



## Reactions and Properties of Fullerene (C<sub>60</sub>)

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### 풀러렌의 성질과 반응

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**ABSTRACT** : In this review, the properties of buckminsterfullerene and its organic and polymeric reactions were focused. In addition, polymer blending with C<sub>60</sub> will be briefly introduced. As soon as C<sub>60</sub> was discovered, chemists put their efforts to explore its reactivity with other compounds. The knowledge of the organic reactions with C<sub>60</sub> was extended to construct different types of fullerene polymers such as side chain fullerene polymers, main chain fullerene polymers, star shaped fullerene polymers, and dendritic fullerene polymers.

**요약** : 논문에서는 풀러렌의 성질, 유기반응, 고분자반응을 설명하였으며, 풀러렌과 고분자의 블렌딩에 대해 소개를 하였다. 또한 다른 화합물과 풀러렌의 반응성을 기술하였다. 풀러렌의 화학 반응은 가지 사슬 풀러렌 고분자, 주 사슬 풀러렌 고분자, 별 모양 풀러렌 고분자, 덴드리머 타입 풀러렌 고분자와 같은 연구에 응용되었다.

**Keywords** : fullerene, reactions, properties, reactivity, fullerene polymers

## I. Introduction

Since the first fullerenes such as C<sub>60</sub>, and C<sub>70</sub> were discovered by Kroto, and Smalley,<sup>1</sup> a lot of scientists have been interested in the properties and reactions of the material. Fullerenes are built up by only carbon like diamond or graphite. Unlike graphite, fullerenes have pentagons as well as hexagons. The pentagon rings made the fullerenes have sphere types structure instead of sheet as graphite. Though there are many fullerene species including C<sub>60</sub>, C<sub>70</sub>, C<sub>76</sub>, C<sub>78</sub>, C<sub>82</sub>, C<sub>90</sub>, C<sub>94</sub>, and C<sub>96</sub>, the most famous fullerene is buckminsterfullerene (C<sub>60</sub>) which consists of sixty carbons. C<sub>60</sub> has destabilization because of the pentagons causing strain energy. Based on the lowest energy Kekulé structure, double bonds are located at the junctions of two hexagons (6-6 double bond) not the junctions of hexagons and pentagons. The soccer ball shaped C<sub>60</sub> was prepared by the resistive heat of graphite to produce carbon soot including fullerenes at the beginning.<sup>2</sup> It was limited to study the reactions of fullerenes and adopt the mass applications of the compounds due to its high cost until other methods were developed to produce large amount of full-

erenes by burning toluene.<sup>3</sup>

The existence of double bonds on fullerenes gives rise to variety of addition reactions for organic chemists. The extension of the reactions prevails in the wide range of polymerization reactions. Adding small amount of C<sub>60</sub> into the polymers can cause a few physical benefits such as photoconductivity,<sup>4</sup> and mechanical property.<sup>5</sup> Another advantage obtainable from polymerization is preventing from aggregations of the fullerene compounds caused by less solubility of C<sub>60</sub> in organic solvents. In this review, we will focus on the representative organic and polymerization reactions with C<sub>60</sub>.

## II. Properties of C<sub>60</sub>

Since double bonds of C<sub>60</sub> are located between two hexagons, the fullerene can be considered to be composed with fused radialenes and cyclohexatrienes. The cyclic voltammetry studies and the theoretical calculation showed that C<sub>60</sub> can be reversibly reduced from one electron to six electrons. It suggested that it was possible to make fulleride anions up to hexaanions by reduction.<sup>6-8</sup> The pyramidalized sp<sup>2</sup> carbons on C<sub>60</sub> can lead to the nucleophilic additions. The driving force of

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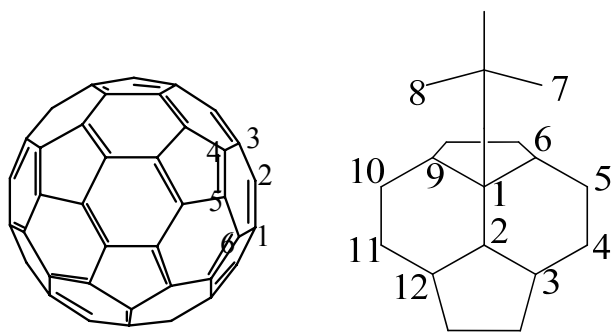


Figure 1. Reaction sites of  $C_{60}$ .

the reaction is the release of the strain energy of pentagons. The addition reaction is regioselective. It is usually minimized to form 5-6 double bonds by the reaction. The most often binding mode with addends is 1,2 addition (binding to both 6-6 double bond) that does not form unfavorable 5-6 double bonds (1,4 addition) (Figure 1). However, the steric hindrance due to bulky additive groups can make 1,4 addition more favorable instead of 1,2 addition that will become more unstable by the strong repulsions between two bulky groups closely located.

### III. Organic reactions

The reactions of  $C_{60}$  extensively include endohedral metal inclusion inside the cage<sup>9</sup> hydrogenation<sup>10,11</sup> and reactions with transition metals such as platinum, palladium, and nickel.<sup>12-15</sup> Besides these broad range of reactions, there are nucleophilic additions, cycloadditions, and radical reactions with  $C_{60}$  that interest both organic and polymer scientists.

The 6-6 double bonds on  $C_{60}$  make it behave as electron deficient alkenes to lead nucleophilic addition reactions when it reacts with organic nucleophiles. The intermediates for the nucleophilic addition were readily prepared by the titration of Grignard reagents or organolithium compounds into the toluene solution with  $C_{60}$ .<sup>16,17</sup> The formed  $R_nC_{60}^{n-}$  intermediates were protonated to give  $C_{60}H_nR_n$ . It is usual to add alkyl halide into the intermediates instead of adding proton to form  $C_{60}R_nR'_n$  compounds as  $CH_3I$  was added to  $R_nC_{60}^{n-}$  to provide  $C_{60}R_n(CH_3)_n$  (Figure 2). The addition is a typical 1,2 addition

to avoid the formation of double bonds at the junctions between hexagon and pentagon on the fullerene. Therefore, the first nucleophilic addition makes C2 the most electron rich carbon followed by C4. This can lead to electrophilic addition to complete the additive reaction unless the addends are so big to bring about steric repulsions between the addends at 1, 2 positions. In the case that R like diethylbromomalonate has a leaving group,  $RC_{60}^-$  can form cyclopropane by intramolecular nucleophilic substitutions.<sup>18</sup> Primary and secondary amines are electron rich groups to react with electron poor  $C_{60}$ .<sup>19,20</sup> Once one electron is transferred from amine to  $C_{60}$ , the radical recombination occurs between positively charged amino radical and the  $C_{60}$  monoanion radical. The reaction is completed by a hydrogen migration from positively charged amino group to negatively charged  $C_{60}$ .

As it was previously shown that 1,2 positions of hexagons are regioselectively accessible for additive reactions, the positions are also applied for cycloaddition reactions. The reaction conditions of [4+2] cycloaddition which is known as Diels-Alder reaction mostly depend on the reactivity of the diene. While it is possible to get monoadduct by reacting  $C_{60}$  with equimolar amount of cyclopentadiene at room temperature, it takes higher energy to obtain monoadduct by reacting excess anthracene to  $C_{60}$ .<sup>21,22</sup> Since some cycloadducts show high thermal stability even up to 400 °C, the derivatives are getting more important in the field of side chain chemistry. [3+2] cycloadditions were achieved as intermediates by reacting  $C_{60}$  to derivatives of diazomethanes,<sup>23,24</sup> diazoacetates,<sup>25</sup> or diazoamides that are 1,3 dipolar reactants.<sup>26</sup> It was actually possible to isolate five-membered [3+2] addition product by reacting diazomethane with  $C_{60}$ . However, after heating or UV irradiation,  $N_2$  extrusion occurred to give 1,2-bridged ring closed structure,<sup>27</sup> or 1,6-ring opened structure resulting in three membered ring (Figure 3).<sup>28</sup> The formation of five-membered intermediate and  $N_2$  extrusion to provide three-membered product was observed when organic azides were reacted with  $C_{60}$ .<sup>29</sup> When the five-membered intermediate was refluxed, aza-bridged fullerene was selectively obtained with 1,6-aza-bridged ring opened structure. The stable five membered  $C_{60}$  compound was constructed by reacting  $C_{60}$  with trimethylene-methane (TMM) well known to undergo [3+2] cycloaddition.<sup>30</sup>

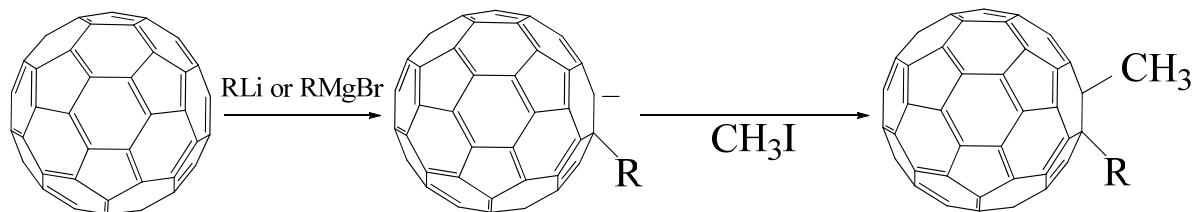
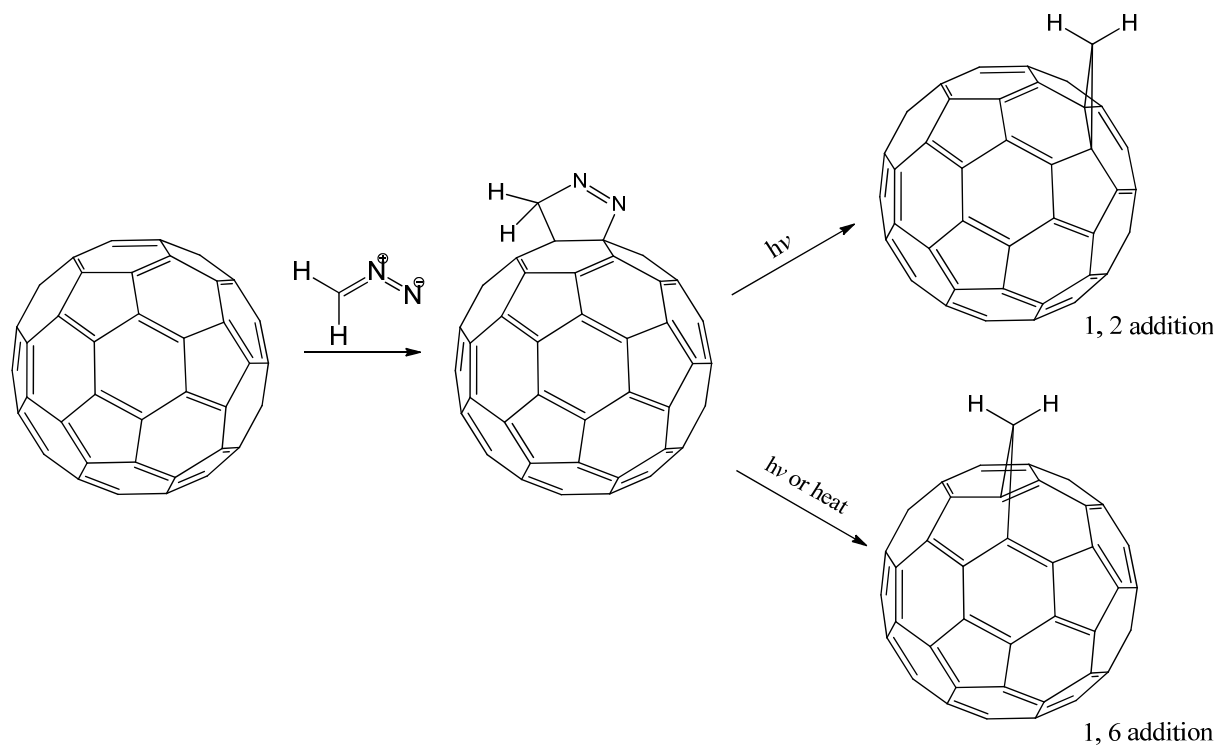


Figure 2. Nucleophilic additive reaction of  $C_{60}$ .



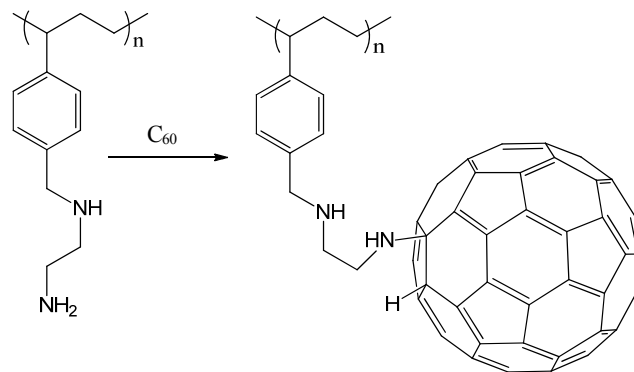
**Figure 3.** [3+2] cycloaddition and its intermediate five-membered ring.

Other examples of stable five-membered geometry with  $C_{60}$  were achieved by azomethine ylides that have chemical formula of  $R-C=N^+(R')-C-R''$ ,<sup>31</sup> nitrile oxides that have general formula  $O-N=C-R$ .<sup>32,33</sup> The four-membered  $C_{60}$  geometry by [2+2] cycloaddition reactions were also observed with benzyne,<sup>34</sup> cyclohexenone derivatives,<sup>35</sup> or N, N-diethylpropynylamine.<sup>36</sup>

As shown in nucleophilic cycloadditions, radical reactions occur when nucleophilic radicals bind to electron deficient  $C_{60}$  to form diamagnetic or paramagnetic radical compounds that are useful for polymerizations. The stability of the radical reaction products such as  $R_nC_{60}^\cdot$  ( $n=1, 3, 5$ ) is relied on the bulkiness of the R group. The radical product composed with R = *t*-butyl group showed higher stability than that of R = H  $C_{60}$  radical compound.<sup>37-40</sup> The radical R groups were prepared by the UV irradiation of alkyl halides, alkyl disulfides, or dialkyl peroxides.<sup>41</sup> Multiple radical addition products were readily prepared by longer UV irradiation of the  $C_{60}$  reaction solution with excess of radical precursors.<sup>42,43</sup>

#### IV. Polymerization

After Krätschmer presented mass preparation of  $C_{60}$ , polymer scientists began to use the fullerene to construct new materials with unusual properties as well as enhanced solubility in different solvents that could not dissolve pure  $C_{60}$ . The use



**Figure 4.** The synthesis of side chain fullerene amino-polymer.

of  $C_{60}$  in the field of polymer was shown as a monomer of polymerization reaction or as a dopant.

When the fullerene was used as a monomer, it could provide different types of polymer  $C_{60}$  derivatives such as side chain polymer, main chain polymer, star shaped polymeric fullerene derivatives, or dendritic fullerene polymer. Side chain fullerene polymers were prepared by reacting  $C_{60}$  to amino polymer,<sup>44</sup> or a polymer with azide group (Figure 4).<sup>45</sup> The former reaction between  $C_{60}$  and amino polymer was addition, and the latter was [3+2] cycloaddition to give side chain polymeric fullerene derivatives. With the concept of nucleophilic addition, polymers containing electron rich carbanions were re-

acted with C<sub>60</sub> to provide fullerenated polymers.<sup>46,47</sup>

Main chain polymeric fullerenes have C<sub>60</sub> on the main backbone of the polymers unlike side chain polymers having C<sub>60</sub> on the branches of the polymers.<sup>48-50</sup> One example of the main chain polymers was prepared by condensation reaction between diaminobenzophenone and *trans*-2-fullerenobisacetic acid in NMP solvent.<sup>51</sup>

Star shaped polymers were prepared by radical polymerization reactions by adding C<sub>60</sub> to distilled styrene,<sup>52,53</sup> or polycarbonate.<sup>54</sup> For the polystyrene-C<sub>60</sub> polymerization, benzoyl peroxide was used as an initiator while AIBN initiator was directly added into the polycarbonate to give polycarbonate fullerene polymer. The UV irradiation or heating at low temperature under 100 °C led to the polymerization for both polymers as well. The C<sub>60</sub> contents of the fullerenated polycarbonate polymers were controlled by varying the amount of C<sub>60</sub> added into the polycarbonate up to 6.3 wt%.

Dendrimers are macromolecules that repeating units regularly spread out from a core. The molecular weight exponentially increases by the increase of the volume of the dendrimer.<sup>55</sup> Dendritic fullerene was synthesized by adopting phenol-functionalized fullerene for the core of poly(aryl ether)-based dendrimer.<sup>56</sup> More fullerodendrimers were prepared by modifying core C<sub>60</sub> moiety to react with dendrimers and using different length of side chains based on poly(aryl ether) dendrimers.<sup>57,58</sup>

Unlike the directly bound fullerene on the polymers, the interaction between C<sub>60</sub> and nonconjugated polymers on fullerene-doped polymers produces new electrical, or optical properties. Polystyrene-fullerene compositions were prepared by blending C<sub>60</sub> with polystyrene.<sup>59</sup> The prepared C<sub>60</sub>-polystyrene film showed higher packing density resulting in slower diffusion rate of gas through the film as compare to that prepared with polystyrene. C<sub>60</sub> doped polyethylene film provides microhardness of the film.<sup>60-62</sup> The hardness of the composites relied on the concentration of C<sub>60</sub> on the film.

## V. Conclusion

The advanced knowledge of organic reactions with C<sub>60</sub> led to the development of polymerization reactions involving the fullerene to provide new properties on the polymers. The known structures of the fullerene polymers include side chain fullerene polymers, main chain fullerene polymer, fullerene dendritic polymer, and star shaped fullerene polymers. Except the polymerization to give rise to new properties, doping polymers with C<sub>60</sub> provides alternatives to accomplish optical or electrical properties. Based on the knowledge previously obtained through organic and polymeric reactions, it affords numerous opportunities to build well designed fullerene polymers for industrial purposes.

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