

Synthesis and Characterization of Three-dimensional Polymer Produced by Mutual Condensation of Ethylenediamine and C₆₀

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Abstract

The polymer with contents of C₆₀ up to 57 wt.% was produced by mutual condensation of fullerene C₆₀ and ethylenediamine. The investigations of this polymer as well as pristine fullerene to comparison were carried out by FT-IR and UV-Vis spectroscopy, ToF-SIMS, TGA, and elemental analysis. At least three kinds of components was revealed as building blocks of polymer. The fullerene cage underwent only distortion but didn't destroy during formation of polymer. The pure fullerene was found as an intermediate of the thermal decomposition of polymer. The conclusion that this polymer could serve as precursor to produce carbon nanomaterial with high concentration curved graphene sheets and can be used for gas adsorption and electrochemical application was made.

Keywords : fullerene, ethylenediamine, polymer, FT-IR, ToF-SIMS, TA

1. Introduction

The great interest to carbon nanomaterial, especially to single wall carbon nanotubes (SWNT) and fullerenes existed today, is due to high prospective of these materials. The main distinction of them from well-know graphite and diamond are caused by curved surface of graphene sheets in nanotubes and fullerenes. That leads to asymmetry of π bonds of graphene layers and to change the chemical and physical properties of nanotubes and fullerenes against graphite. The chemical activity should be higher if the curvature of the molecule sheet is greater. The fullerene C₆₀ has the larger one as compared with SWNT. However, there are several reasons limited a use of a fullerene as carbon material with high curved graphene structure. The first of ones is that the fullerene crystal called fullerite has closed packed structure (*fcc*) under ambient condition, that don't allow to posses high adsorption surface [1]. The second reason is that fullerene is close like cage molecule so it inner surface does not accessible for other molecules to take place chemical reactions or adsorption. The strategy to overcome these difficulties could include the producing of three dimensional (3-D) polymer which consist C₆₀ molecules cross linked by the short chains. The partially destroying of such polymer could resulted in 3-D carbon network consisted high concentration of fullerene fragments that are curved graphene sheets. Such materials widely tested for gas adsorption and electrochemical application, for example, as an anode of lithium secondary batteries [2]. Therefore a usage of materials based on partially destroyed fullerene

polymer is very promising.

There are many publications devoted to production and investigation of polymers that includes C₆₀ [3-6]. But the case of 3-D polymer, which consists C₆₀ multi-bonded by short chains, was rarely been paid attention until these days.

Fullerene C₆₀ is a molecule with the many equal electrophilic reactivity sites. They cause of difficulty to obtain monoaddition products but the other way existing these sites would be advances to produce 3-D polymeric net based on fullerene. Nucleophilic addition of amines is a widespread reaction that used to attach other molecules to C₆₀ through these sites [7-11]. Many researchers also use this reaction to graft fullerene onto the surface or to polymers [3, 12-17].

If the diamines are utilized in the reaction of nucleophilic addition of amines to fullerene this reaction possess all attributes of polycondensation reaction used to produce polymers. Therefore to our mind a usage of this reaction should lead to success in production of 3-D polymer based on fullerene.

W.L. Bell *et al.* [18] have produced already copolymer of C₆₀/C₇₀ with ethylenediamine insoluble in either toluene or water by refluxing the fullerenes in mixture of ethylenediamine and toluene as well as fullerene/melamine/formaldehyde polymer. The average 14 ethylenediamine units per fullerene in copolymer of C₆₀/C₇₀ with ethylene diamines of were estimated from elemental analysis. No detail investigation of the structure and the properties of these polymers were carried out.

N. Manolova *et al.* [19] has reported the synthesis of in-chain derivatives of fullerene with precursor polymers includ-

ing O,O'-bis(2-aminopropyl)poly(oxypropylene) and O,O'-bis(2-aminopropyl)poly(oxyethylene). But the long polymeric chains consist only two active aminogroups able to connect with fullerene that caused a low fullerene concentration in 3-D polymers. K E. Geckeler and A. Hirsch [20] have carried out titration of fullerene solution in toluene by poly(ethylenimine) ($M=35000$) and poly[4-[(2-aminoethyl)imino]methyl]styrene, ($M=20000$) and obtained polymeric products of molar ratio polymer/fullerene equals 18:1, 19:1 and fullerene capacity 230, 180 mg/g respectively. The obtained polymers were characterized as monoaddition fullerene products. No cross linking of neat polymers by fullerene was claimed.

Our purpose is to produce and to investigate a 3-D polymer with high concentration of C_{60} . We used the similar way to W.L. Bell's [18]. There are two reasons caused the choice of ethylenediamine as bonding agent of C_{60} molecules. The first one is low molecular mass of it that permits to produce polymer with high concentration of C_{60} , the second one is the length of aliphatic chain. The ethylenediamine skeleton -N-C-C-N- is enough flexible to be rearmament in 3-D structure but also it is so sort and inflexible to form inner cycles.

The products that could yield during the addition of ethylenediamine to fullerene are shown on Fig. 1 according literature analysis [4, 8, 21-23]. Only a few ethylenediamine molecules attached to fullerene are shown for clarity of picture. The substances "a" is a product of nucleophilic addition ethylenediamine to fullerene. The substances "b" obtained when dehydrogenation takes place during or after nucleophilic addition. The epoxide oxygen originated from air stabilizes dehydrogenated structure "b" that results in substances "c". When $R=H$ that the like-star products are formed terminated by hydrophilic aminogroups. These sub-

stances have to be soluble in water. When R is C_{60} that the cross linking 3-D polymers are obtained. This polymer will insoluble both water and toluene with high probability. The gross formulas $C_{60n}(EDA)_m$ and $C_{60}(EDA)_n$ for products with $R=C_{60}$ and $R=H$ respectively could be introduced, where EDA means ethylenediamine. These formulas include "a", "b", and "c" structures.

2. Experimental

The sample 1 described in [18] as polymeric was produced according following procedure. 100 ml solution of C_{60} in toluene (125 mg C_{60}) was heated up to 70°C . After that 2.5 ml of neat ethylenediamine was dropped to this solution. During the first three hours solution grow turbid and changed color to brown. Addition 7 ml of ethylenediamine was dropped along the next 25 hours. Total time of synthesis was 45 hours and the amount of added ethylenediamine (EDA) was 9.5 ml. The molar ratio is $C_{60}:EDA = 1:960$. The clear dark red-brown solution and brown precipitate were obtained and separated by centrifugation. The precipitate was washed 3 times by acetone and dried at 50°C overnight. The yield of product equals 110 mg. The reaction did not stop in the solution, the precipitate has continued slowly formed.

The substances numerated as 2 prepared according technique [8]. The 158 mg of C_{60} (0.219 mmol) was added to 50 ml (0.75 mol) of neat ethylenediamine under room temperature. The solution became dirtily green and self-refrigerated. After heated up to 35°C the color of solution changed to brown during 0.5 hour. A clear brown solution results in keeping the reaction mixture under this condition during 47 hours. The solution was consecutively concentrated with rotary pump, precipitated by THF, washed by

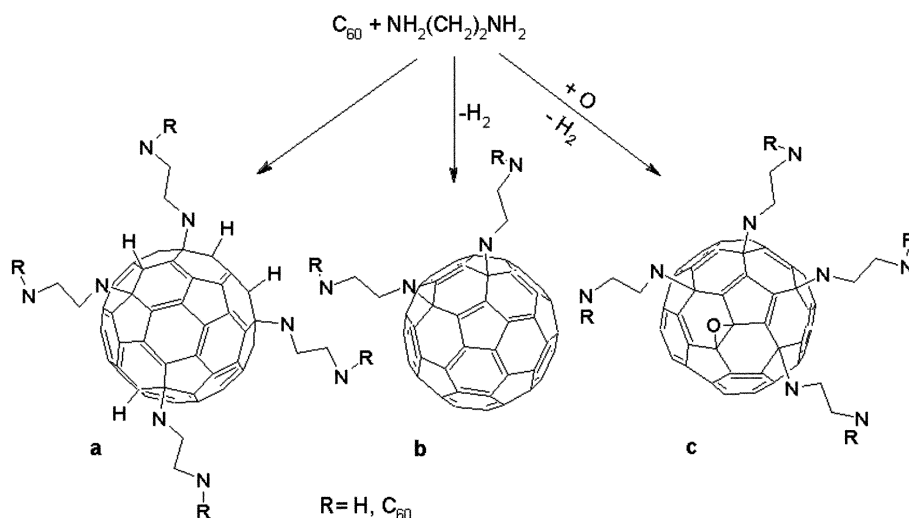


Fig. 1. Scheme of possible products resulted in C_{60} with ethylenediamine condensation. When $R=H$ like star products yielded, if $R=C_{60}$ —3-D polymer obtained. **a**—hydroaminated fullerene, **b**—dehydroaminated fullerene, **c**—oxo-dehydroaminated fullerene.

THF 3 times, dissolved in water, again precipitated by THF, washed by THF and acetone.

Reagents: C_{60} (99 wt.%) was produced by Astrin Inc. (St. Petersburg, Russia) and was supported by Technlife Co. Ltd, Seoul, Korea, ethylenediamine, anhydrous (99%) was supported by Kanto Chemical Co. Inc. (Japan), toluene (grade guaranteed reagent, 99%) and tetrahydrofurane (extra pure, 99%) were from Junsei Chemical Co. Ltd. (Japan), acetone (extra pure 99.5%) was from DC Chemical Co. Ltd (Korea). All reagents were used without additional purification.

The FT-IR analysis of samples were carried out using KBr pallets on Magna IR 750 Spectrometer with resolution 1 cm^{-1} . UV-vis spectra were recorded on Agilent 8453 UV-visible Spectrometer with resolution 1 nm . SDT 2960 Simultaneous DTA-TGA system (TA Instruments, USA) was used for thermal analysis. A linear heating $10^\circ\text{C}/\text{min}$ up to 800°C was utilized. The ToF-SIMS and elemental analysis were performed by Advanced Analysis Center of Korea Institute of Science and Technology.

3. Results and discussion

The obtained products vary in their water and toluene solubility. The sample **1** is practically insoluble in toluene and water (the solution is colorless for naked eyes), the sample **2** possess high solubility in water (bright yellow solution is formed) and insoluble in toluene. The sample **2** has like star structure with high hydrophilic NH_2 groups on the outer-shell that corresponds the case $R=\text{H}$ for the substances **a**, **b**, and **c** on Fig. 1 and can be expressed by gross formula $C_{60}(\text{EDA})_n$. The action of terminated primary aminogroups with solute provides high solubility of **2** in water. Non-solubility of **1** in water and toluene can be explained through that the sample **1** is polymer which consists of fullerene molecules cross linked by ethylenediamine bridges. The structure of the sample **1** could corresponded the structures **a**, **b**, and **c** with $R=C_{60}$ from the scheme on Fig. 1 and can be expressed by gross formula $C_{60n}(\text{EDA})_m$.

3.1. FT-IR spectra of products of C_{60} with ethylenediamine condensation.

The FT-IR spectra of products of C_{60} with ethylenediamine condensation are very similar, as can be seen the spectra 1 and 2 on Fig. 2. The spectra of both samples didn't reveal modes at $\nu=527, 576, 1182, 1428\text{ cm}^{-1}$ attributed to original C_{60} . That means strong distortion of C_{60} cage due to multiaddition of ethylenediamine molecules. The amine groups bands are shown in the both of the spectra.

The strong stretching N-H modes at $\nu=3277\text{ cm}^{-1}$ and bend (scissoring) NH_2 modes at $\nu=1584\text{ cm}^{-1}$ appeared. Two bands at $\nu=1110$ and $\nu=1074\text{ cm}^{-1}$ attributed to stretching C-N vibrations of nitrogen bonded with fullerene

cage and aliphatic carbon of ethylenediamine, respectively.

Also the contribution of ethylenediamine in spectra represented by the two bands at $\nu=2932\text{ cm}^{-1}$, and $\nu=2870\text{ cm}^{-1}$ corresponded to C-H stretching symmetry and asymmetry vibrations and band at $\nu=1435\text{ cm}^{-1}$ attributed to bend CH_2 mode. The multiaddition of diamine to fullerene cage and its distortion resulted in many double C=C bonds asymmetrically substituted. They stretching adsorption represented by the band at $\nu=1632\text{ cm}^{-1}$. The band at $\nu=1324\text{ cm}^{-1}$ attributed to bend C-H vibration of the hydrogen atom bonded to fullerene cage. This is the evidence that the structure like **a** (see Fig. 1) there is in the samples **1** and **2**. The presence of structural fragment like **c** (see Fig. 1) in both samples confirmed by the band at $\nu=817\text{ cm}^{-1}$ that corresponds to vibration of epoxide ring.

Unfortunately, the FT-IR spectra of sample **1** and **2** didn't show the significant difference between structure of these samples.

3.2. Elemental analysis and ToF-SIMS of the condensation product of C_{60} and ethylenediamine.

The elemental analysis of sample **1** was carried out. The determined content of C, N, H showed 71.1, 16.1, 4.4 wt.%, respectively. The residue 8.4 wt.% was caused by the

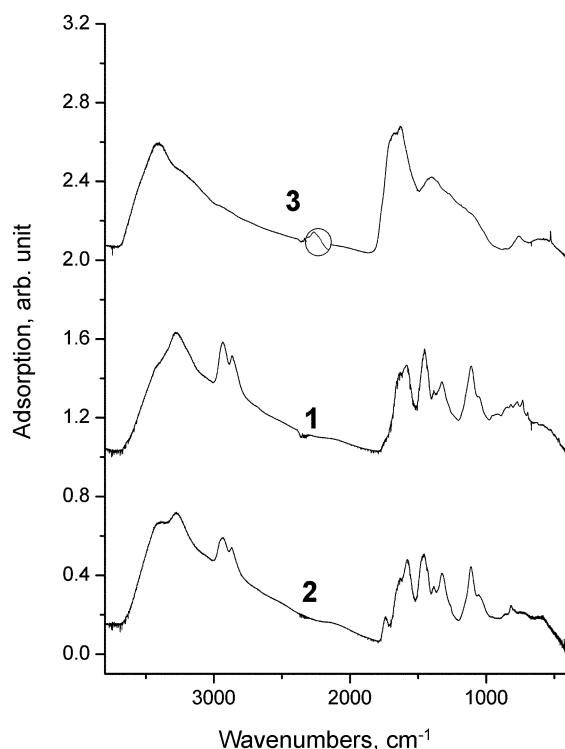


Fig. 2. FT-IR spectra: 1- sample **1** insoluble both toluene and water polymer $C_{60n}(\text{EDA})_m$; 2- sample **2**, water soluble like star $C_{60}(\text{EDA})_n$, 3- residue of thermal annealing of sample **1** at 250°C during 30 min in nitrogen. Assignment of adsorption bands see in text.

existence of oxygen. The gross formula is C_{5.92}N_{1.15}H_{4.4}O_{0.525} or in more suitable expression C₆₀(C₂N₂H₈)_{7.2}H_{2.6}O_{6.6}. It means that samples **1** is the mixture of substances with average number of ethylenediamine molecules attached to fullerene cage of 6~8. The negative index of H atom indicates that the samples **1** consists dehydrogenated substances like **b** (see Fig. 1). Oxygen could be related to adsorbed water or is consumed on epoxide functionality. The contents of C₆₀ in polymer consists 57 wt.% and is more higher than in previously obtained polymers that include fullerene [18-20].

The elemental analysis of original fullerene C₆₀ reveals 99.4 wt.% of C and 0.5 wt.% of H. The hydrogen originated from toluene which used in fullerene production technology. Such spread sheet corresponds for molar ration C₆₀: C₆H₅CH₃ = 1:0.45 or 5.4 wt.% of toluene in the original sample of C₆₀.

The Time of Flight Secondary Ion Mass-spectrometry (ToF-SIMS) was applied to analysis of origin C₆₀ and product of mutual condensation C₆₀ with ethylenediamine (sample **1**). The samples were strewed on carbon strip. The Cs⁺ ion beam with 7.9 keV was applied to ionize the samples and to produce mass-spectra. Both positive and negative ions of mass-spectra were collected and examined up to 3000 Dalton.

The selected ions both positive and negative with related intensity are given in Tables 1, 2 respectively. The ion selection was made according to interest on discussion of difference between original C₆₀ and sample **1** and don't include all observed peaks. The total ion current concentrates

Table 1. Selected positive ions of ToF-SIMS mass-spectrum of sample **1** and origin C₆₀

| Sample 1 | | C ₆₀ | | Ions (+) |
|-----------------|------|-----------------|------|---|
| M/z | Int. | M/z | Int. | |
| 736 | 11 | | | (C ₆₀ +NH ₂) (C ₆₀ +O) |
| 735 | 8 | | | (C ₆₀ +CH ₃) |
| 734 | 6 | 734 | 2 | (C ₆₀ +CH ₂) |
| 720 | 52 | 720 | 17 | C ₆₀ |
| 696 | 10 | 696 | 3 | (C ₆₀ -2C) |
| 685 | 3 | | | (C ₆₀ -3C+H) |
| 672 | 5 | 672 | 2 | (C ₆₀ -2C ₂) |
| 648 | 4 | | | (C ₆₀ -3C ₂) |
| | | 149 | 2920 | C ₁₂ H ₅ |
| 91 | 11 | 91 | 280 | C ₇ H ₉ (toluene) |
| 56 | 54 | | | C ₃ H ₆ N |
| 44 | 108 | | | C ₂ H ₆ N |
| 42 | 95 | | | C ₂ H ₄ N |
| 30 | 129 | | | CH ₂ NH ₂ |
| 18 | 14 | | | NH ₄ |

up to 150 Daltons in the both samples for both kinds of ions.

In the high mass region the positive ion mass-spectrum of C₆₀ consists molecular ion (720 m/z) and satellites that corresponding a loss of 2 and 4 carbon atoms, as well as the loss three C atoms with simultaneously attachment one hydrogen. A peak 734 m/z resulted in attachment of CH₂ groups also is revealed in this region of mass-spectrum. The most intensive peak of mass-spectrum is 149 m/z, which probably attributed to fragment of C₆₀ cage formed by two six and one five rings condensed together. The toluene peak (91 m/z) was found in spectrum that confirms the presence of this solute in original C₆₀.

The positive ion mass-spectrum of the sample **1** could be divided on two part, the first one is close to 720 m/z, the second one is up to 150 m/z. No ion was detected in the mass region far than 750 m/z. The intensity of C₆₀⁺ (720 m/z) is higher than in origin C₆₀, but the fragmentation is very similar. Due to high intensity the losses of three pairs of

Table 2. Selected negative ions of ToF-SIMS mass-spectrum of sample **1** and origin C₆₀

| Sample 1 | | C ₆₀ | | Ions (-) |
|-----------------|-------|-----------------|------|---|
| M/z | Int. | M/z | Int. | |
| 736 | 27 | 736 | 3 | (C ₆₀ +NH ₂) (C ₆₀ +O) |
| 735 | 23 | | | (C ₆₀ +CH ₃) |
| 734 | 23 | 734 | 5 | (C ₆₀ +CH ₂) |
| 720 | 159 | 720 | 24 | C ₆₀ |
| 709 | 21 | 709 | 2 | (C ₆₀ -C+H) |
| 696 | 25 | 696 | 3 | (C ₆₀ -C ₂) |
| 685 | 9 | 685 | 1 | (C ₆₀ -3C+H) |
| 672 | 17 | 672 | 1 | (C ₆₀ -2C ₂) |
| 648 | 12 | | | (C ₆₀ -3C ₂) |
| 624 | 8 | | | (C ₆₀ -4C ₂) |
| 220 | 2 | | | C ₁₆ N ₂ |
| 218 | 3 | | | C ₁₇ N |
| 208 | 4 | | | C ₁₅ N ₂ |
| 206 | 4 | | | C ₁₆ N |
| 184 | 11 | | | C ₁₃ N ₂ |
| 182 | 11 | | | C ₁₄ N |
| 170 | 30 | | | C ₁₃ N |
| 160 | 13 | | | C ₁₁ N ₂ |
| 158 | 14 | | | C ₁₂ N |
| 146 | 48 | 146 | 2 | C ₁₁ N, C ₁₂ H ₂ |
| 136 | 19 | | | C ₉ N ₂ |
| 134 | 26 | | | C ₁₀ N |
| 122 | 127 | | | C ₉ N |
| 112 | 24 | | | C ₇ N ₂ |
| 110 | 36 | | | C ₈ N |
| 50 | 1050 | | | C ₃ N |
| 26 | 18900 | | | CN |

carbon atoms is observed. The attachment of O or NH₂ (736 m/z) and CH₃ (735 m/z) to C₆₀ was revealed as well as CH₂, which is in the origin C₆₀ mass-spectrum. In the low mass region of mass-spectrum the nitrogen containing ions with mass 18, 30, 42, 44, 56 appeared. The four first ones could be originated from ethylenediamine whilst the last consist three carbon atoms that is evidence of the bonding ethylenediamine with fullerene. The peak of 149 m/z with high intensity in C₆₀ mass-spectrum disappeared in this mass-spectrum that points out that the pass of fragmentation of C₆₀ cage is changed.

The negative ion ToF-SIMS mass-spectrum of primary C₆₀ consists molecular ion 720 m/z surrounded by satellites both fragment and adducts (see Table 2) and is a very similar to positive ion mass-spectrum of C₆₀. The losses of one and two pairs of C atoms as well as eliminating odd numbers of carbon atoms with simultaneously attachment of one hydrogen were observed. The adduct (C₆₀+CH₂)⁻ was revealed also. In the low mass region the series of C_nH⁻ (n=9~18) were detected (no include in the Table 2).

The ToF-SIMS negative ion mass-spectrum of the sample **1** is characterized by the peak at 720 m/z with satellites both lower and higher masses and set of peaks up to 300 m/z. No peaks higher than 750 m/z were detected. The peak of C₆₀⁻ (720 m/z) is more intensive than in all discussed mass-spectra of sample **1** and C₆₀ as negative both positive. A vicinity of 720 m/z is the similar to previously observed mass-spectra. The high intensity allows to detect more deep fragmentation (up to a loss of four C pairs) but no principal differences were revealed in this range of spectrum. In the low mass region most intensive ion is CN⁻ (26 m/z). New ion sets of C_xN⁻ and C_xN₂⁻ were detected this mass-spectrum (see Table 2) as well as the C_nH⁻ series similar one of C₆₀ mass-spectrum.

The presence of the peak 720 m/z originated from C₆₀ in the ToF-SIMS of sample **1** points on that a pass way of ion fragmentation with C₆₀ intermediate there is. But the difference between sets of low mass fragments and availability nitrogen containing ions in mass-spectrum of sample **1** shows that the substance consisting C₆₀ with (EDA) adducts exists really. Its formula can be expressed as C_{60n}(EDA)_m. But no peaks corresponding this formula were detected. It can be explained high degree of cross linking between C₆₀ and ethylenediamine molecules that causes thermal decomposition of polymer down to C₆₀ before ionization under secondary ion bombardment.

3.3. TG analysis of sample **1** and original C₆₀

A TGA up to 800°C of C_n(EDA)_m (sample **1**) with linear rate 10°C/min was made as well as pristine fullerene C₆₀ for comparison (see fig. 3). The thermal stability of C₆₀ is higher than its adduct with ethylenediamine (**1**). The weight loss of **1** amounts to 88% against 21% of the pure C₆₀. A detail examination of differential TG curve of **1** that are presented

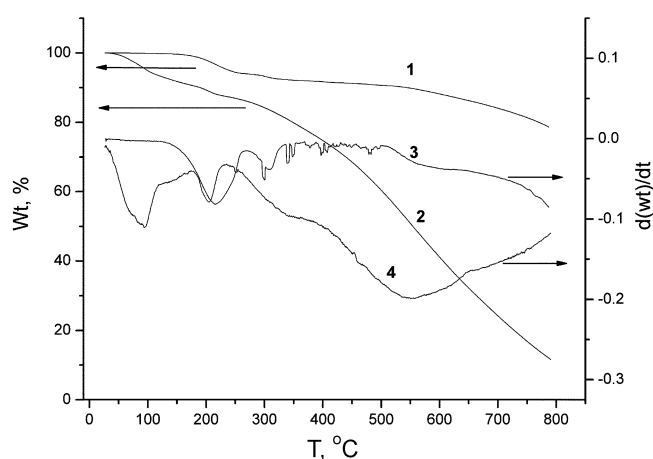


Fig. 3. 1- TA curve of pristine C₆₀; 2- TA curve of sample **1**, polymer resulted in condensation of C₆₀ with ethylenediamine; 3- DTA curve of pristine C₆₀; 4- DTA curve of sample **1**, polymer resulted in condensation of C₆₀ with ethylenediamine.

on Fig. 3 reveals three peaks. The first one at 100°C corresponds of water desorption, the second peak centered at 215°C could attributed out gassing of solute like toluene. This peak also was revealed on DTG curve of original C₆₀. It is additional evidence of the attribution this peak to toluene, which usually utilized in fullerene production technology and can remained in the sample of C₆₀. The toluene was also discovered in original C₆₀ by ToF-SIMS (see previous chapter).

Over the 250°C the sample of C_{60n}(EDA)_m begins to loss weight intensively. The wide DTG peak with a center of 553°C is a response of this process. This peak could be deconvoluted on three components (don't show on fig. 3) with the maximums at 322, 543, 761°C. The last two maximums also were revealed on DTG curve of pure C₆₀ and attributed to evaporation of fullerene. The peak at 322°C concerns to decomposition of polymer structure. Therefore could be supposed that the intermediates of thermal decomposition of C_{60n}(EDA)_m are the fullerene C₆₀ or the structures liked fullerene cage (also see part devoted to mass-spectrometry).

3.4. Annealing of C_{60n}(EDA)_m

The sample **1** (C_{60n}(EDA)_m) was annealed in the flow of N₂ during 30 min at 250°C that corresponds of the foot of decomposition peak on DTG curve. A weight loss of 1 wt.% was revealed during the isothermal annealing after sample reached the evaluated temperature. After the annealing the sample color changed from brown to black. A FT-IR spectrum of residue is quite different from initial sample (see spectrum 3 on Fig. 2).

The bands of vibrations at $\nu = 3278 \text{ cm}^{-1}$ and $\nu = 1584 \text{ cm}^{-1}$ attributed to N-H₂ stretching and deformation scissor vibrations respectively disappeared. All bands corresponding

to C-H vibrations, namely, stretching modes at $\nu = 2867\text{ cm}^{-1}$, $\nu = 2932\text{ cm}^{-1}$, bending mode CH₂ at $\nu = 1453\text{ cm}^{-1}$, C-H bending mode of methine hydrogen atom connected to fullerene cage also disappeared. The band attributed to triple C = C bond at 2226 cm^{-1} risen. It is shown in ring on graf 3 of Fig. 2. These changes point on outcoming of hydrogen from the sample. The band at $\nu = 817\text{ cm}^{-1}$ attributed to epoxide functional group disappeared also. The most probable pathway to outlet this group is CO evolving that have to led partial destroying of fullerene cage.

The band at $\nu = 528\text{ cm}^{-1}$ of mode corresponded to C₆₀ cage appeared. This is $F_{1u}(1)$ mode and usually it intensity in the C₆₀ IR spectra depends on depth of distortion C₆₀ cage. For example, it has observed yet it monoaddition products of C₆₀ (see supplement materials of [20]), in dimmers (C₆₀)₂ [24], but it disappeared in multiaddition products of C₆₀ or deep polymerized C₆₀ [20, 25].

Revealing of fullerene mode at $\nu = 528\text{ cm}^{-1}$ in residue of C₆₀(EDA)_m annealing allows to suggest that in the products of decomposition there is fullerene.

The UV-vis spectra of toluene extracts of sample **1** and its residue after annealing were measured. The toluene solubility of both samples are very low. But the solution of sample **1** was colorless for the naked eye whilst the solution of its annealed residue was colored in typical C₆₀ purple color of very low intensity and its UV-vis spectra was typical for C₆₀ (see Fig. 4). The extract of sample **1** also adsorbs at 335 nm, but this maximum is 15 times less than for the annealed sample. No any proof about the presenting of molecule with fullerene structure in this solution can be made based on this spectra.

The three dimensional polymer with 57 wt.% content of fullerene was produced by mutual condensation of fullerene and ethylenediamine. This polymer includes a few kinds of

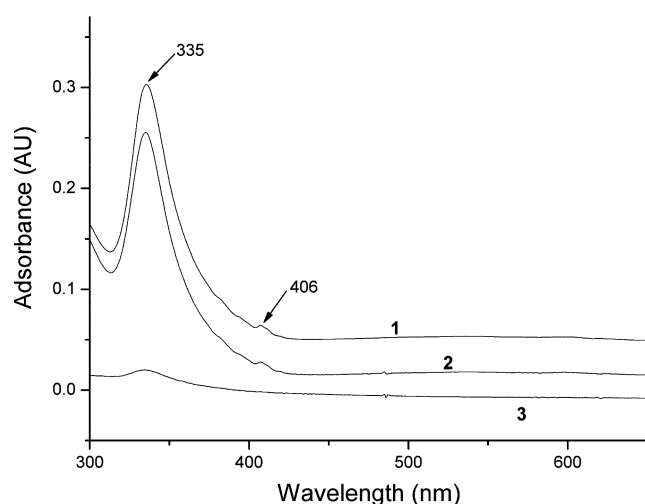


Fig. 4. UV-vis spectra: 1- original C₆₀ in toluene; 2- toluene extract of residue of sample **1** after thermal annealing at 250°C in nitrogen; 3- toluene extract of sample **1**.

substances that can be formed under nucleophilic addition of ethylenediamine to fullerene C₆₀. The first of one are multiadducts of ethylenediamine addition C₆₀H_n(NHCH₂-CH₂NH₂)_n (see substances **a**, Fig. 1). Its presence is proven by mode at $\nu = 1324\text{ cm}^{-1}$ attributed to the C-H bend vibration of the tertiary hydrogen atom attached to fullerene cage. The availability of the dehydrogenated products signed as C₆₀(NHCH₂CH₂NH₂)_m (see substances **b** fig. 1) was deduced from elemental analysis. The epoxide product like substances **c** fig. 1 were revealed also in the content of polymer due to band at $\nu = 817\text{ cm}^{-1}$.

The mass-spectrometry analysis by ToF-SIMS shows that the fullerene cage don't collapse under formation of polymer. The TG analysis led to similar conclusion. The formation of fullerene as intermediate products during thermal decomposition of this polymer was revealed by both linear and isothermal heating of polymer. The ethylenediamine bridges between fullerene molecules have lost hydrogen and failed under heating before fullerene fragments collapse or evaporate.

Likely the structure of polymer after annealing consists of fullerene molecules and/or they large fragments separated by the net from products of thermal decomposition of ethylenediamine.

The extraction of fullerene by toluene from the residue of thermal annealing of polymers shows that this net isn't tight and allows to surface of fullerene molecules could be easy of access for other molecules in the body of polymer. This phenomena could be used to create new carbon nanostructural materials with high concentration of curved graphene sheets.

4. Conclusions

The three dimensional polymer with 57 wt.% content of fullerene molecule was produced by mutual condensation of ethylenediamine and fullerene C₆₀. The investigation of this polymer by FT-IR and UV-Vis spectroscopy, ToF-SIMS, TGA, and elemental analysis shows that it consists at least three kinds of substances: hydroaminated fullerene, dehydroaminated fullerene, and oxo-dehydroaminated fullerene that resulted in ethylenediamine addition to fullerene. The pathway of thermal decomposition of this polymer includes formation of fullerene or like fullerene structures as intermediate. It is a perspective precursor for development carbon nanostructural materials with high concentration of curved graphene sheets that can be used for gas adsorption or/and electrochemical applications.

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References

- [1] Gusev, V.; Ruetsch, S.; Popeko, L. A.; Popeko, I. E. *J. Phys. Chem. B* **1999**, *31*, 6498.
- [2] Wang, Q.; Li, H.; Chen, L.; Huang, X. *Solid State Ionics* **2002**, *152-153*, 43.
- [3] Innocenzi, P.; Brusatin, G. *Chem. Mater.* **2001**, *13*, 3126.
- [4] Chen, Y.; Huang, Z.-E.; Cai, R.-F.; Yu, B.-C. *Eur. Polym. J.* **1998**, *2*, 137.
- [5] Dai, L. *J. M. S.-Rev. Macromol. Chem. Phys.* **1999**, *C39(2)*, 273.
- [6] Geckeler, K. E.; Samal, S. *Polym. Int.* **1999**, *48*, 743.
- [7] Seshadri, R.; Govindaraj, A.; Nagarajan, R.; Pradeep, T.; Rao, C. N. R. *Tetrahedron Letters* **1992**, *15*, 2069.
- [8] Wudl, F.; Hirsch, A.; Klemm, K. C. *et al.* "Fullerenes: Synthesis, properties, and chemistry of large carbon clusters" ed. G. S. Hammond, V. J. Kuck, ACS Symposium Series ISSN 0097-6156, 481, **1992**.
- [9] Lawson, G. E.; Kitaygorodskiy, A.; Sun, Y.-P. *J. Org. Chem.* **1999**, *64*, 5913.
- [10] Inoue, M.; Machi, L.; Brown, F.; Inoue, M. B.; Fernando, Q. *J. Molecular Structure* **1995**, *34*, 113.
- [11] Samal, S.; Choi, B.-J.; Geckeler, K. E. *Chem. Commun.* **2000**, 1373.
- [12] Voigt, I.; Simon, F.; Esthel, K.; Spange, S. Friedrich, M. *Langmuir* **2001**, *17*, 8355.
- [13] Jensen, A. W.; Daniels, C. *J. Org. Chem.* **2003**, *68*, 207.
- [14] Choi, S. Y.; Lee, Y.-J.; Park, Y. S.; Ha, K.; Yoon, K. B. *J. Am. Chem. Soc.* **2000**, *122*, 5201.
- [15] Chen, K.; Caldwell, W. B.; Mirkin, C. A. *J. Am. Chem. Soc.* **1993**, *115*, 1193.
- [16] Mirkin, C. A.; Caldwell, W. B. *Tetrahedron* **1996**, *14*, 5113.
- [17] Bae, J. S.; Kim, E.-R.; Lee, H. *Synthetic Metals* **1995**, *71*, 2063.
- [18] Bell, W. L.; Jiang, Z.; Dietz, S. D. "Fullerenes: Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials" eds. Kadish, K. M., Ruoff, R. S., The Electrochem. Soc. Inc.: Pennington, NJ, **1994**; Vol. 94-24, p 92.
- [19] Manolova, N.; Rashkov, I.; Beguin, F.; van Damme, H. *J. Chem. Soc., Chem. Commun.* **1993**, 1725.
- [20] Geckeler, K. E.; Hirsch, A. *J. Am. Chem. Soc.* **1993**, *115*, 3850.
- [21] Schick, G.; Kampe, K.-D.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1995**, 2023.
- [22] Isobe, H.; Ohbayashi, A.; Sawamura, M.; Nakamura, E. *J. Am. Chem. Soc.* **2000**, *122*, 2669.
- [23] Hirsch, A. *J. Phys. Chem Solids* **1997**, *11*, 1729.
- [24] Davydov, V. A.; Kashevarova, L. S.; Rakhmanina, A. V.; *et al.* *Phys. Rev. B* **2000**, *61*, 11936.
- [25] Rao, A. M.; Eklund, P. C.; Hodeau, J.-L.; Marques, L.; Nunez-Regueiro, M. *Phys. Rev. B* **1997**, *55*, 4766.