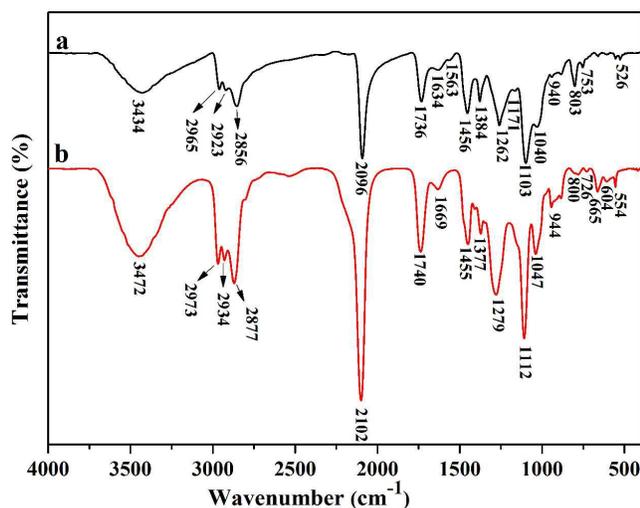
Figure 2. ATR-FTIR absorption spectra of BM-PAMMO and C_{60}-PAMMO. (a) C_{60}-PAMMO and (b) BM-PAMMO.
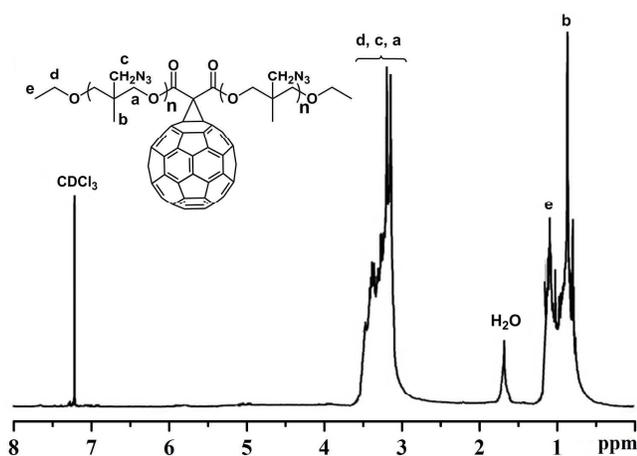
Figure 3. ^{1}H NMR spectrum of C_{60}-PAMMO.

The ^{1}H NMR spectrum also confirmed the successful introduction of PAMMO to C_{60} cage. Figure 3 shows the ^{1}H NMR spectrum of C_{60}-PAMMO. As shown in Figure 3, the peaks at around 3.10 and 3.60 ppm are attributed to the methylene protons of the main chain -CH_2O- protons (denoted a and d) and the methylene protons of the side chain -CH_2N_3 protons (denoted c). The methyl protons of the CCH_3 (denoted b) and CH_3CH_2O- (denoted e) appear at 0.75-1.20 ppm.
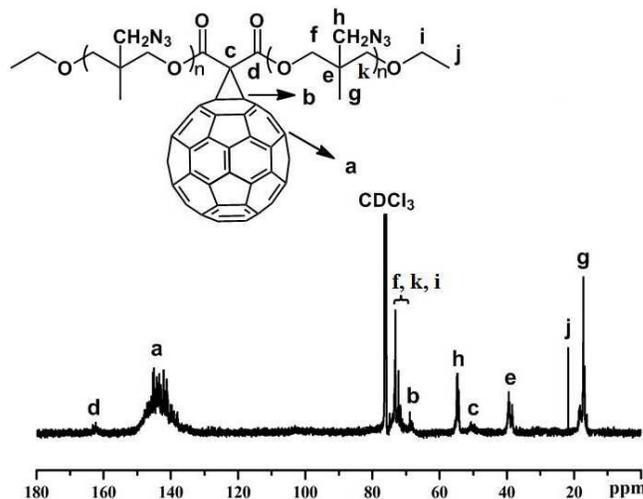
Figure 4. ^{13}C NMR spectrum of C_{60}-PAMMO.

The ^{13}C NMR spectrum of C_{60}-PAMMO is presented in Figure 4. The signals of the carbonyl carbon (–C=O, denoted d) and the quaternary carbon bounding to C_{60} (denoted c) appear at δ = 162.20–163.00 ppm and δ = 50.20 ppm, respectively.[47] The signals at around 74.00 and 71.20 ppm are attributed to the methylene carbons of the main chain -CH_2O- group (denoted f, k and i). The signals from 54.22 ppm to 52.34 ppm are attributed to the azidomethyl carbon of the side chain -CH_2N_3 group (denoted h). The quaternary carbon (denoted e) of the main chain appears at around 39.52 ppm. The methyl carbons of the side chain (denoted g) and terminal CH_3CH_2O- group (denoted j) appear at around 16.68 ppm and 20.89 ppm respectively. The two sp^3-carbons of the C_{60} cage (denoted b) appear at 68.34 ppm, and 58 sp^2-carbons of fullerene cage (denoted a) overlap and appear from 150.00 ppm to 135.40 ppm as a broad peak.[48]

Thermal analysis

The thermal stability of energetic materials has an important effect on the preparation, storage, processing, and application scope. Thus, DSC and TGA methods were adopted to evaluate the decomposition behavior of C_{60}-PAMMO.

The DSC curve of C_{60}-PAMMO under air atmosphere is showed in Figure 5. Three exothermic peaks were observed from 100 °C to 600 °C. The first exothermic peak under atmosphere at 157 °C is probably caused by the initial intramolecular or intermolecular reaction of the -N_3 group and fullerene carbon cage.[49] The second exothermic peak at 324 °C is due to the decomposition of PAMMO main chain. The third peak at 513 °C can be attributed to the decomposition of the C_{60} skeleton. In addition, the decomposition enthalpies of the three exothermic peaks are 39 J/g, 2858 J/g and 1005 J/g respectively.

In order to well understand the thermal decomposition mechanism of C_{60}-PAMMO, thermogravimetric analysis tandem infrared spectrum (TGA-IR) was used to rapidly identify the constituents of the thermal decomposition gas (Figure 6). As shown in Figure 6(a), the TGA and DTG curves show the three-step thermal degradation

of C_{60}-PAMMO under air atmosphere. The first thermal degradation appears at 148 °C, with around 10.36% weight loss. Thereafter, two thermal degradations appear at 323 °C and 512 °C with approximately 35.99% and 51.91% weight losses, respectively. Figure 6(b) shows the IR spectra of the thermal decomposition gas of C_{60}-PAMMO at 323 °C and 512 °C, respectively. As depicted in Figure 6(a), the decomposed products of C_{60}-PAMMO at 323 °C under air atmosphere are mainly CO_2 (2310 and 2367 cm^{-1}), CO (2185 and 2110 cm^{-1}) and C=O (1749 cm^{-1}), and the decomposed products at 512 °C under air atmosphere are mainly CO_2 (2302 and 2364 cm^{-1}), CO (2109 and 2177 cm^{-1}), N_2O (2247 cm^{-1}) and H_2O (3543 cm^{-1}). Obviously, these results are different from the previously reported that the thermal degradation of azide polymer appears at around 200 °C, and the main gas products are CO, HCN, HCHO and NH_3. Thus, these results indicate that the first thermal degradation of C_{60}-PAMMO at 148 °C is probably due to the decomposition of the -N_3 group, and decomposition mechanism is probably through the initial intramolecular or intermolecular cycloaddition of -N_3 and fullerene carbon cage and subsequent decomposition to release nitrogen (Scheme 2).

Scheme 2. The decomposition mechanism of C_{60}-PAMMO.

In order to demonstrate this decomposition mechanism, in situ FTIR was used to rapidly identify the constituents of decomposition condensed-phase residue. Figure 7(a) shows the infrared spectra of C_{60}-PAMMO decomposition condensed-phase residue at 27 °C, 127 °C, 152 °C, 172 °C, 207 °C and 262 °C under air atmosphere, respectively. Figure 7 (b) shows the infrared absorption intensity ratio of -N_3 ($\nu = 2096$ cm^{-1}) and C=O ($\nu = 1736$ cm^{-1}), C_{60} ($\nu = 526$ cm^{-1}) and C=O ($\nu = 1736$ cm^{-1}) in C_{60}-PAMMO decomposition condensed-phase FTIR spectra at specified temperatures. As shown in Figure 7, both the infrared absorption intensity ratio of -N_3 ($\nu = 2096$ cm^{-1}) and C=O ($\nu = 1736$ cm^{-1}) ($A_{-N3}/A_{C=O}$) and the infrared absorption intensity ratio of C_{60} ($\nu = 526$ cm^{-1}) and C=O ($\nu = 1736$ cm^{-1}) ($A_{C60}/A_{C=O}$) were rapidly decreased at 148 °C. The decrease of $A_{-N3}/A_{C=O}$ shows that the -N_3 started rapid decomposition at 148 °C, and the reduction of $A_{C60}/A_{C=O}$ at 148 °C indicates that the decomposition of -N_3 group is accompanied with the damage of fullerene conjugated structure. Thus, in situ FTIR analytical results strictly corroborate the TGA-IR analyses that C_{60}-PAMMO decomposition at 148 °C is through the initial intramolecular or intermolecular reaction of -N_3 and the fullerene carbon cage.

Figure 5. DSC curve of C_{60}-PAMMO under air atmosphere.
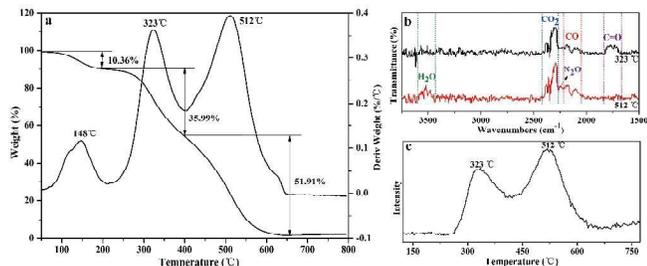
Figure 7. (a) TGA and DTG curves of C_{60}-PAMMO under atmosphere; (b) IR spectrum of the thermal decomposition gas of C_{60}-PAMMO at 323 °C and 512 °C under atmosphere; (c) Thermal decomposition gas intensity under different temperature.
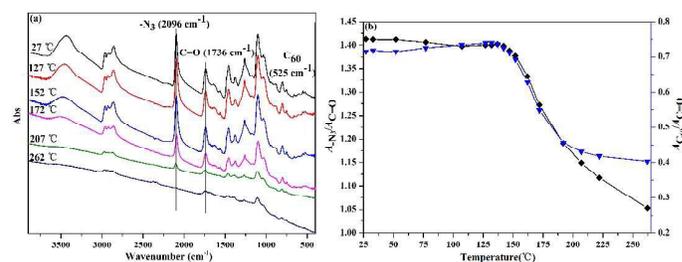
Figure 8. (a) IR spectra of the thermal decomposition remaining solid of C_{60}-PAMMO at 27, 127, 152, 172, 207 and 262 °C respectively; (b) Ratio of the IR absorption peak of -N_3 (v = 2096 cm^{-1})/-COO- (v = 1736 cm^{-1}) and C_{60} (v = 526 cm^{-1})/C=O (v = 1736 cm^{-1}) at different temperatures.

Conclusions

A new energetic polymer, [60]fullerene-poly(3-azidomethyl-3-methyl oxetane) has been successfully synthesized through the

Bingel reaction of BM-PAMMO and C_{60}. Its structure was systematically characterized by FTIR, UV-vis, ^{1}H NMR and ^{13}C NMR spectroscopy analyses. The thermal stability and thermal decomposition mechanism of [60]fullerene-poly(3-azidomethyl-3-methyl oxetane) was analyzed by DSC. TGA-FTIR, and in situ FTIR. The results showed that the initial decomposition of [60]fullerene-poly(3-azidomethyl-3-methyl oxetane) at 148 °C could be ascribed to the intramolecular or intermolecular reaction of the -N_3 group and fullerene carbon cage.

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Notes and references

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