

# Fullerene Polymers: Synthesis and Properties

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## 1. Introduction

The synthesis and development of macromolecules represents one of the main achievements of chemists in the search for new materials for practical applications. In this regard, although polymer science is nowadays well-developed and can be considered to be perfectly settled down, this is not the case for polymers containing fullerenes, which have only been prepared during the past decade.

Fullerenes, first reported by Curl, Kroto, and Smalley 20 years ago,<sup>1</sup> are highly symmetric cage-shaped molecules constituted only by carbon atoms, which have been thoroughly studied during the last two decades. Since the preparation of fullerene C<sub>60</sub> in multigram amounts in 1990,<sup>2</sup> a wide variety of chemically modified fullerenes have been synthesized and outstanding structural,<sup>3</sup> magnetic,<sup>4</sup> superconducting,<sup>5</sup> electrochemical,<sup>6</sup> and photophysical<sup>7</sup> properties reported.<sup>8</sup> This unabated interest in fullerenes has allowed exploring the many possibilities that these carbon nanostructures have in biological applications<sup>9</sup> and, particularly, materials science as well as in the emerging field of nanoscience and nanotechnology.<sup>10</sup>

Combination of fullerenes and polymer chemistry is a new interdisciplinary field in which all knowledge on the synthesis and study of natural as well as artificial macromolecules can be applied to fullerenes to achieve novel fullerene-based architectures with unprecedented properties and realistic applications. The aim of this review is 5-fold: (i) to extend the scope of fullerene chemistry to a macromolecular level, showing how fullerenes can be covalently incorporated into

a polymer chain, forming side-chain polymers, main-chain polymers, cross-linked polymers, or star-shaped polymers; (ii) to show that the presence of one or two fullerene units in the end-capped or star-shaped polymers can drastically modify the properties of the parent polymer; (iii) to discuss from a chemical point of view the less-known all-C<sub>60</sub> polymers in which the fullerene units are directly connected between them, giving rise to a singular class of fullerene-based polymers; (iv) to present an elegant and rational concept for design of the so-called "double-cable" approach in which the  $\pi$ -conjugated semiconducting polymer (p-type cable) is endowed with covalently connected fullerene units able to interact between them (n-type cable), thus forming a "double-cable" with a priori remarkable advantages for construction of photovoltaic devices; and (v) to highlight the supramolecular polymer chemistry of fullerenes as a new and versatile concept to prepare a wide variety of new C<sub>60</sub>-based polymer materials governed by weak intermolecular interactions, showing unprecedented architectures and enormous potential applications (see Figure 1 for the schematic representation).

Because of their original structure, three-dimensional fullerenes as well as polymers are intrinsically useful scaffolds for construction of high molecular weight structures. Therefore, combination of both systems has led to a wide variety of new materials showing appealing features based on the possibility of tuning their properties by modifying the chemical nature of the components or the chemical linkage between them. Several reviews have previously been reported in the literature.<sup>11,12</sup> However, most of them have been focused on partial aspects or considered within a broader context of general aspects of fullerenes. The aim of the present work is to update the most recent advances on the topic, gathering the huge amount of work reported along the years in a rational and systematic way. Therefore, in this comprehensive review we present the most significant achievements in the field according to the different type of chemical structures and, consequently, their properties and potential applications. Furthermore, in the proposed classification two different classes of C<sub>60</sub>-based polymers not considered in previous reviews have now been included. Thus, the less conventional all-C<sub>60</sub> and related polymers are discussed for the first time in a more detailed way from a chemical viewpoint in connection with other polymer types. In addition, a detailed discussion is presented on the C<sub>60</sub>-based supramolecular polymers as a new class of supramolecular ensembles which have been developed during recent years and exhibit a wide range of potential applications.

A significant aspect which has also been considered in the present work is to comment on the properties and applications of the discussed polymers in connection with

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their different chemical structures. Finally, all the most relevant examples reported in the literature from 2003 have also been collected in the present review. Therefore, this over 460 references revision is a timely and updated mosaic of the state of the art of this new avenue in chemistry combining the outstanding properties of fullerenes with the versatility and processability of polymers.

## 2. All-C<sub>60</sub> and Related Polymers

All-carbon poly[60]fullerenes, or intrinsic polymeric fullerenes, are those materials constituted only by C<sub>60</sub> molecules connected by covalent bonds without any additional linking groups or side groups. This definition also can be extended to those polymers that contain a metal or another element other than carbon in the polymer backbone, and we will refer to such a class of compounds as related heteroatom-containing all-C<sub>60</sub> polymers.

First, we have to clarify that a deeper treatment of this topic is out of the scope of this review since the major efforts devoted to these “polyfullerenes” have been focused on from a physics viewpoint. Furthermore, the reader is referred to some previous reviews<sup>13,14</sup> and a special issue of *Applied Physics A* in which this topic is addressed in more detail.<sup>15</sup> In this section, we will show a general “panoramic sight” on this peculiar class of C<sub>60</sub> polymers.

To date, a number of different strategies have been exploited in order to prepare the so-called all-carbon polyfullerenes. Among them, photopolymerization, pressure-induced polymerization, and charge-transfer polymerization mediated by metals are the most widely investigated, even though some other strategies such as electron beam-induced<sup>16</sup> and plasma-induced polymerization<sup>17,18</sup> have also been studied.

Since the first example of polyfullerene synthesized at high pressure (piezopolymerization) in 1994,<sup>19</sup> a huge amount of



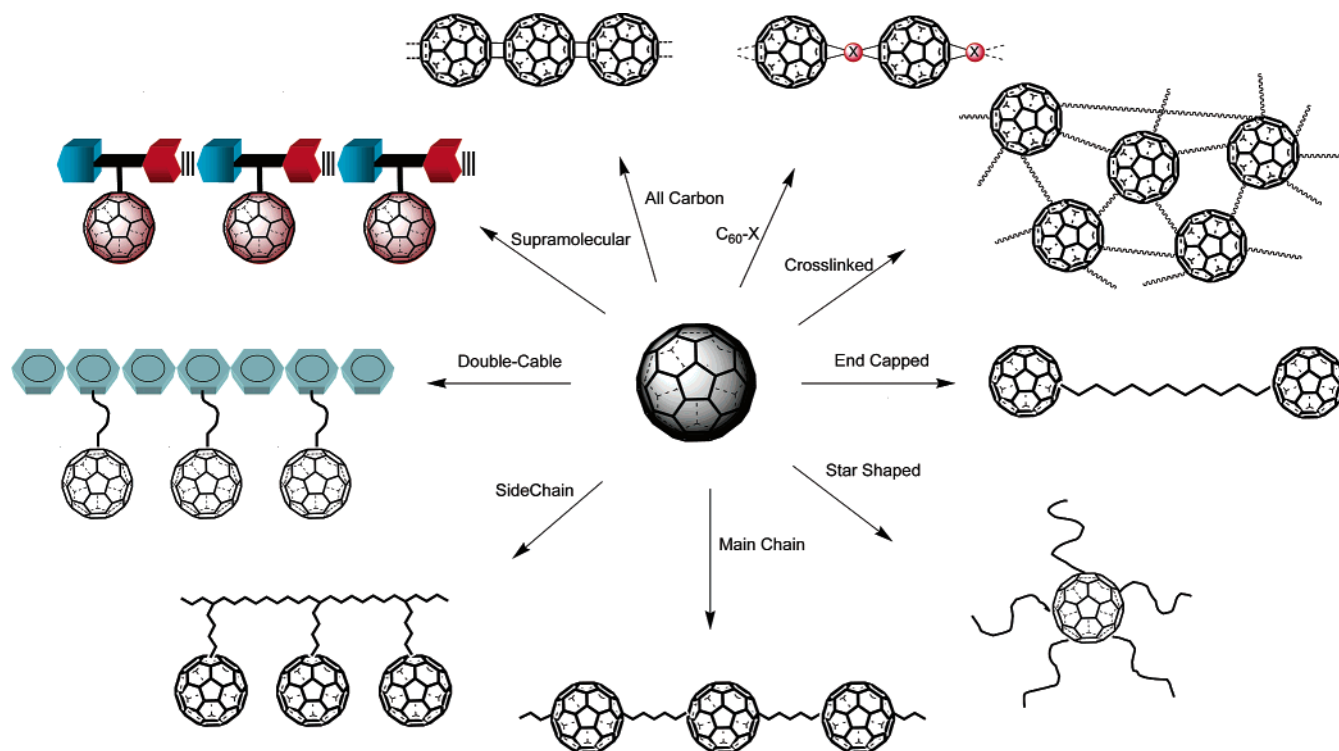
Nazario Martín is a graduate of the University Complutense of Madrid (UCM), where he obtained his Ph.D. degree in 1984. He worked as a postdoctoral fellow (1987–1988) with Michael Hanack on electrically conducting organic materials at the Institut für Organische Chemie der Universität Tübingen. In 1994 he was a Visiting Professor at the Institute for Polymers and Organic Solids (IPOS) at the University of California, Santa Barbara (UCSB), working with Fred Wudl on fullerenes. He is currently Full Professor of Organic Chemistry at the UCM. His research interests span a range of targets with emphasis on the chemistry of carbon nanostructures such as fullerenes and carbon nanotubes,  $\pi$ -conjugated systems as molecular wires, and electroactive molecules, namely, tetrathiafulvalenes (TTFs), in the context of electron-transfer processes, photovoltaic applications, and nanoscience. He has been a visiting professor at UCLA and Angers (France) universities. He is currently a member of the Editorial Board of *Chemical Communications*, and he has served as General Editor of the Spanish journal *Anales de Química* (2000–2005) and a member of the international editorial advisory board of *The Journal of Materials Chemistry*. He is the Regional Editor for Europe of the journal *Fullerenes, Nanotubes and Carbon Nanostructures*. He is a fellow of The Royal Society of Chemistry, and currently he is the President of the Spanish Royal Society of Chemistry.

work has been done in that direction in order to characterize the final product and clarify the mechanism underlying in the process of polymerization.<sup>20</sup> In particular, the influence of the *P/T* treatment on polymerization,<sup>21</sup> the IR, Raman, and vibrational properties,<sup>22</sup> as well as photoluminescence<sup>23</sup> and magnetism<sup>24</sup> have been well investigated.

For the polymerization process, [2+2] cycloaddition reaction between two 6–6 double bonds of two neighboring C<sub>60</sub> molecules seems to be the most likely reaction pathway (Scheme 1). In this reaction a new cyclobutane ring is formed connecting the two fullerene cages.<sup>20a</sup> Proof for polymerization is given by the extreme insolubility of the resulting material in those solvents that do solubilize C<sub>60</sub><sup>19</sup> and by the splitting in the degenerate vibrational modes due to the diminished molecular symmetry.<sup>22b</sup> It has been claimed that these fullerene polymers revert to the pristine monomer upon heating at  $T > 200$  °C.<sup>25</sup>

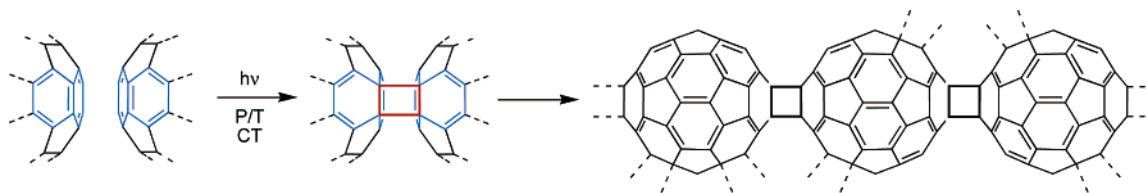
When hydrostatic or quasi-hydrostatic pressure is applied to a sample of pristine C<sub>60</sub> three different scenarios could be presented: pressures up to 25 GPa and  $T \geq 300$  K give rise to metastable materials that return to the starting [60]-fullerene with release of pressure;<sup>26</sup> pressures of several GPa and temperatures of several hundreds of degrees Celsius afford polymeric and metastable materials; high pressures at high temperatures yield polymeric products but with the C<sub>60</sub> cages broken and, sometimes, extremely hard diamond-like materials.<sup>20e,26</sup>

For better comprehension, Figure 2 summarizes the *P* vs *T* phase distribution diagram for C<sub>60</sub> polymerized under pressure. Among all the previously reported investigations, the final polymer has orthorhombic, cubic, rhombohedral,



**Figure 1.** Schematic representation of  $C_{60}$ -containing polymers.

**Scheme 1. Formation of All- $C_{60}$  Polymers by [2+2] Cycloaddition of Pristine  $C_{60}$**



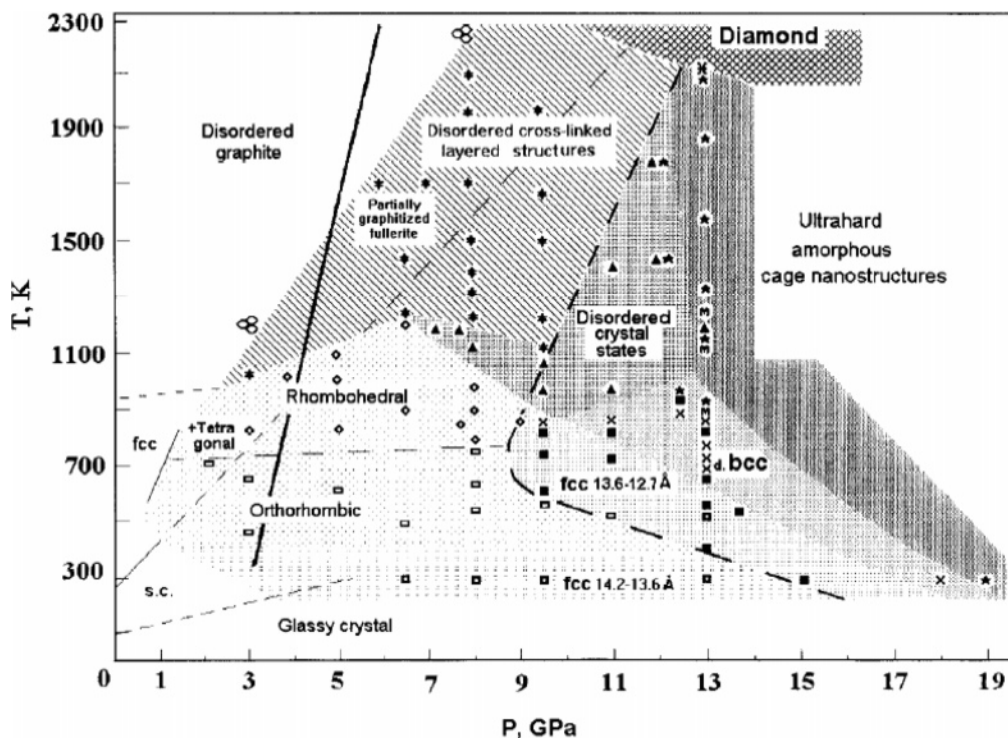
or cross-linked phases. The only documented example of linear polyfullerene has recently been reported by Sun and Reed.<sup>27</sup> They cocrystallized  $C_{60}$  molecules together with *p*-bromocalix[4]arene propyl ether and afterward applied a 5 GPa pressure over 30 min followed by heating at 200 °C for 1 h. Spectroscopic proof that polymerization took place was furnished by IR and Raman spectra, where new signals appear due to the lowering in the fullerene symmetry. In this elegant way the authors prepared a nanofuse rather than a nanowire.

As stated before, photopolymerization is another extensively investigated procedure to polymerize [60]fullerene. Again, a [2+2] cycloaddition reaction mechanism has been proposed for the photopolymerization process.<sup>28</sup> Even though it has been argued that the [2+2] cycloaddition for the neutral  $C_{60}$  can become thermally allowed for charged fulleride anions,<sup>29</sup> this reaction can also be explained in terms of a [2+2] cycloaddition through the excited triplet state of  $C_{60}$  (Scheme 2).<sup>30</sup> This finding is strongly supported by the fact that photopolymerization does not take place in air-saturated cluster solutions.

For the photopolymerized  $C_{60}$  a number of investigations on its bulk<sup>31</sup> and electronic<sup>32</sup> structure, IR,<sup>33</sup> Laser desorption mass spectrometry,<sup>34</sup> as well as magnetic,<sup>35</sup> photophysical, and nonlinear absorptive optical limiting properties<sup>36</sup> have been carried out. The latter are significantly different than those of pristine fullerene. The polymer solution shows much weaker fluorescence, scarcely detectable triplet-state absorption, and marginal optical limiting response.

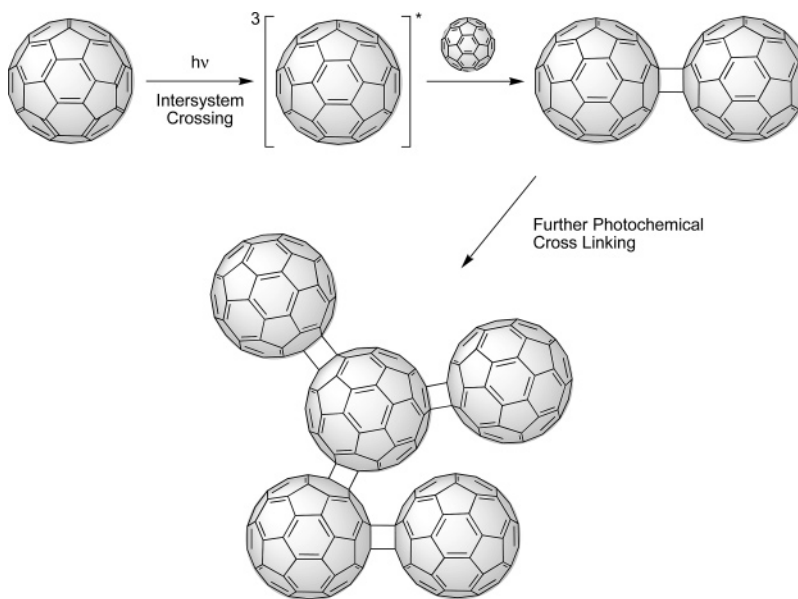
On the other hand, a huge amount of work has been focused on polymeric materials derived from metal doping of  $C_{60}$ , thus obtaining the charge-transfer polymer.<sup>20d</sup> The starting point was the discovery that fulleride phases  $AC_{60}$ , where A is K, Rb, or Cs,<sup>37</sup> undergo [2+2] cycloaddition producing polyfullerene with alkali metals in the crystal voids. It is thought that  $AC_{60}$  phases provide an example of a thermal phase transition driven by the reversible formation and breaking of covalent bonds.<sup>37a</sup> Interestingly, at low temperatures  $RbC_{60}$  and  $CsC_{60}$  become insulators with a phase transition at  $\sim 50$  K, while  $KC_{60}$  behave like a metal for all the low  $T$  investigated. Such a difference is thought to have its origin in the different dimensionality of the system:  $KC_{60}$  is considered a 3D metal, whereas  $RbC_{60}$  and  $CsC_{60}$  are quasi-monodimensional polymers. Other examples of alkali-metal-doped fullerenes are represented by those with Na and Li ions. For  $Na_4C_{60}$  phase a single intermolecular bond form between the fullerene cages was argued,<sup>38</sup> but a different behavior was found for the  $LiC_{60}$  polymers.<sup>39</sup> In fact, the single inter- $C_{60}$  bond form has been proposed by Strasser and Ata as a simple intermediate in the mechanism that leads to formation of [2+2] cycloadduct when  $Li^+$  is used (see Figure 3).<sup>39a</sup>

Nonetheless, the first example of an organometallic polymer of  $C_{60}$  ever reported was described in 1992 by Nagashima and co-workers.<sup>40</sup> They mixed fullerene and  $Pd_2(dba)_3$  (dba = dibenzylideneacetone) in a 1:1 Pd: $C_{60}$  stoichiometry, obtaining a one-dimensional  $C_{60}Pd_1$  polymer. As depicted in Scheme 3, changing the Pd/ $C_{60}$  ratio or heating



**Figure 2.** Map of the pressure–temperature plane showing the various phases of  $C_{60}$  created under different conditions. Symbols denote some of the  $P$ – $T$  coordinates where the experiments have been carried out and samples have been treated for at least 1 min. (—) Denotes the diamond/graphite equilibrium line, while (---) divides semimetal and semiconductor states at  $T > 1100$  K and “soft” and “hard” states at  $T < 1100$  K. (Reprinted with permission from ref 14. Copyright 1998 Elsevier Ltd.)

#### Scheme 2



the monodimensional polymer results in formation of a three-dimensional polymer. Furthermore, when  $Pd_2(dba)_3$  and  $C_{60}$  were mixed in a  $Pd/C_{60}$  ratio  $\geq 4:1$  the corresponding polymer contained Pd atoms deposited in the surface able to catalyze heterogeneous hydrogenation reaction of alkenes.<sup>41</sup>

On the other hand, Balch et al. carried out the study of fullerene/Pd films. They showed that in these systems the polymeric network is formed via covalent bonding between the palladium complexes and fullerene.<sup>42</sup> Due to the electron-accepting properties of  $C_{60}$ , those films present  $n$ -doping properties and can be reversibly reduced at negative potentials. In addition, the doping process is accompanied by

transference of cations from the electrolyte into the solid film deposited on the electrode surface.<sup>42b</sup>

In 2003, a kind of double-cable polymer was prepared by electroreduction of ferrocenylfulleropyrrolidine (**1**) in the presence of palladium(II) acetate trimer.<sup>43</sup> The resulting polymer **2** has a “main chain” constituted by alternating Pd and  $C_{60}$  units, with the ferrocene moiety covalently linked to the latter (Scheme 4).

The authors tried to create a polyfullerene with both  $p$ - and  $n$ -doping properties derived from the presence of the electron donating ferrocene and accepting  $C_{60}$ . It was observed that reduction and reoxidation of the  $Fc-C_{60}/Pd$

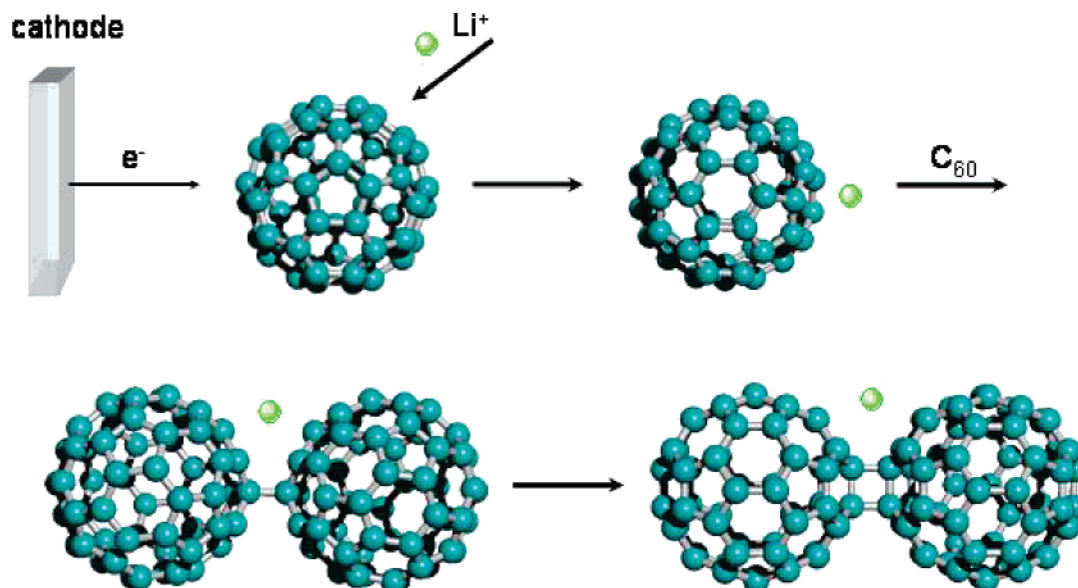
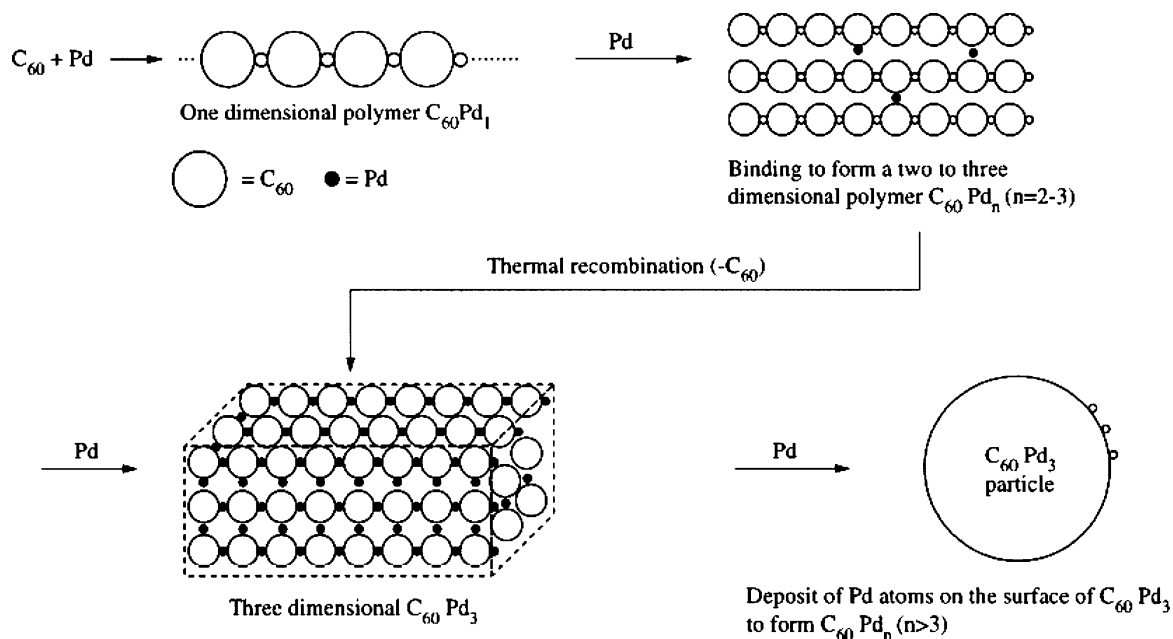


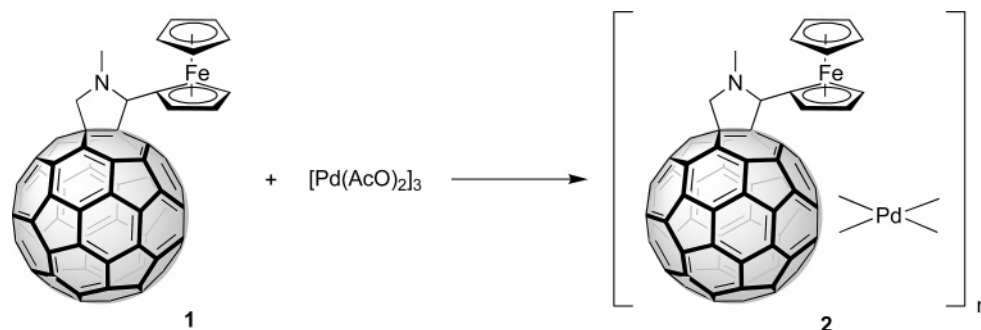
Figure 3. Possible initial formation process and polymerization of C<sub>60</sub>Li.

Scheme 3<sup>a</sup>



<sup>a</sup> Reprinted with permission from ref 40. Copyright 1992 The Royal Chemical Society of Chemistry.

Scheme 4



film involves cation transport between the film and the solvent. On the contrary, oxidation of Fc units occurs via a process of sequential electron self-exchange between Fc groups and is accompanied by anion transport between the solution and the film.

Very recently, C<sub>60</sub>Pd<sub>n</sub> polymers have been successfully employed as gas adsorbents toward volatile and toxic organic compounds.<sup>44</sup> It is interesting to note that the adsorptivity toward toluene was retained even at concentrations as low as 1000 ppb, which is close to the actual toluene concentra-

tion in the environment. The authors proposed a mechanism in which the partially positive Pd atoms attract the  $\pi$  cloud of toluene electrons, as displayed in Figure 4.

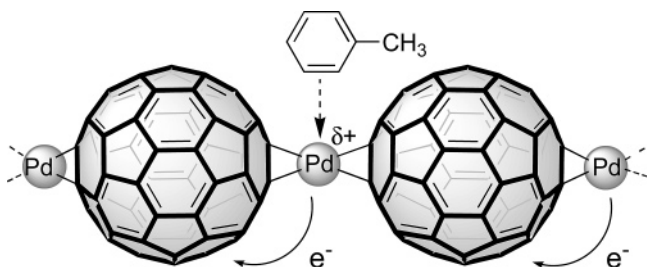


Figure 4.

On the other hand, films of  $(C_{60}O)_n$  have also been synthesized by electroreduction of fullerene epoxide.<sup>45</sup> These films strongly adhere to a variety of electrodes and have the ability to store up to eight electrons per  $C_{60}$  unit with potential application as an energy storage battery.<sup>45a,46</sup> Further improvement in the production of  $(C_{60}O)_n$  films relies on reduction of  $C_{60}$  in the presence of limited amounts of  $O_2$  in a toluene/acetonitrile mixture<sup>47</sup> or in the prolonged ozonation of fullerene.<sup>48</sup> In both approaches the advantage is represented by the fact that in doing so it eliminates the need to prepare  $C_{60}O$ .

Finally, samples of polyfullerene oxide have been synthesized by electron bombardment on thermally activated films of hexanitrofullerene deposited on gold. The proposed mechanism involves, first, cleavage of  $-NO$  bonds with release of gaseous nitric oxide. Thus, following formation of fullerene oxy radicals  $C_{60}-O_6^{\cdot}$  results in formation of cross-linked polymeric network (Scheme 5) that has a thermal stability of up to 900 K.<sup>49</sup>

### 3. Cross-Linked Polymers

Cross-linked polymers containing  $C_{60}$  often represent a less elegant category under a strictly “chemical structure” viewpoint. However, in some cases, when the design of very complex monomer molecules is researched, the three-dimensional polymer that is obtained usually results simply wonderful. Anyway, the latter cases are usually very rare since the syntheses of cross-linked polymers proceed from random and quick reactions that take place, this time with the help of the  $C_{60}$  cage, in the three dimensions.

Furthermore, careful control of the addition reactions to the multiple reactive fullerene double bonds is required since, otherwise, the dimensionality of the final products can increase drastically. In fact, a number of examples in which the monomers, including  $C_{60}$ , are blended and polymerized randomly without a real control on the possible chemical

structure of the resulting material have been reported in the literature. In this light, styrene and fullerene in solution produce randomly branched copolymers with heterogeneous composition especially when free-radical copolymerization takes place.<sup>50</sup> In some particular case, random PS- $C_{60}$  polymers (PS = polystyrene) showed outstanding optical limiting properties.<sup>51</sup>

Obviously, in the preparation of cross-linked polymers, “classical” polymers have been widely employed. Among them, styrene and its derivatives have been extensively used as comonomer to react together with  $C_{60}$  via both free-radical polymerization<sup>52,53</sup> and “living” anionic polymerization.<sup>54,55</sup> Interestingly, when  $C_{60}$  and styrene are reacted in bulk under radical copolymerization conditions, the molecular structure of poly( $C_{60}$ -*co*-St) changes depending upon the  $C_{60}$  content. The higher the amount of fullerene employed in the copolymerization, the more branched the molecular structure.<sup>53</sup> In this investigation the authors compared the  $M_w$  data obtained with a size-exclusion chromatograph (SEC) coupled with a multidetector system, concluding that  $M_w$  values calculated from a refractive index detector are always lower than those obtained by means of absolute methods like differential viscosimetry (DV) and right-angle laser light scattering (RALLS)

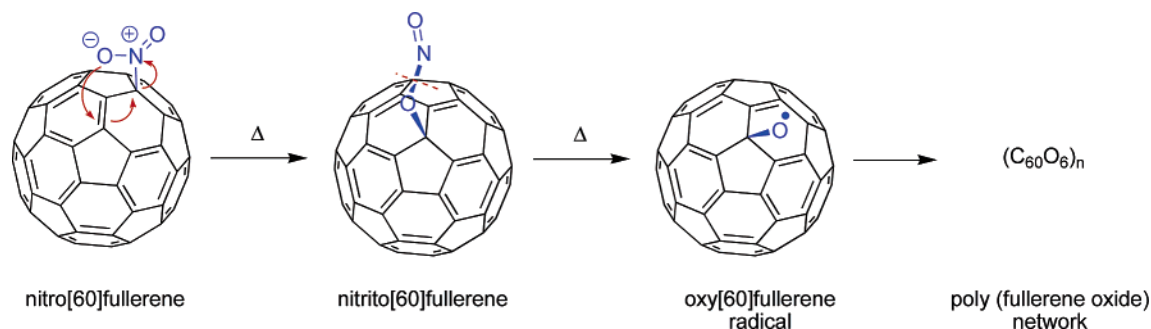
When 4-vinylbenzoic acid is used in the copolymerization instead of styrene, the resulting PS- $C_{60}$  copolymer has a polyelectrolyte character.<sup>52</sup> When NaOH is added to an aqueous dispersion of such polymer, complete solvation takes place due to formation of polycarboxylate anions. The authors, in addition, claim that although such copolymers form clear solutions, they are solubilized microgel dispersions, as deduced by the significant scattering of UV and near-visible radiation. The same phenomenon seems to occur for PS-*co*- $C_{60}$  obtained by living anionic polymerization, even though the authors did not comment on it. In fact, the UV spectra they reported clearly proceed from the scattering of UV radiation.<sup>55</sup>

Finally, two different degrees of cross-linking have been reported by Mathis reacting styrene and divinylbenzene with  $C_{60}$ , employing potassium naphthalate as anionic initiator.<sup>54</sup>

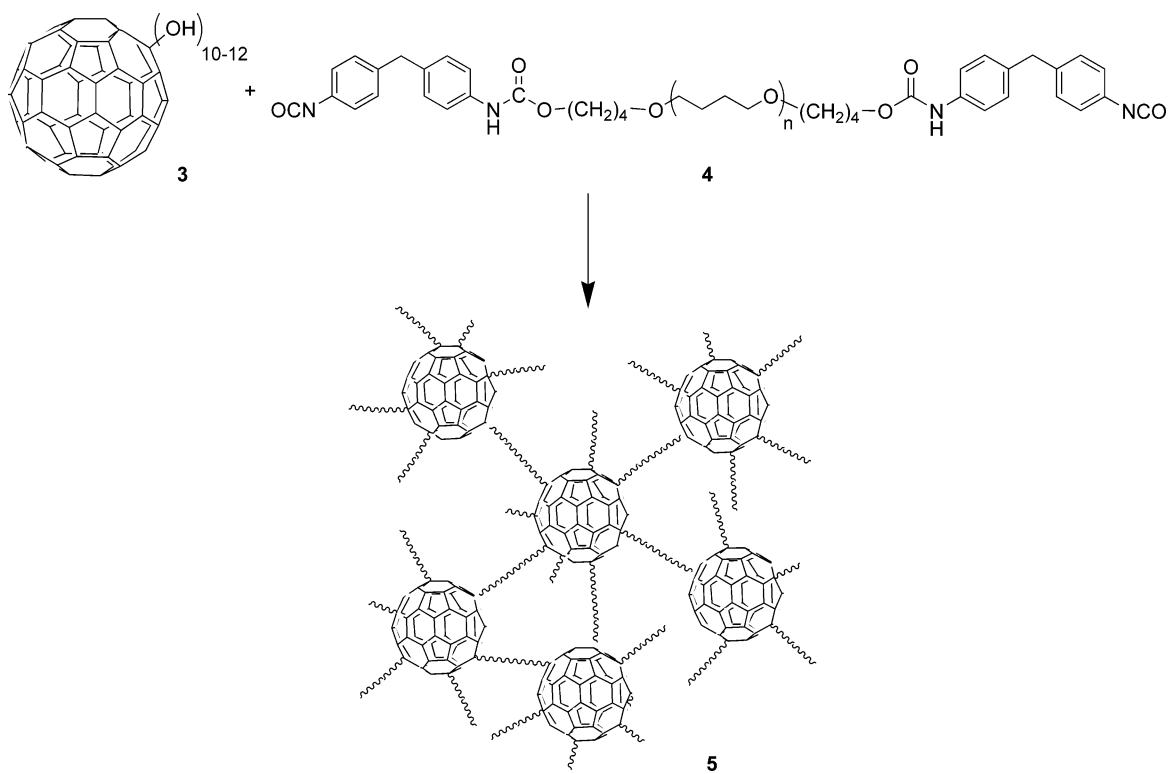
Despite these radical anionic polymerizations, attempts to polymerize styrene and  $C_{60}$  under high pressure resulted in a polymer gel with a content in  $C_{60}$  of 0.1–0.5 wt % with a huge  $M_w$  distribution (from 4000 to  $10^8$  Da).<sup>56</sup>

Another class of polymers which has been widely employed in the synthesis of  $C_{60}$ -containing cross-linked networks is represented by polyurethanes. The first example described by Chiang et al. involves the synthesis of polymer **5** by reacting fullerenols,  $C_{60}(OH)_{10-12}$  (**3**), with a suitably diisocyanate-functionalized prepolymer **4** (Scheme 6).<sup>57</sup>

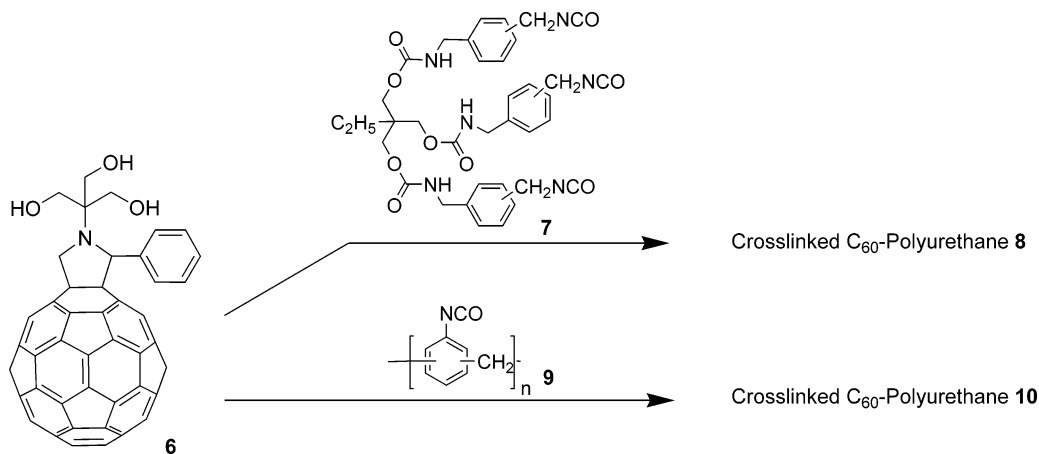
Scheme 5



Scheme 6



Scheme 7



Thermal mechanical analysis of **5** demonstrated that use of fullereneols as cross-linkers improves the properties of polyurethane elastomers as well as the tensile strength at break.

In another investigation fullerene-containing cross-linked polyurethanes displayed optical limiting properties in film with a modulation in the transmittance that depends linearly with the amount of C<sub>60</sub> present in the material.<sup>58</sup>

In a parallel work two new cross-linked polyurethanes containing C<sub>60</sub> has a third-order nonlinear optical (NLO) response.<sup>59-61</sup> These polymers were synthesized using trihydroxy-C<sub>60</sub> derivative **6** and the commercially available isocyanates, **7** and **9**, as depicted in Scheme 7.

As stated before, such polymers showed the largest third-order NLO response within a range of 1150–1600 nm with a  $\chi^3$  of  $9.74 \times 10^{-11}$  esu at 1550 nm. This 1–2 orders of enhancement in comparison with other C<sub>60</sub> materials is probably due to the successful incorporation and good

dispersion of large amounts of C<sub>60</sub> (as high as 19.1 wt % for polymer **7**) into a highly cross-linked polymer.

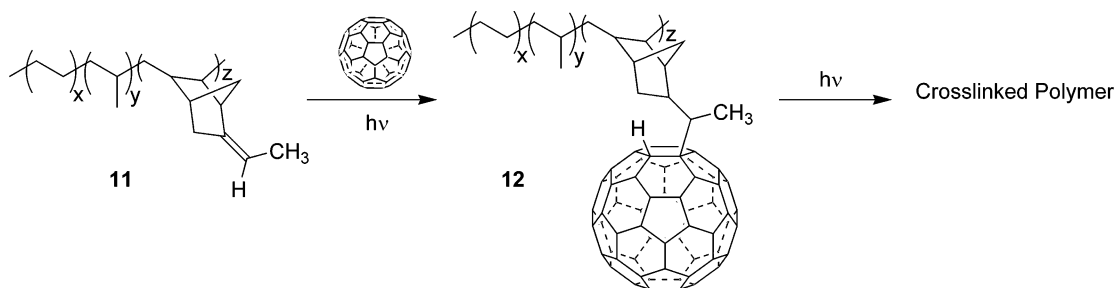
On the other hand, amino-containing polymers have also been used in the preparation of cross-linked-C<sub>60</sub> polymers using *O,O'*-bis(2-aminopropyl)poly(oxypropylene) and *O,O'*-bis(2-aminopropyl)poly(oxyethylene) as precursor polymer.<sup>62</sup>

When a film of a terpolymer constituted by ethylene-propylene ethylidene norbornene (**11**) was irradiated with light in the presence of pristine C<sub>60</sub>, the corresponding ene reaction cross-linked polymer was formed (Scheme 8).<sup>63</sup>

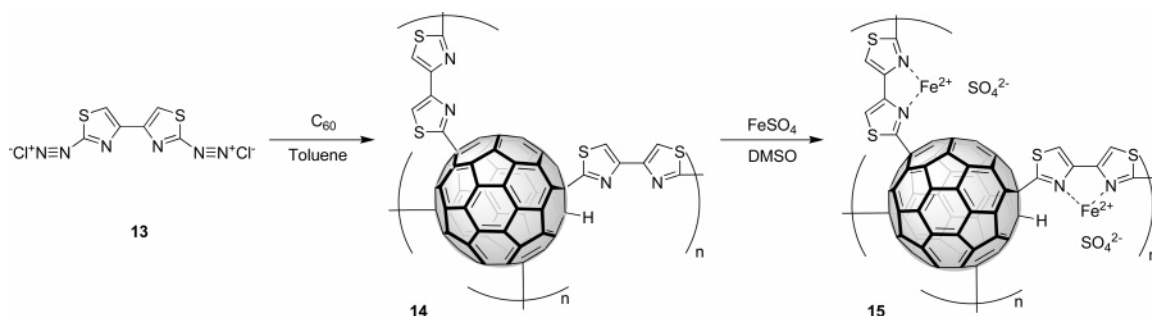
Anionic polymerization reactions take place in the preparation of a C<sub>60</sub>-PVK network (PVK = polyvinyl ketone).<sup>64</sup> The resulting layered structure had good photoconductivity as well as an unusual temperature dependence of the ESR spectrum.

Recently, Sun and co-workers prepared a novel cross-linked copolymer with magnetic behavior by reacting the

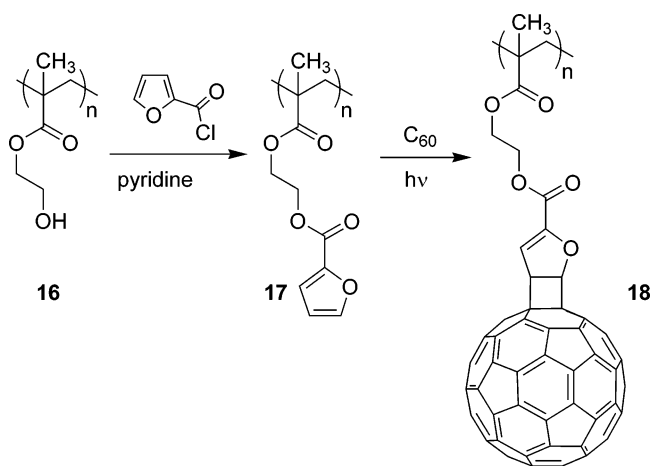
Scheme 8



Scheme 9



Scheme 10



diazo salt derived from bithiazole (13) and [60]fullerene, as displayed in Scheme 9.<sup>65</sup>

Interestingly, after copolymerization, they also prepared the corresponding ferro complexes by treating polymer 14 with FeSO<sub>4</sub> in DMSO solution at 60 °C. The so-obtained derivative 15 had soft magnetic properties, whereas the precursor polymer 14 behaves as an anti-ferromagnetic material.

As stated at the beginning of this section, C<sub>60</sub>-containing cross-linked polymers can be obtained from functionalized polymers. Following this strategy, Tajima and co-workers prepared a poly(2-hydroxyethyl methacrylate) (PHMA) functionalized with a furan ring (17) that after irradiation with visible light incorporated C<sub>60</sub> as side substituent. Further irradiation of the side-chain polymer so obtained led to the corresponding cross-linked polymer 18 (Scheme 10).<sup>66</sup>

Bayerl, Hirsch et al. reported the photochemical synthesis of a lipofullerene (20) by photo-cross-linking of the hexakis-adduct monomer 19, which was in turn prepared following a synthetic strategy in three steps (Scheme 11).<sup>67</sup>

The symmetrical T<sub>h</sub> shape of hexakis-adduct 19 allows formation of a perfect three-dimensional network by an

isotropic polymerization. After irradiation of an aqueous dispersion of multilamellar dipalmitoylphosphatidylcholine (DPPC) vesicles with 15 mol % of monomer 19, polymerization takes place. DPPC was then removed by extraction with organic solvents. The authors pointed out that such polymerization can be assumed to be a kind of emulsion polymerization in which the monomers are dispersed in an aqueous solution and polymerized in the presence of a detergent. Attempts to polymerize 19 in the absence of DPPC afforded only low yields of an amorphous material. Finally, a similar approach has recently been followed for the cross-linking of a C<sub>60</sub> derivative endowed with two diacetylene moieties to measure the exciton diffusion length in a conjugated PPV.<sup>68</sup>

#### 4. End-Capped Polymers

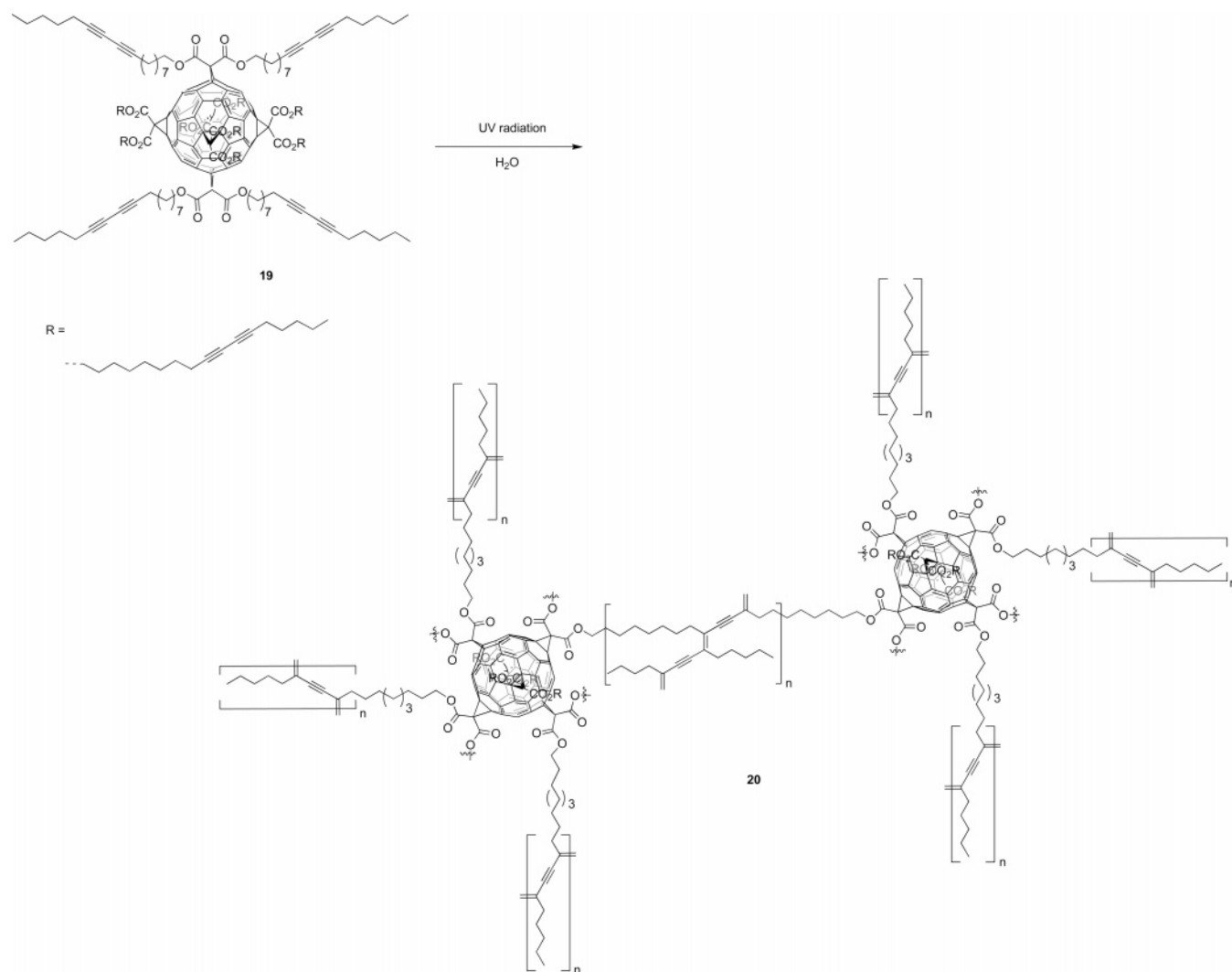
An interesting class of C<sub>60</sub>-containing macromolecules is represented by the C<sub>60</sub>-end-capped polymers, sometimes referred as “telechelic”, in which the C<sub>60</sub> units are located at the terminal positions of the polymer chain. In fact, by introducing one or two fullerene moieties at the end of the chain it is possible to modify the hydrophobicity of the parent polymer, thus drastically changing its behavior in blends of H-donor/H-acceptor polymers.

Goh and co-workers devoted much effort in the preparation and study of mono- and bi-C<sub>60</sub>-end-capped poly(ethylene glycol)s (PEG).<sup>69</sup> The syntheses of 23 and 25 macromolecules are depicted in Scheme 12 and take place in a similar way by treating PEG and PEG–monomethyl ether with thionyl chloride. Reaction of mono-chloro- and bi-chloro-PEG with sodium azide, followed by refluxing the azido-PEG so obtained in the presence of C<sub>60</sub> in chlorobenzene, affords water-soluble mono- (23) and bi-C<sub>60</sub>-end-capped PEG (25), respectively, with narrow polydispersity indexes.

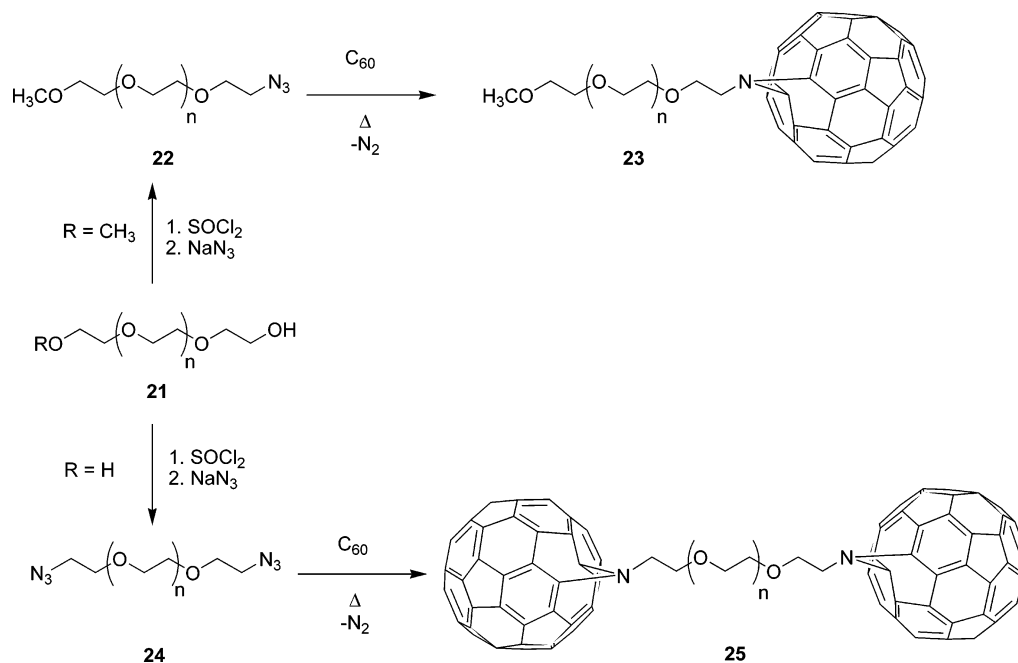
These macromolecules show hydrogen-bonding interactions forming interpolymer complexes (IC) with a number of H-donating polymers such as poly(*p*-vinylphenol),<sup>69</sup> poly(vinyl chloride),<sup>70</sup> poly(methacrylic acid),<sup>71</sup> and poly(acrylic acid).<sup>72</sup> Furthermore, by melt blending of poly(methyl



Scheme 11

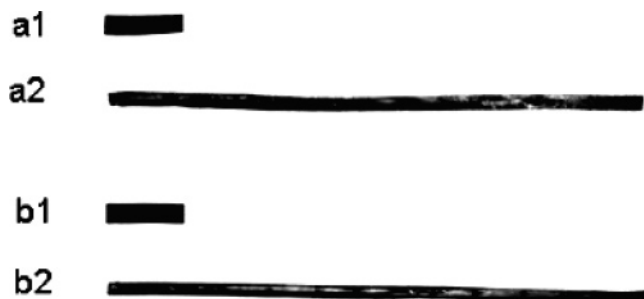


Scheme 12



methacrylate) (PMMA) and **25**, pseudo-semi-interpenetrating polymer networks (pseudo-SIPN) have been prepared show-

ing a storage modulus as high as 42 kPa, 16 times larger than that of PMMA.<sup>73</sup> Very recently, Inoue showed that **25**

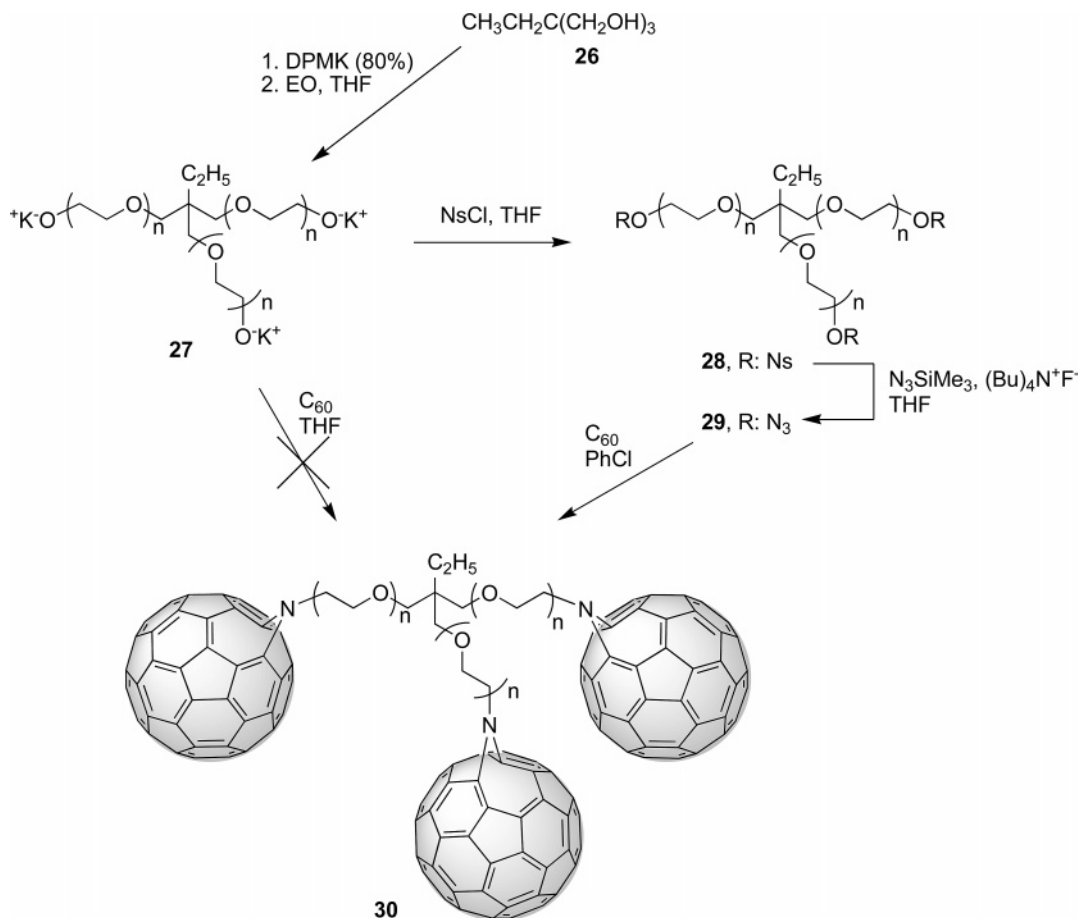


**Figure 5.** Polymer **23** (PEG with  $M_w = 10\,000$ ) specimen before (a1) and after (a2) deformation; polymer **25** (PEG with  $M_w = 20\,000$ ) specimen before (b1) and after (b2) deformation. (Reprinted with permission from ref 75. Copyright 2003 Elsevier Ltd.)

forms pseudo-SIPN when mixed with the biodegradable poly-(L-lactic acid) (PLLA), improving the PLLA fracture strain about 100 times.<sup>74</sup>

Films of double  $C_{60}$ -end-capped PEG **25** have been prepared and tested in mechanical measurements having good mechanical properties stemming from a network-like structure due to the strong aggregation of fullerene.<sup>75</sup> The authors found a value of 20.1 MPa for the tensile strength as well as a very large resistance to elongation that exceeds 640% of the original size (Figure 5). These values for the mechanical properties are as good as and in some case better than those of PEG/polybutylene terephthalate (PBT) thermoplastic elastomers.<sup>76</sup> On the other hand, significant improvements in dynamic mechanical and tensile properties have been achieved from pseudo-SIPN formed by mixing poly-vinyl chloride with doubly  $C_{60}$ -end-capped poly(*n*-butyl methacrylate) in THF.<sup>77</sup>

#### Scheme 13



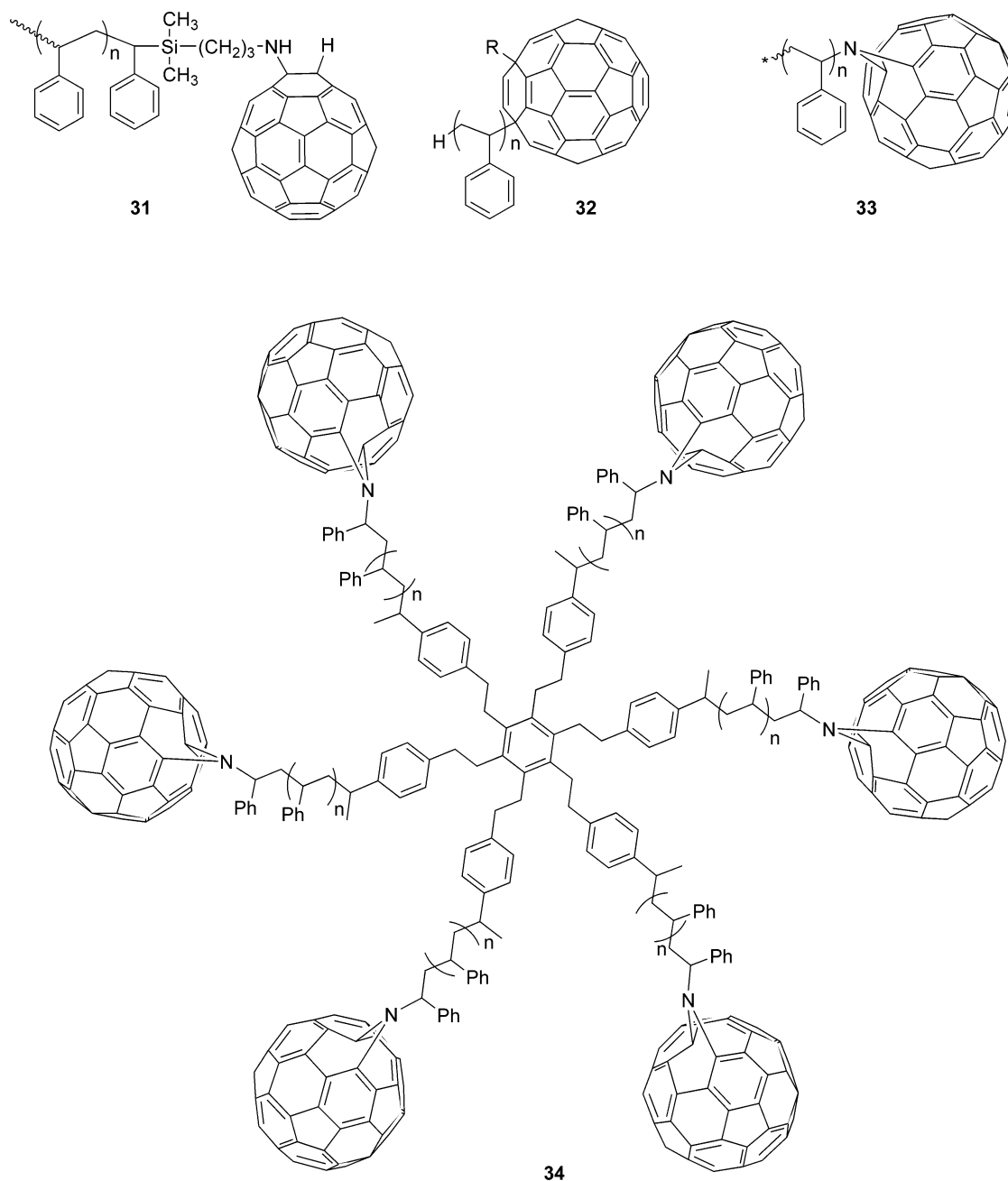
Goh et al. also investigated the crystallization<sup>78</sup> as well as aggregation behavior<sup>79</sup> of these two  $C_{60}$ -end-capped polymers (**23** and **25**). The latter study revealed that the polymers formed aggregation possessing a large and complex structure with many small core-shell-like aggregates. Inclusion complexes have been prepared employing **23** and cyclodextrins (CD).<sup>80</sup> In fact, by mixing **23** together with  $\alpha$ - and  $\gamma$ -CD, 1:1 and 2:1 complexes are formed, respectively.

Very recently, Qin and co-workers described two analogues PEG- $C_{60}$  mono- and di-end-capped polymers prepared incorporating fullerene to amine-terminated poly(ethylene glycol) with an average molecular weight of  $2 \times 10^4$ .<sup>81</sup>

Four-arm  $C_{60}$ -end-capped PEG have also been prepared starting from a commercially available star-shaped PEG.<sup>72</sup> On the other hand, a  $C_{60}$ -end-capped three-branch PEG has been synthesized from triol **26** as shown in Scheme 13.<sup>82</sup>

Synthesis starts with a "living" anionic polymerization of ethylene oxide using 1,1,1-tris(hydroxymethyl)propane as three-arm precursor in order to prepare PEG stars.<sup>83</sup> However, attempts to react  $C_{60}$  directly after the polymerization process were unfruitful. The authors decided to follow a new route involving formation, first, of nosylate groups (4-nitrobenzenesulfonate- Ns) and, second, substitution to azido groups prior to incorporation of fullerene moieties. The star polymer **30** so prepared forms highly expanded Langmuir monolayers.

In 1995, Frey et al. first described an example of  $C_{60}$ -end-capped polystyrene by reacting an amino-terminated PS, prepared by living polymerization, with [60]fullerene<sup>84</sup> (see **31** in Chart 1).

Chart 1. Chemical Structure of Some C<sub>60</sub>-End-Capped Polystyrene Systems

Although such polymer can easily be processed to homogeneous and transparent films containing up to 27 wt % of C<sub>60</sub>, the amount of fullerene incorporated was much less than that in the feed.

To establish the structure–property relationship of C<sub>60</sub>-containing macromolecules it is necessary to know the exact content of fullerene in the polymers. With this aim, one of the possible strategies involves employing a synthetic procedure able to reach well-defined polymers with narrow  $M_w/M_n$  ratios through precise polymerization.

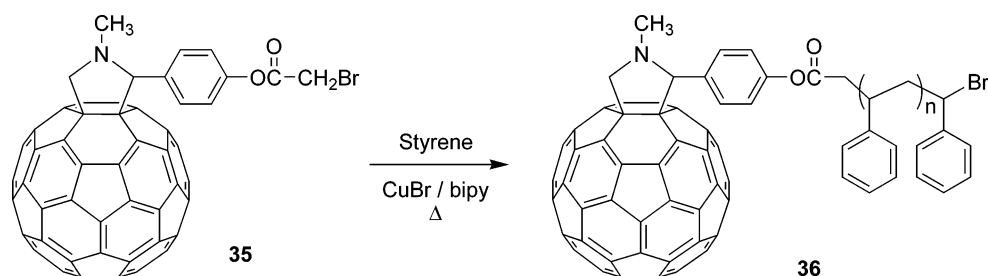
In this sense, attempts to control radical polymerization with [60]fullerene to prepare C<sub>60</sub>-end-capped PS have been carried out using TEMPO-terminated PS (**32**)<sup>85</sup> (TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy) or TEMPOL-terminated PS<sup>86</sup> (TEMPOL = 4-hydroxyl-2,2,6,6-tetramethylpiperidinyloxy). In the latter case, mono-end-capped PS with narrow polydispersity has been prepared showing good conductivity.

A very interesting structure has been proposed by Astruc et al., who prepared a hexaarm hexachloro PS star polymer via living cationic polymerization with a  $M_w$  of 3000 per branch<sup>87</sup> (see **34** in Chart 1).

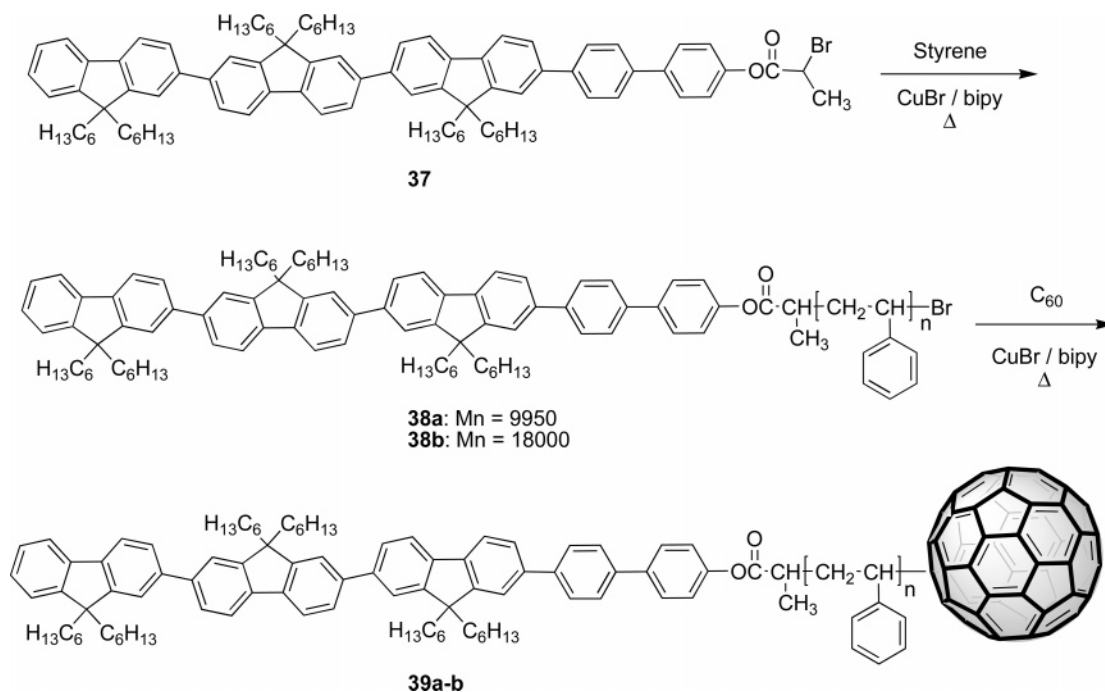
After reaction with sodium azide followed by heating in the presence of a 2-fold excess of C<sub>60</sub>, the hexafulerene-end-capped **34** was prepared.<sup>88,89</sup> Derivatization of the six-branch termini into as many C<sub>60</sub> was not hindered by steric constraints because the size of the PS arms was large enough to avoid mutual interferences. Moreover, the CV of **34** showed three reversible waves at  $E^\circ = -1.00$ ,  $-1.40$ , and  $-1.90$  V vs ferrocene–ferrocinium, corresponding to the three first reduction processes of fullerene-derived compounds,<sup>6b,90</sup> thus constituting a huge polyelectronic reservoir system.

Better results have been obtained employing atom-transfer radical polymerization (ATRP),<sup>91,92</sup> whose major advantage is that polymerization can be performed according to the

Scheme 14



Scheme 15



ordinary free-radical polymerization procedure, thus avoiding the stringent polymerization conditions such as those required for living anionic polymerization needed.

This method has been successfully exploited by Wang<sup>93</sup> and Li,<sup>94,95</sup> who prepared two different well-defined C<sub>60</sub>-end-capped PS with low  $M_w/M_n$  values following two different strategies. In the first approach, they initially prepared a bromo-terminated PS which was in turn transformed into an azido group able to react with C<sub>60</sub> to afford **33**. In the second one, a C<sub>60</sub> derivative was first prepared (**35**) to subsequently undergo a ATRP reaction, thus avoiding formation of bisadducts and multibranched polymers (Scheme 14).<sup>83</sup>

Synthesis of a rod-coil PS polymer end-capped with C<sub>60</sub> in one side and with a terfluorene segment on the other is shown in Scheme 15.<sup>96</sup> Preparation of such a rod-coil polymer was carried out from the properly functionalized terfluorene oligomer **37** followed by incorporation of the polystyrene part by ATRP polymerization in two different degrees of chain extension. Afterward, reaction of **38a** ( $M_n = 9950$ ) and **38b** ( $M_n = 18\,000$ ) with C<sub>60</sub> in the presence of CuBr and bipyridine afforded the corresponding end-capped polymers **39a,b**, which exhibited excellent solubility in organic solvents and were stable materials for polymeric light-emitting diodes (PLED's).

A new example of C<sub>60</sub>-end-capped PS synthesized by ATRP was reported by Li in 2000 together with the preparation of a C<sub>60</sub>-end-capped poly(methyl methacrylate).<sup>97</sup> In both cases, the polydispersity indexes were narrow and the

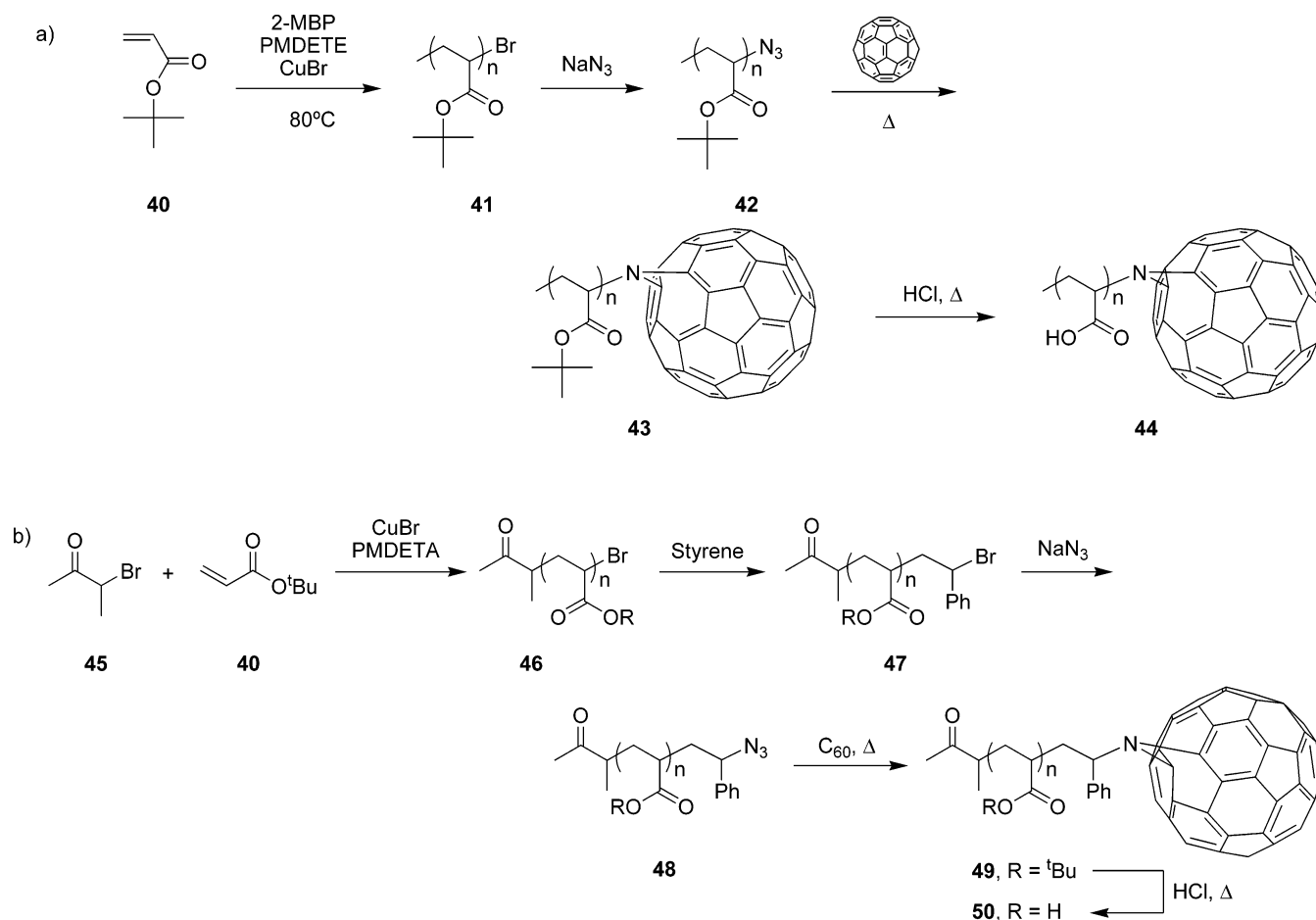
PMMA-based polymer showed a quenching of the fluorescence when mixed together with triethylamine or fumaronitrile, thus indicating that C<sub>60</sub> still maintains its strong electronic properties.

It is remarkable how the ATRP method has been the most used technique for preparation of PMMA and poly(butyl methacrylate) (PBMA)<sup>98,99</sup> as well as for synthesis of poly(*tert*-butylacrylate) (PtBA) and poly(acrylic acid) (PAA).<sup>100</sup> In the first two examples an equilibrium exists in THF between individual polymer chains and micelle-like core-shell aggregates, the shell being made of highly stretched polymeric chains. On the other hand, PtBA (**43**, **49**) and PAA C<sub>60</sub>-end-capped (**44**, **50**) and C<sub>60</sub>-terminated PtBA-PS block copolymer,<sup>101</sup> which were prepared following a multistep synthetic procedure (Scheme 16), had a dramatic enhancement in photoconductivity, which increases linearly with the C<sub>60</sub> content.

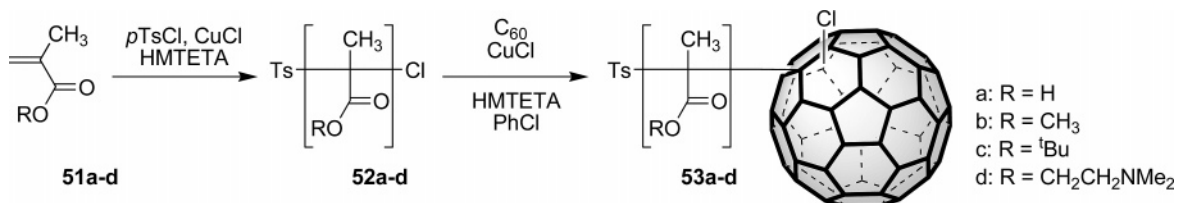
Very recently, syntheses of PMAA (**53a**),<sup>102,103</sup> PMMA (**53b**),<sup>104</sup> PtBMA (**53c**),<sup>105</sup> and poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA) (**53d**)<sup>106</sup> and its sulfobetaine derivative<sup>107</sup> end capped with C<sub>60</sub> via ATRP reaction have been described, as depicted in Scheme 17.

Tam et al. showed that while C<sub>60</sub>-end-capped PMMA presented pH-responsive and water-soluble properties at high pH,<sup>103</sup> the aggregation behavior of C<sub>60</sub> end-capped PDMAEMA in aqueous solution can be tuned by adjusting pH or temperature. At low pHs micellar aggregates coexist with unimeric C<sub>60</sub>-PDMAEMA **53d** in solution. However,

## Scheme 16



## Scheme 17



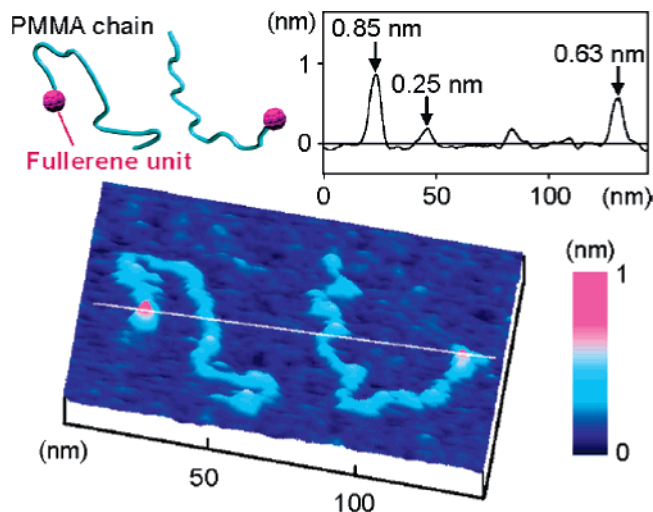
at high pH insoluble C<sub>60</sub>-PDMAEMA suspensions are produced at high temperatures and transform into unimeric particles at lower critical solution temperature (LCST) of PDMAEMA via formation of the charge-transfer complex. The pH and temperature stimuli-response properties of a C<sub>60</sub>-containing block-copolymer poly(MAA-*b*-DMAEMA) in aqueous solution have also been investigated by the same authors.<sup>108</sup>

On the other hand, Gan et al. prepared an amphiphilic doubly C<sub>60</sub>-end-capped ABA triblock polymer via ATRP strategy.<sup>109</sup> This water-soluble poly(2-(dimethylamino)ethyl methacrylate)-*b*-poly(ethylene oxide)-*b*-poly(2-(dimethylamino)ethyl methacrylate) capped with C<sub>60</sub> at both ends forms flower micelle-shaped aggregates with a low critical micelle concentration value (2.1 mg dm<sup>-3</sup>), suggesting potential use as a carrier for drug/gene delivery application. Yajima and co-workers earlier presented a research in which a poly(*N*-isopropylacrylamide) ended with an azofullerene moiety shows rapid and reversible dispersion–aggregation changes in response to a narrow range temperature alternation across its lower critical solution temperature in water.<sup>110</sup> This new stimuli-responsive polymer could be used for development

of a smart material in biomedical fields as well as the fullerene-tagged poly(L-glutamic acid), formerly synthesized, which is able to remove the biologically important superoxide radical, thus mimicking the superoxide dismutase.<sup>111</sup>

In 2005 a very important investigation was reported by Yashima et al., who prepared high molecular weight isotactic PMMA–C<sub>60</sub> synthesized by anionic living polymerization and whose single molecule could be observed with AFM microscopy.<sup>112</sup> They were able to separate PMMA–C<sub>60</sub> chains from PMMA prepolymer by self-assembly of the C<sub>60</sub>-polymer followed by size-exclusion chromatography. Furthermore, they obtained AFM images of single PMMA–C<sub>60</sub> molecules, as displayed in Figure 6.

It is noteworthy that analyzing *M<sub>n</sub>* and *M<sub>w</sub>* results obtained by GPC the examples of C<sub>60</sub> end-capped PS fit well with the weights estimated for the parent PSs.<sup>84,85,97,113</sup> This fact can be better understood taking into account that the standard polymers used for the GPC curve calibration were PSs, thus justifying the good agreement observed. However, this is not true for the PMMA-, PAA-, and PDMAEMA-based C<sub>60</sub>-end-capped polymers in which the [60]fullerene has a smaller impact on the weight's values than that expected due to the



**Figure 6.** Tapping-mode AFM height images of isolated PMMA- $C_{60}$  spin cast from a dilute solution in chloroform on mica. The height profile measured along the white line in the image is also shown. (Reprinted with permission from ref 112. Copyright 2005 American Chemical Society.)

low compact effect that  $C_{60}$  has on the overall hydrodynamic volume.<sup>98,100,103,105</sup>

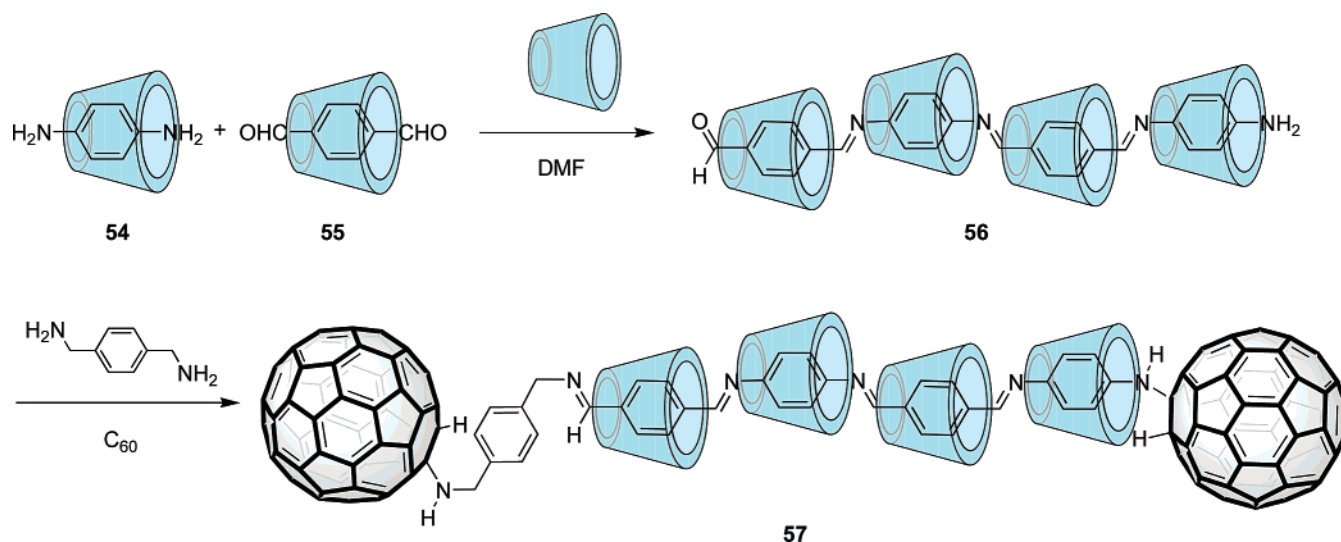
In 2003 Geckeler reported on the synthesis of an aromatic poly(azomethyne) rotaxane by condensing terephthalaldehyde and *p*-phenylenediamine in the presence of large amounts of  $\beta$ -CD (Scheme 18).<sup>114</sup>

The only way to retain the CD units in the chain was capping both extremes with  $C_{60}$ , which will act as stopper and in the meantime as self-dopant for the polyrotaxane. The efficiency of fullerene as chain blocker was proved by  $^1H$  NMR. In fact, pseudo-rotaxane **57** without stoppers at the ends had 71.65 CD protons for each  $-CH=N-$  proton (a molecule of  $\beta$ -CD contains 70 protons). In this nice example the CD covering could be used both to enhance the solubility of high molar mass poly(azomethyne) without making any structural changes as well as a good electrical insulator for electroluminescence purposes.

## 5. Star-Shaped Polymers

Star-shaped fullerene-containing polymers, also known as “flagellenes”, are comprised from 2 to 10 long and flexible

**Scheme 18**



polymer chains covalently linked to a fullerene cage with topologies similar to that of sea stars or resembling the shape of flagellate-unicellular protozoa. In this section we will not refer to the  $C_{60}$  content of such macromolecules, rather low in all cases, ranging from of only one to two  $C_{60}$  units in each star.

Some authors usually refer to the paper of Olah and co-workers<sup>115</sup> as the first example of this class of compounds. However, they described the synthesis of a  $C_{60}$ -benzene multiadduct catalyzed by  $AlCl_3$ . The real first example of  $C_{60}$ -star-shaped polymer was published just 1 year later by Bohme, who used  $C_{60}^{2+}$  and  $C_{70}^{2+}$  as initiators for polymerization of gaseous butadiene.<sup>116,117</sup>

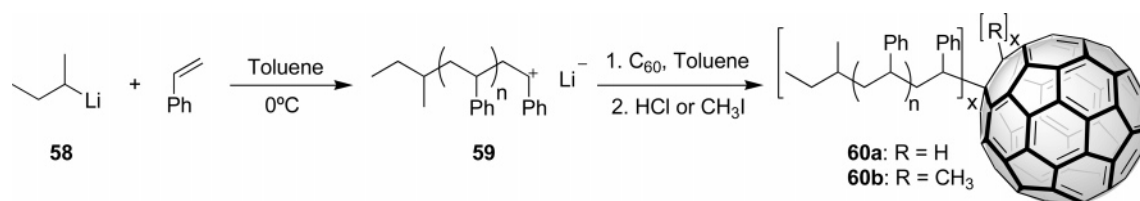
On the other hand, “living” anionic polymerization has been the most employed method for the preparation of PS- $C_{60}$  star polymers. In fact, as stated previously in this review, “living” anionic polymerization allows better control of the molar weights as well as their distributions. The first PS-containing flagellene was prepared following the synthetic route displayed in Scheme 19.<sup>118,119</sup>

Such  $C_{60}(PS)_x$  (**60a,b**) were found to be highly soluble and, due to their melt processable properties, may be spin-coated, extruded to fiber and films, or solvent casted. A lot of effort has been done by Mathis and Ederlé in the synthesis and investigation of  $C_{60}(PS)_x$ .<sup>120</sup> They showed that, under high-purity conditions, addition of “living” polymers can be well controlled both in number of chains linked to the  $C_{60}$  and in dimensions of the final products, reaching well-defined architectures.<sup>121–123</sup> Physicochemical studies on  $C_{60}(PS)_6$  revealed that upon decreasing the molecular weight from  $2 \times 10^6$  to  $5 \times 10^5$ , a change from random coil-type behavior toward a dense sphere can be observed.<sup>124</sup> In addition,  $C_{60}(PS)_6$  possessing  $M_w$  in the 3000–50 000 range gave rise to porous membranes with a honeycomb shape when  $CS_2$  solutions of these polymers were evaporated.<sup>125</sup>

Thermal stability as well as the anomalies in glass transitions<sup>126</sup> of  $C_{60}(PS)_6$  have also been investigated. The former studies revealed that the degradation reaction follows a stepwise “breaking” mechanism in which the 6-arm star is first converted to a 5-arm and so on, successively down to the  $C_{60}$  (Figure 7).<sup>127,128</sup>

Several strategies have been followed in order to prepare palm-tree architectures derived from  $C_{60}$ -containing polymers. One involves initially the synthesis of an end-capped-

## Scheme 19



PS joined to C<sub>60</sub> via an azido group, which in turn has been used to covalently graft five polystyryllithium or polyisopropyllithium arms.<sup>129</sup> A second approach permits obtaining dumbbell-like polymer architectures starting from palm-tree-C<sub>60</sub>(PS)<sub>6</sub> polymers, as shown in Scheme 20.<sup>130,131</sup>

After attaching six PS<sup>-</sup>Li<sup>+</sup> chains on the C<sub>60</sub> cage, only one of the six carbanions formed is able to initiate polymerization of styrene or isoprene, affording the corresponding palm-tree-like structure **62**. Two equivalents of such a “living” polymer in turn react with dibromoxylene, dibromooctane, or fullerene itself to form the very nice dumbbell structure **63a–c**.

Living anionic polymerization has also been employed to produce C<sub>70</sub>-containing star-shaped polymers.<sup>132,133</sup>

In addition to the anionic polymerization,<sup>134</sup> PS chains have been grafted onto C<sub>60</sub> to form starlike polymers via free radical,<sup>135</sup> ATRP on C<sub>60</sub>,<sup>136</sup> C<sub>60</sub>Cl<sub>n</sub>,<sup>137</sup> as well as through “living” radical polymerization.<sup>138</sup> The latter issue has been well developed by Fukuda et al., who reported on the synthesis of 1,4-dipolystyryldihydro[60]fullerene starting from narrow polydispersity polystyryl adducts TEMPO-end-capped (Scheme 21).<sup>138a–c</sup>

The C<sub>60</sub>(PS)<sub>2</sub> (**65a,b**, **66**) thus prepared gave UV–vis spectra characteristic for 1,4-bisadducts and also retained the redox properties of [60]fullerene. At the same time light-scattering studies revealed that C<sub>60</sub>(PVP)<sub>2</sub> (**65b**) and C<sub>60</sub>(PS–PVP)<sub>2</sub> (**66**) in THF form multilamellar micelles.<sup>138b</sup>

Recently, a two-arm poly(“butyl acrylate), prepared via ATRP, has been grafted onto a C<sub>60</sub> cage through a Bingel reaction, leading to a well-defined polymeric methanofullerene.<sup>139</sup>

On the other hand, improvements by ~5 and ~20 times the quantum efficiency and emitted light power were obtained using the (PS)<sub>x</sub>C<sub>60</sub>(PMMA)<sub>y</sub> star polymer as active layer in a ITO/MDMO–PPV/(PS)<sub>x</sub>C<sub>60</sub>(PMMA)<sub>y</sub>/Al device.<sup>140</sup> A very interesting synthetic strategy has been adopted by Hiorns et al. for synthesis of C<sub>60</sub> star block copolymer C<sub>60</sub>(PS-*b*-PPP)<sub>6</sub> (**71**) and C<sub>60</sub>(styrene-PPP-*b*-PS)<sub>6</sub> (**76**).<sup>141</sup> As depicted in Scheme 22, they first prepared poly(1,3-cyclohexadiene) (PCHD, **68**) by living anionic polymerization as precursor for the block copolymer PS–PCHD (**69**), which was in turn reacted with C<sub>60</sub> and oxidized with DDQ to afford C<sub>60</sub>(PS-*b*-PPP)<sub>6</sub> **71**. An analogous route was followed for C<sub>60</sub>(styrene-PPP-*b*-PS)<sub>6</sub> **76**.

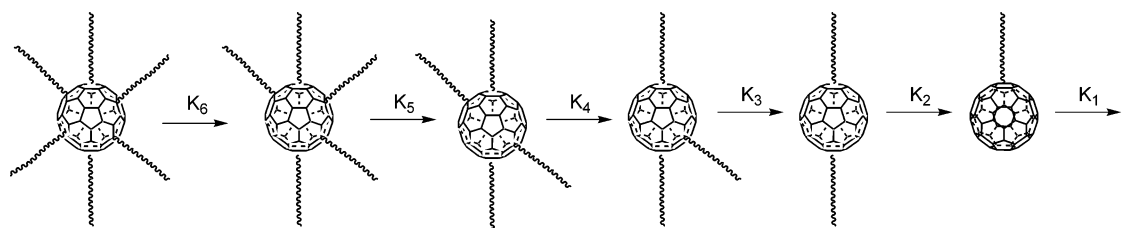
Again, C<sub>60</sub> was observed to limit the number of linked polymeric chains to six even if a 10:1 stoichiometry arm:

C<sub>60</sub> is used, probably due to the strong steric hindrance around the fullerene core. Furthermore, **76** had an effective quenching of PPP fluorescence that was considered indicative for a charge transfer from the donor fragment PPP to the acceptor C<sub>60</sub>.

As already seen in the previous paragraphs, PVK has been widely employed to prepare polymers and copolymers with C<sub>60</sub>. PVK-based star-shaped-C<sub>60</sub> polymers with three arms have been recently described.<sup>142,143</sup> In one case, (PVK)<sub>3</sub>C<sub>60</sub> has been used as hole-transporting layer in an electroluminescent ITO/(PVK)<sub>3</sub>C<sub>60</sub>/CPDHFPV/Al device (CPDHFPV = poly(9,9′-dihexylfluorene-2,7-divinylene-*m*-phenylenevinylene-*stat-p*-phenylenevinylene), resulting in quenching of the electroluminescence.<sup>143</sup> On the contrary, when a new PVK layer was added, the new device showed 3-times improvement in the emitted light power. (PVK)<sub>4</sub>C<sub>60</sub> star polymers have also been synthesized starting from C<sub>60</sub>Cl<sub>20</sub> as the central core in the radical ATRP polymerization.<sup>144,145</sup>

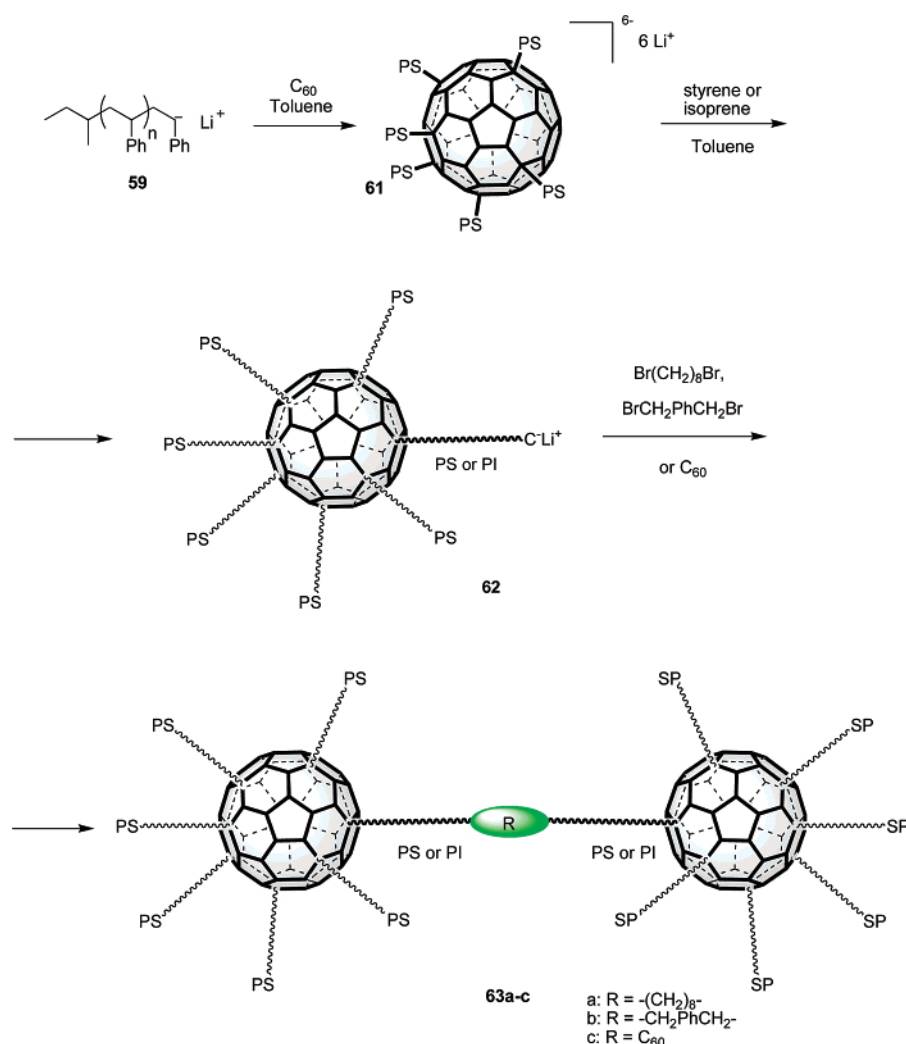
Use of a multisubstituted fullerene as the central core is not a novel approach since it was adopted in several C<sub>60</sub>-cross-linked polymers.<sup>57</sup> The most used C<sub>60</sub>-multiadduct in the preparation of star-shaped polymers is fulleranol, C<sub>60</sub>(OH)<sub>n</sub> (**3**). In this regard, Goswami and co-workers prepared ether-connected star-shaped C<sub>60</sub>-polymer, reacting fulleranol together with a cycloaliphatic epoxy resin **77** in order to form the corresponding hemiketals (**78**, Scheme 23).<sup>146</sup> Moreover, fullerenols have been employed as suitable reactants for the synthesis of several polyurethanes by reaction with isocyanates (see polymers **80** and **82** in Scheme 23).<sup>147,148</sup> The synthesis and aggregation behavior of a two-arm fullerene-containing poly(ethylene oxide) **80** has been described by Goh and Tam.<sup>149</sup> They reacted C<sub>60</sub>(OH)<sub>10–12</sub> with PEO-monocyanate **79** in a 1:2 stoichiometry, thus forcing the amphiphilic two-arm product that in polar solvents forms large spherical aggregates with an average size of 540–1020 single polymer chains.

Other examples of star-shaped C<sub>60</sub>-containing PEO<sup>150</sup> prepared by reaction of C<sub>60</sub> with “living” PEO–K<sup>+</sup> chains<sup>151</sup> with PEO–N<sub>3</sub><sup>152</sup> or PEO–NH<sub>2</sub> chains<sup>153</sup> are also known in the literature. In the above-mentioned examples the fullerene core was surrounded by 3–7 PEO arms. Other examples involve the synthesis and characterization of star-shaped C<sub>60</sub>-poly(vinylpyrrolidone),<sup>154</sup> (CH<sub>3</sub>)<sub>3</sub>–C<sub>60</sub>–PMS<sub>3</sub>,<sup>155</sup> and C<sub>60</sub>-polyacrylonitrile polymer.<sup>156</sup> When the latter polymer was pyrolyzed, the appearance of C=N chains was evidenced



**Figure 7.** Thermal-degradation mechanism of C<sub>60</sub>(PS)<sub>6</sub> stars.

Scheme 20



by in-situ IR measurements and followed by formation of aromatic rings when the temperature was further increased.<sup>157</sup>

On the other hand, fullerene  $\text{C}_{60}$ , besides being incorporated as the core of a star-shaped polymer, can act as a cocatalyst provided that a determined reaction takes place. In this light, it has been demonstrated that whereas W-based catalysts such as  $\text{WCl}_6\text{-Ph}_4\text{Sn}$  polymerize terminal acetylenes, such catalysts are not able to polymerize disubstituted ones.<sup>158</sup> In fact, only 0.5% yield on the polymerization of 1-phenyl-1-propyne has been obtained, while when  $\text{C}_{60}$  is present even in small amounts, the polymer yield dramatically increases to 77%.<sup>159</sup> Moreover, the PD indexes were lowered from 1009 to 2.2 at the same time that the  $M_w$  were increased.

The reaction sequence that affords the star-shaped polymer **88** is shown in Scheme 24. Polymerization propagates via a wolframa-carbeno-mediated metathesis mechanism, and the polymeric chains are finally linked to  $\text{C}_{60}$  via a carbene addition to a double bond, producing a new cyclopropane ring. It is worth noting that polymer **88** emits a strong blue light upon excitation, higher than that of pure polymer without fullerene.<sup>160</sup>

Finally, Chiang and co-workers described the gradual synthesis of hexaarm oligoaniline and polyaniline- $\text{C}_{60}$  star polymer.<sup>161,162</sup> The polymers were prepared by nucleophilic substitution of the tertiary  $\text{NO}_2$  groups (used as good leaving groups) from the hexanitrofullerene  $\text{C}_{60}\text{-(NO}_2)_6$  replaced with aniline, oligoaniline, and polyaniline. Photoexcitation of such

materials produced photoinduced intramolecular electron transfer from benzenoid moieties of oligoaniline arms to the  $\text{C}_{60}$  sphere.<sup>163</sup> The same authors synthesized a palm-tree polymer series **91a-d** by capping the poly(dimethylsiloxane) **90** with hexanitro[60]fullerene followed by substitution with oligoaniline (Scheme 25).<sup>164</sup>

## 6. Main-Chain Polymers

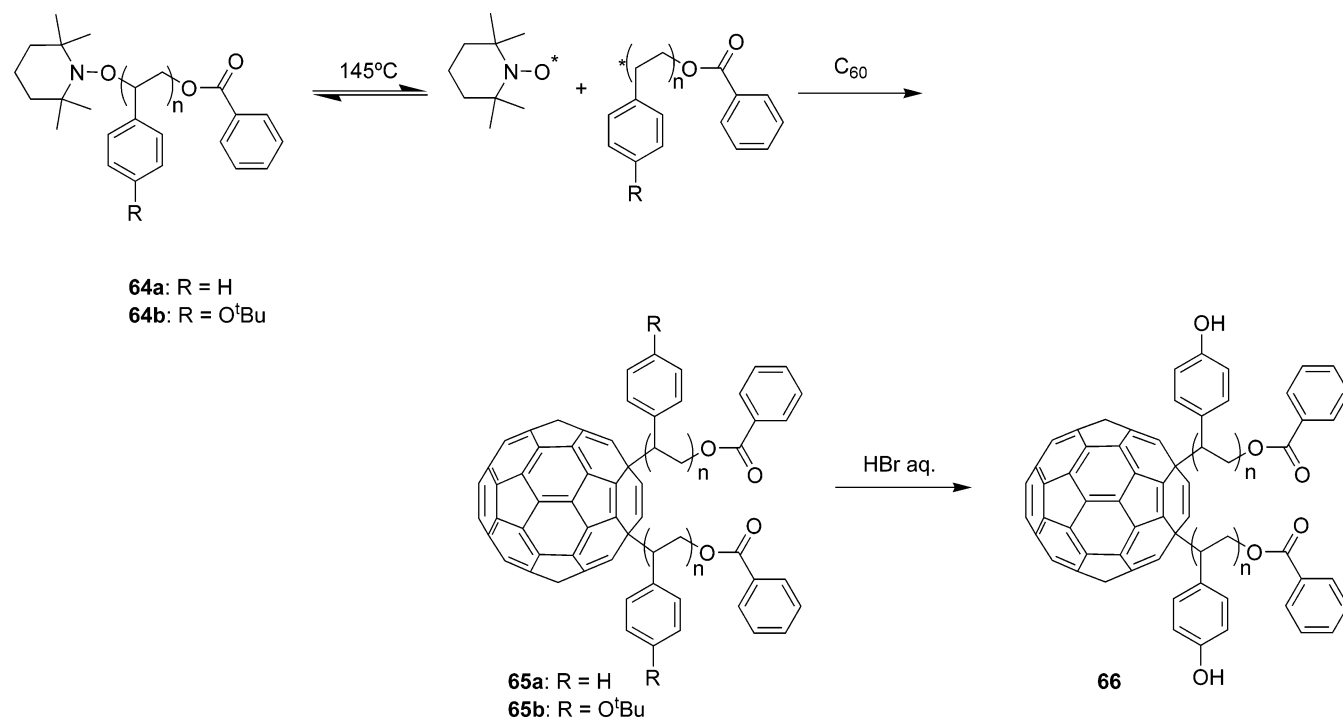
Whereas the synthesis of [60]fullerene side-chain polymers has been widely developed as discussed in the next section, copolymers with  $\text{C}_{60}$  units in the main chain of the polymer are only scarcely known. This fact can be accounted for by the low regioselectivity found in the double addition on the  $\text{C}_{60}$  sphere, resulting in formation of the regioisomeric mixture as well as possible formation of the cross-linking products by multiple additions on the  $\text{C}_{60}$  units.

To prepare such in-chain polymers two different synthetic strategies are possible: (i) direct reaction between the  $\text{C}_{60}$  cage and a suitable symmetrically difunctionalized monomer and (ii) polycondensation between a fullerene bisadduct (or a mixture) and a difunctionalized monomer.

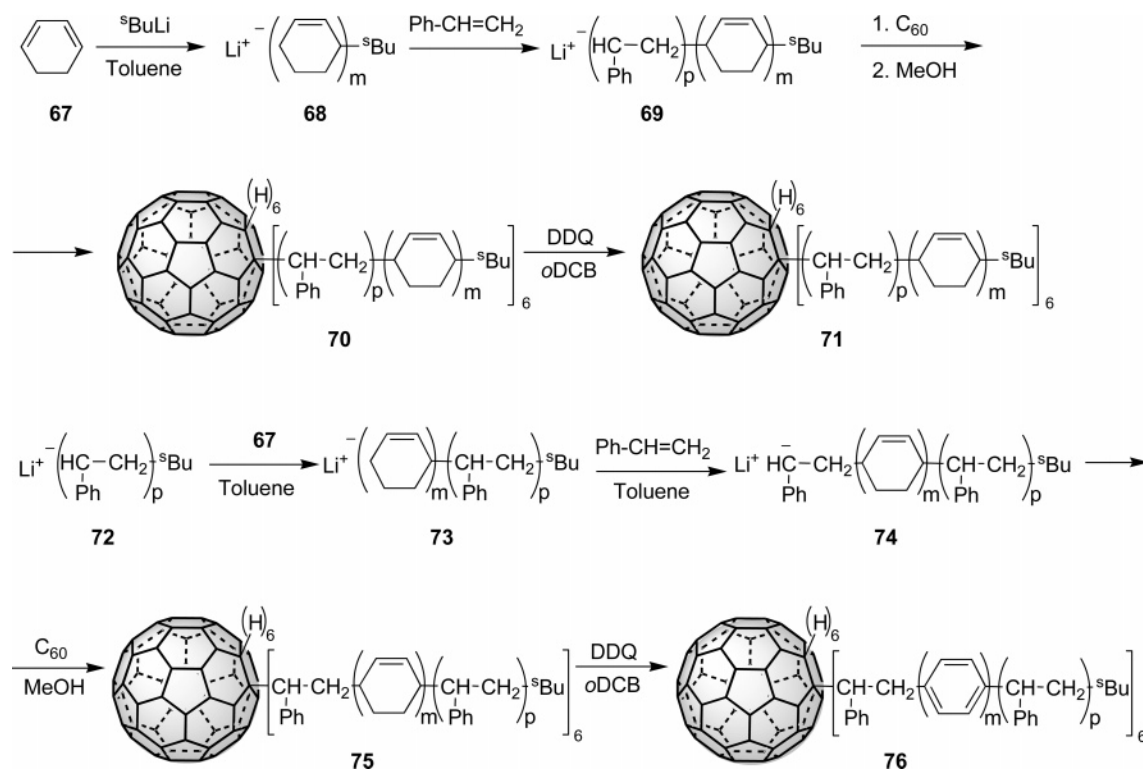
The first example of in-chain  $\text{C}_{60}$  polymers was reported in 1992 by Loy and Assink,<sup>165</sup> although TG analysis finally revealed that such  $\text{C}_{60}$ -xylylene copolymer was prevalently cross-linked. Analogous materials were prepared by covalently attaching PPV fragments directly on the  $\text{C}_{60}$  units,



Scheme 21



Scheme 22



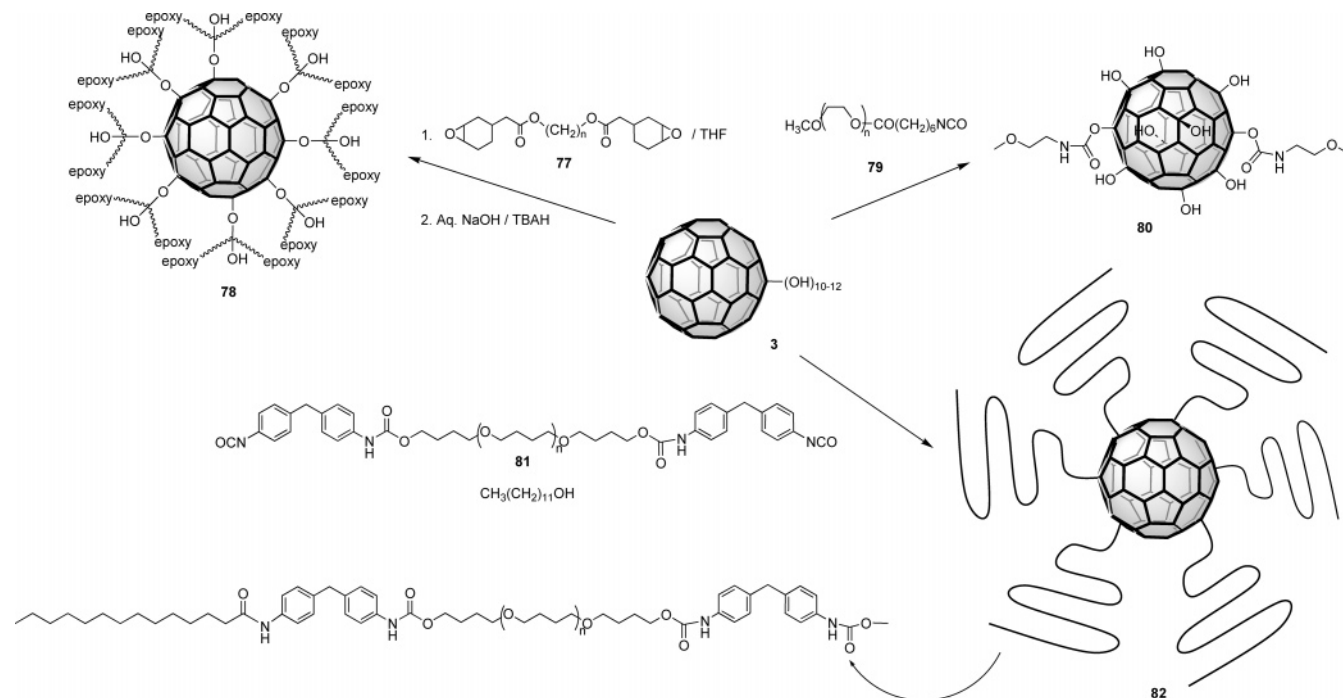
reducing  $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*p*-xylylene in the presence of fullerene,<sup>166</sup> or reducing C<sub>60</sub> in solution in the presence of a PPV precursor.<sup>167</sup>

Cross-linking also took place in an attempt to further increase the molecular weight of the oligomeric mixture **94** ( $n = 1-5$ ) when treated with an additional equivalent of the bis-sulfone **92** (Scheme 26).<sup>168</sup>

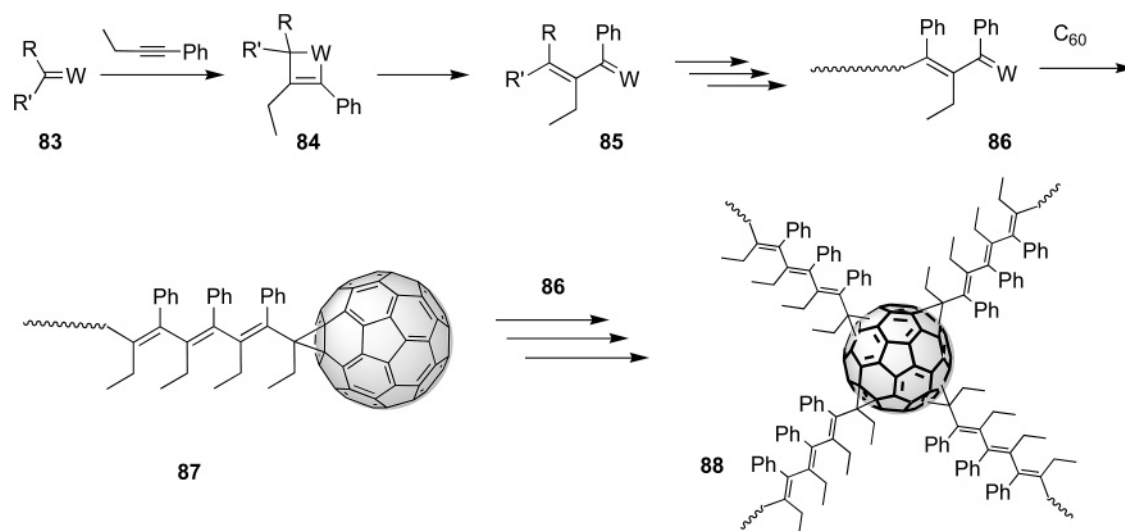
To avoid the undesired cross-linking and obtain more extended polymers, a new reaction was carried out adding

one equivalent of a mixture of bis-sulfone **92** and mono-sulfone **95** (7:3) to fullerene. This process led again to a soluble mixture of oligomers **96** ( $n_{\max} = 3$ ), but this time further reaction with a new equivalent of **92/95** mixture (7:3) afforded a higher  $M_w$  and completely soluble polymer ( $M_w = 34\,000$ ) in which the presence of lateral mono-*o*-quinodimethane moieties effectively suppressed the cross-linking and in the meantime enhanced the solubility of the resulting material.

Scheme 23



Scheme 24



A new typology of C<sub>60</sub> polymer was introduced by Rotello and Nie in 1997, who first reported on a thermoreversible material based in [60]fullerene in the main chain.<sup>169,170</sup> They used a poly-Diels–Alder cycloaddition strategy employing a bis-anthracene derivative (**98**) which readily reacts with C<sub>60</sub> at room temperature, thus avoiding homocoupling side reactions (Scheme 27).

After 168 h the reaction was complete and workup provided a THF-soluble fraction consisted of oligomers and polymers with an estimated molecular weight range of 3000–25 000. However, the authors pointed out that these values should be higher due to the lower hydrodynamic radius of **99** relative to polystyrene. This was mainly evidenced by the *M<sub>w</sub>* peak of 540 found for unreacted C<sub>60</sub> in the GPC (instead of 720!).

The most outstanding property of such materials is, however, that when heated between 60 and 75 °C they readily undergo a cycloreversion to afford the starting materials **98** and C<sub>60</sub> and the polymerization–depolymerization process

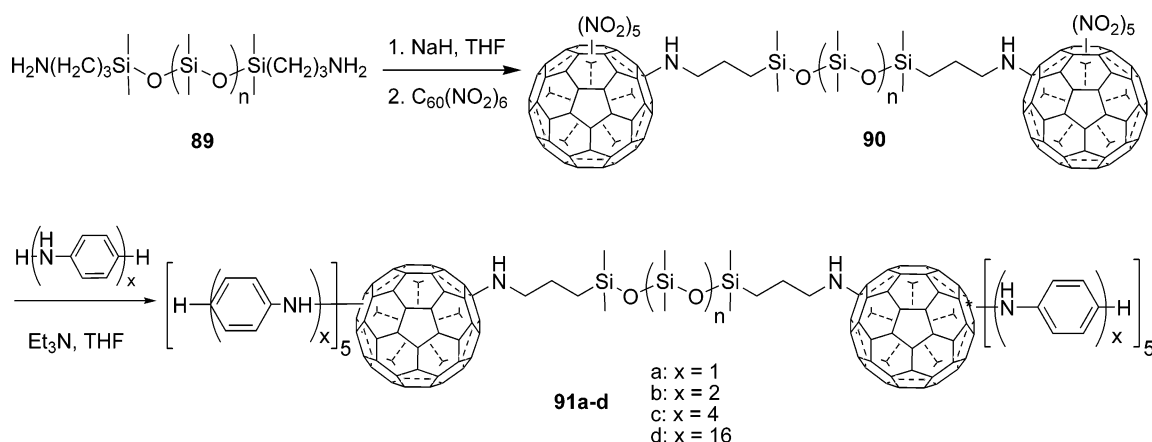
could be repeated several times without decomposition (for comparison see Figure 8a and 8b).

Although the low range of temperatures between the two processes prevents use of this polymer for practical purposes, it paves the way for further investigations in the field of thermoreversible materials based on fullerenes with larger different temperatures of polymerization–depolymerization in order to obtain recyclable and thermally processable polymers.

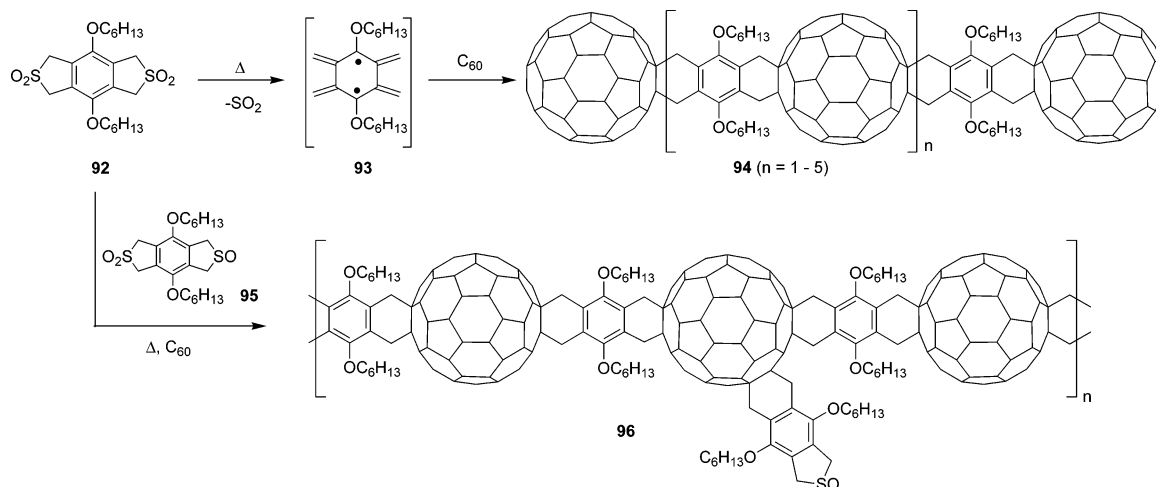
Since poly(dimethylsiloxane) (PDMS) showed extraordinarily high chain mobility,<sup>171</sup> resulting in a very good solubility as well as a high thermal stability, Müller and co-workers incorporated this kind of polymer to prepare an extremely soluble in-chain fullerene polymer (Scheme 28).<sup>172</sup>

Synthesis of polymer **103** was carried out through a poly-SNA reaction between the commercially available amino-propyl-end-capped-PDMS **102** (*M<sub>w</sub>* 35 000) and a mixture of C<sub>60</sub>-bis adducts **101**, which was in turn prepared by the

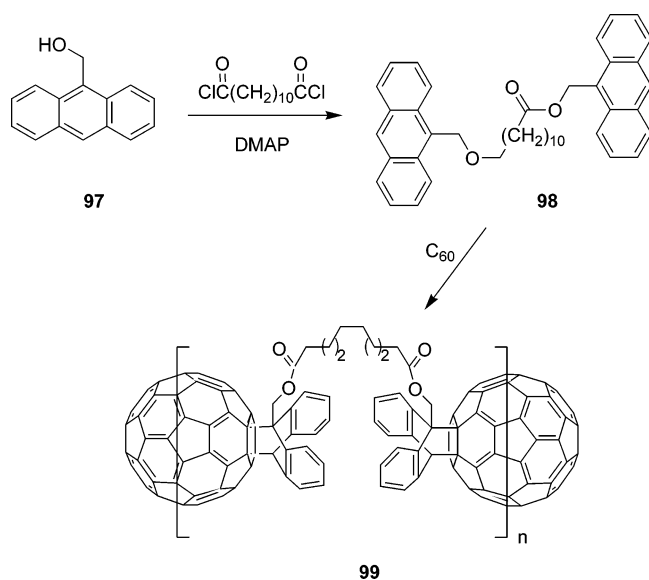
## Scheme 25



## Scheme 26



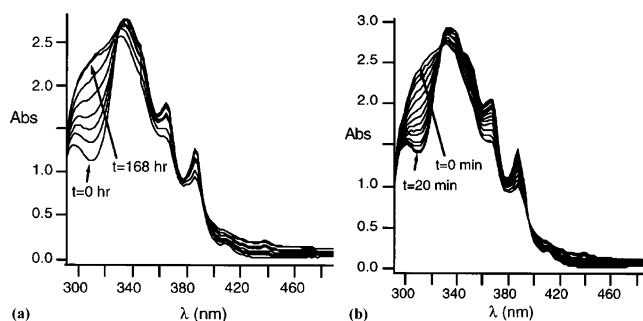
## Scheme 27



*o*-xylylene method.<sup>169,173</sup> After SEC purification the resulting material had a high average molecular weight > 50 000 and a  $M_w$  of 150 000. However, the authors pointed out how SEC analyses of C<sub>60</sub>-containing polymers tend to reveal lower than expected molecular weights.<sup>172</sup> This fact can be ascribed to the  $\pi$ - $\pi$  interaction between the fullerene units and the phenyl groups of the PS stationary phase, which leads to major elution values with the subsequent lowering in the

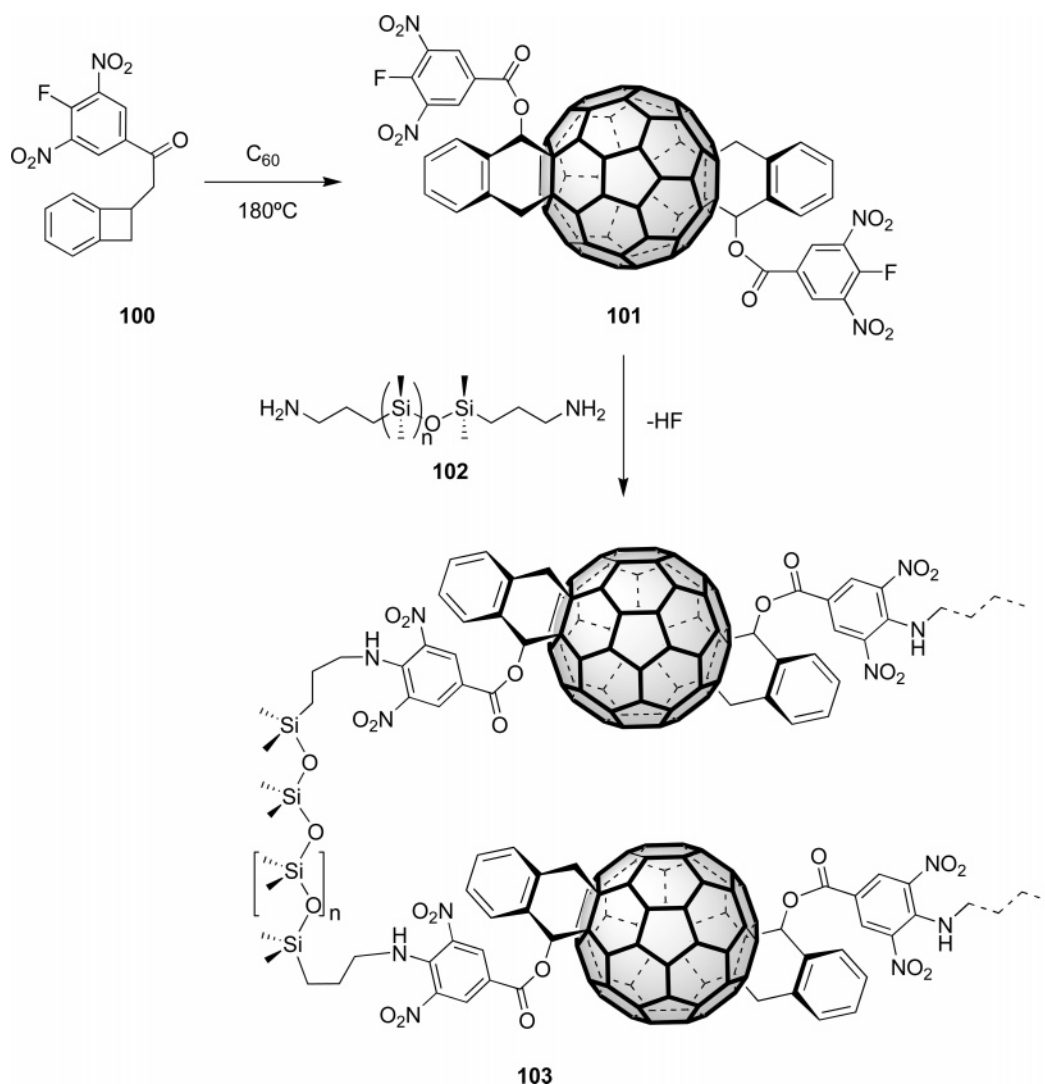
apparent  $M_w$ . This disagreement has been quantified as a character factor of approximately 2 by comparing the SEC data with an absolute method such as vapor pressure osmometry. Therefore, taking into account such correction, polymer **103** consists of nine PDMS and fullerene units and the high molecular weight resulted in a high solubility and excellent film building properties as well as a high thermal stability up to 435 °C.

A new class of C<sub>60</sub>-based polyamides has been prepared using a direct polycondensation method in the presence of triphenyl phosphite and pyridine. The novelty was that after preparation of bisadducts **104** by reacting [60]fullerene with dimethylsulfonium ethoxycarbonylmethylide, the mixture was chromatographically separated in order to use pure



**Figure 8.** UV spectra for reaction of bisanthracene ether **98** with C<sub>60</sub> in toluene: (a) polymerization reaction at room temperature; (b) depolymerization at 75 °C. (Reprinted with permission from ref 169. Copyright 1997 American Chemical Society.)

Scheme 28



regioisomers for the subsequent polymerization reaction (Scheme 29).

In the first example, only the *trans*-2 isomer of **104** was reacted together with 4,4'-diaminobenzophenone to afford polymer **105**,<sup>174,175</sup> in which MALDI-TOF experiments revealed a maximal peak at  $m/z$  45 000 that fit well with the  $M_w$  53 000 value found by GPC measurements. Use of LiCl avoids the exclusive formation of oligomers, cleaving the inter- and intramolecular hydrogen bonds, thus improving polymer solubility.

On the other hand, mixtures of **104b** (equatorial isomer) and isophthalic acid (molar ratio 1:50, 1:5, 1:1, 1:0) were reacted with an equimolar amount of 4,4'-diaminodiphenyl ether, obtaining **106a–d** in fiber to powder shape.<sup>176</sup> The  $M_w$  decreases linearly with **104b** content (i.e.,  $3 \times 10^5$  to  $3 \times 10^3$ ) as well as the thermal stability as observed by TGA and DSC analyses.

One of the first main-chain fullerene polymers was synthesized by Taki et al. in 1997.<sup>177</sup> They prepared two in-chain polymers reacting a mixture of C<sub>60</sub> bisphenol (**107**) with an equimolar amount of dibasic acid dichloride at room temperature. Sebacyl chloride or a 1:1 mixture of isophthaloyl chloride/terephthaloyl chloride was chosen to afford linear polyesters containing the fullerene moiety in the main chain **109a,b** (Scheme 30). These two macromol-

ecules had good solubility in DMF, although low molecular weights were obtained (4000–6000 Da).

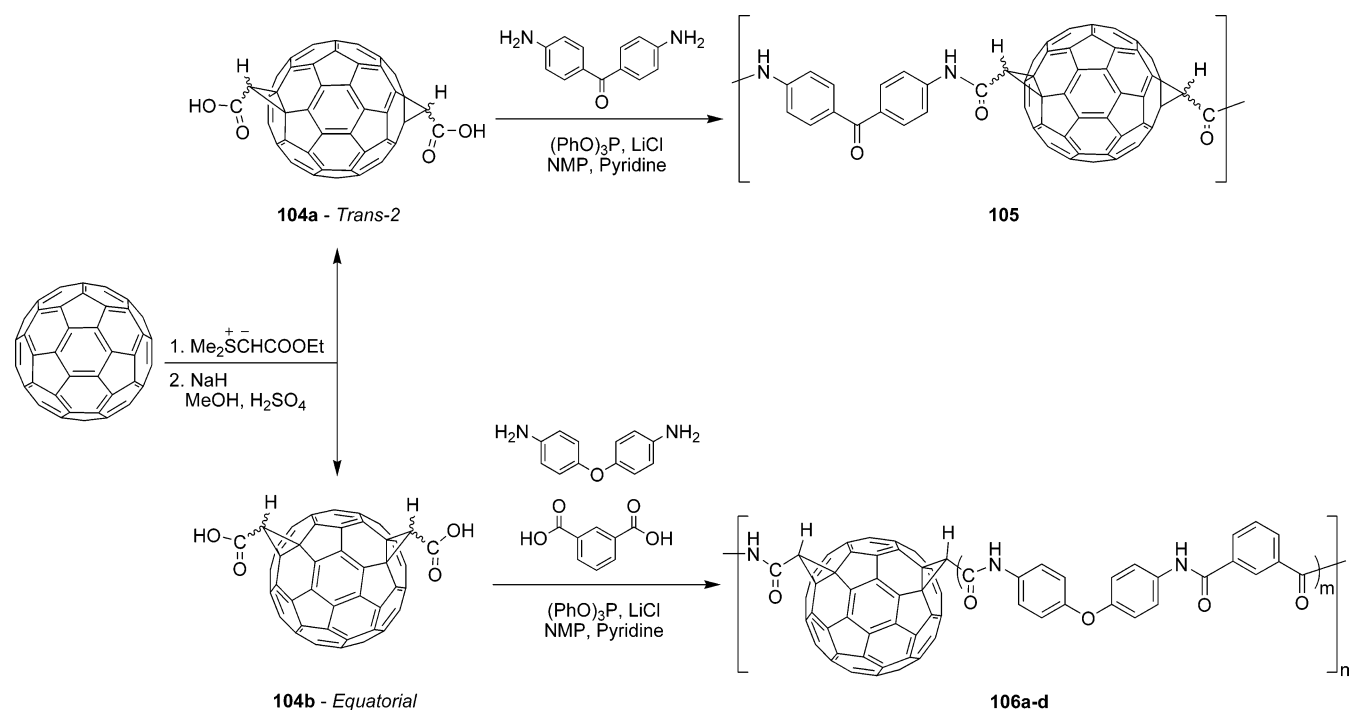
In 1999 Scamporrino et al., following a similar strategy to that just reviewed, described two different fullerene-main-chain polymers based on 61,61'-bis(*p*-hydroxyphenylmethano)-[60]fullerene (**112**, isomeric mixture) (Scheme 31).<sup>178</sup>

Polymers **115** and **116** were synthesized by a condensation reaction between an isomeric mixture of fullerene derivative **112** and bisphenol A (**113**) or 1,20-bis(bisphenoxy-A)-eicosane (**114**) in the presence of NaOH. These macromolecules were soluble enough materials with good thermal stability, presenting a relatively high  $M_w$  (**115**, 151 200; **116**, 18 170). The exact fullerene content (in molar percent) in the copolymers was established spectroscopically, considering the absorption values at 320 nm, using Beer's law employing the molar absorption of monomer **111** as standard (**115**, 0.43%; **116**, 2.5%).

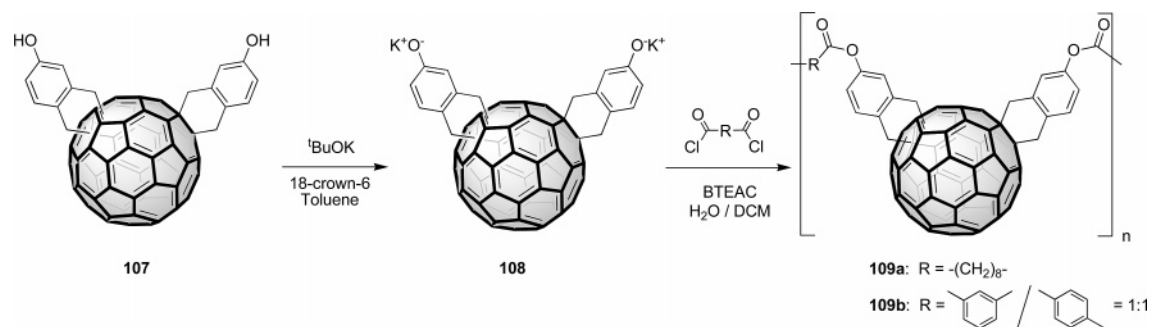
Recently, Saigo followed a similar strategy for preparation of a pearl-necklace polyiminofullerenes starting from enantiopure equatorial bis(formylmethano)[60]fullerenes and the aromatic diamine 4,4''-diamino-2',5'-bis(dodecyloxy)-*p*-terphenyl.<sup>179</sup> The macromolecular product obtained showed excellent processability.

On the other hand, free-radical polymerization initiated by AIBN between methyl or ethyl methacrylate and a mixture

Scheme 29



Scheme 30



of bis-phenylaminofullerene ( $\text{C}_{60}\text{H}_{1.9}(\text{NHC}_6\text{H}_5)_{1.9}$ ) afforded [60]fullerene main-chain copolymers with good  $M_w$  and optical limiting properties.<sup>180</sup>

A very interesting example of the first water-soluble main-chain polyfullerene has been described by Geckeler and co-workers (Scheme 32).<sup>181</sup> Synthesis of **118** has been carried out by mixing the  $\beta$ -cyclodextrin-bis(*p*-aminophenyl) ether complex **117** (CD-BPE) with a solution of  $\text{C}_{60}$  via a nucleophilic polyaddition reaction. A similar attempt of polymerization employing *p*-phenylenediamine failed due to the scarce length of such amine that was unable to react with two different fullerene units staying complexed in a cyclodextrin (CD). The resulting polymer **118** exhibited an extraordinary solubility in water ( $>10 \text{ mg mL}^{-1}$ ) as well as a very narrow polydispersity index of 1.06 ( $M_w$  20.0  $\text{kg mol}^{-1}$ ;  $M_n$  18.9  $\text{kg mol}^{-1}$ ).

In this approach the CD moieties play a crucial function since, in a comparative study, reaction between  $\text{C}_{60}$  and BPE give rise to an insoluble polysubstituted fullerene. This fact pointed out that CD not only furnished water solubility to the final polymer but also prevented further branching in the  $\text{C}_{60}$  cage due to its bulkiness. Interestingly, this polymer has been successfully employed as a highly efficient DNA-cleaving agent under visible light conditions.<sup>182</sup> The quantitative DNA-cleaving achieved suggests strong application

prospects of water-soluble  $\text{C}_{60}$ -polymers in photodynamic cancer therapy.

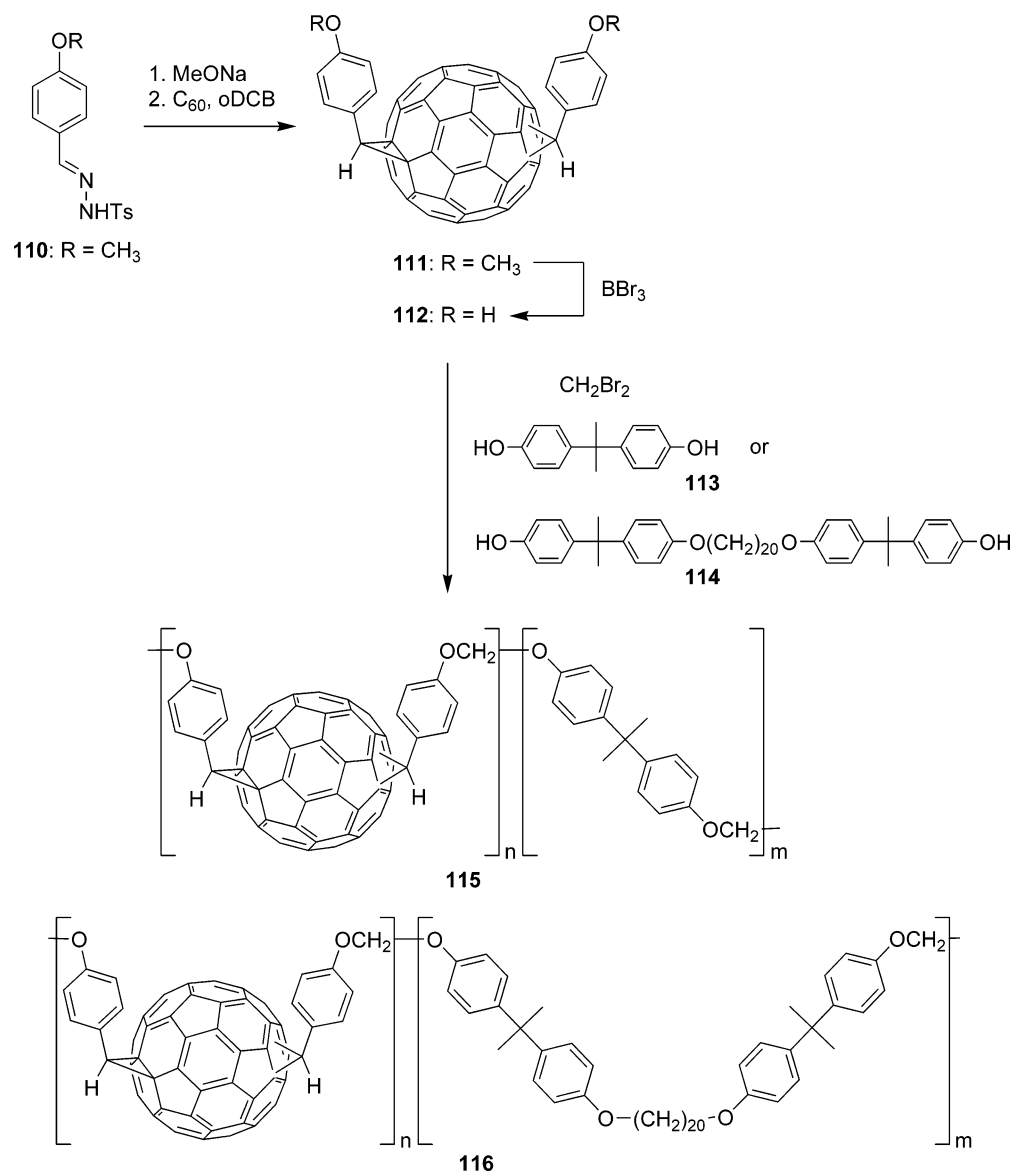
## 7. Side-Chain Polymers

One of the main classes of  $\text{C}_{60}$ -based polymers is represented by those in which the  $\text{C}_{60}$  units are localized as pendants of the main polymer chain. In the so-called side-chain polymers chemists find a huge degree of freedom in order to create a wide variety of polymers, ranging from the simplest to the hardest, in which the finest chemical strategies are followed to obtain  $\text{C}_{60}$ -based designed polymers. From a synthetic standpoint, two different approaches are possible: (i) direct introduction of fullerene itself or of a  $\text{C}_{60}$  derivative monomer into a previously prepared polymer and (ii) synthesis of a  $\text{C}_{60}$  derivative which can be in turn directly polymerized or copolymerized together with other/s monomer/s.

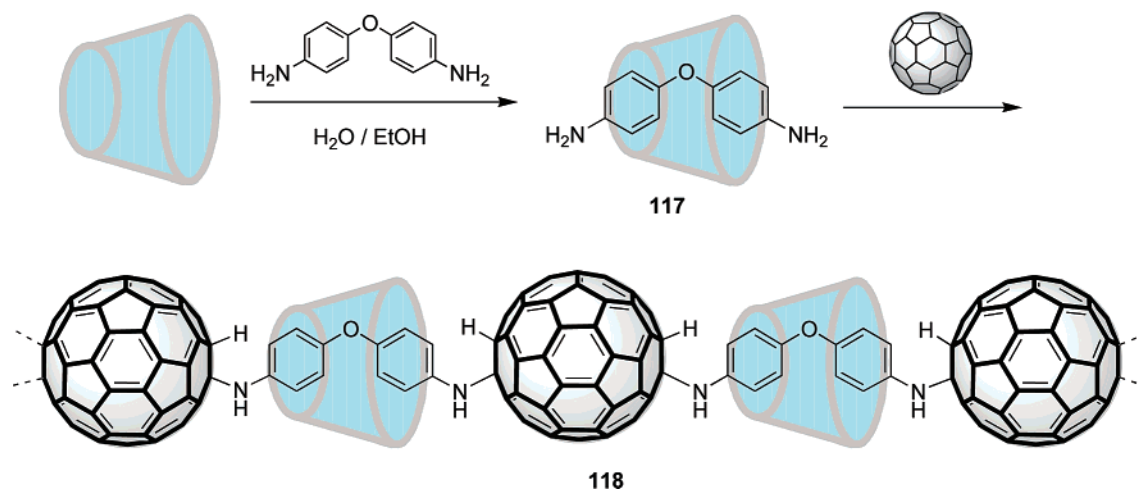
In this section we will summarize the most relevant syntheses of fullerene side-chain polymers which have been classified according to their structure.

The first example of  $\text{C}_{60}$  side-chain polymers was reported by Wudl et al. in 1992.<sup>183</sup> They prepared a polyester (**120**) as well as a polyurethane (**121**) by polycondensation reaction from bis-hydroxydiphenylmethanofullerene (DPM = **119**)

Scheme 31



Scheme 32

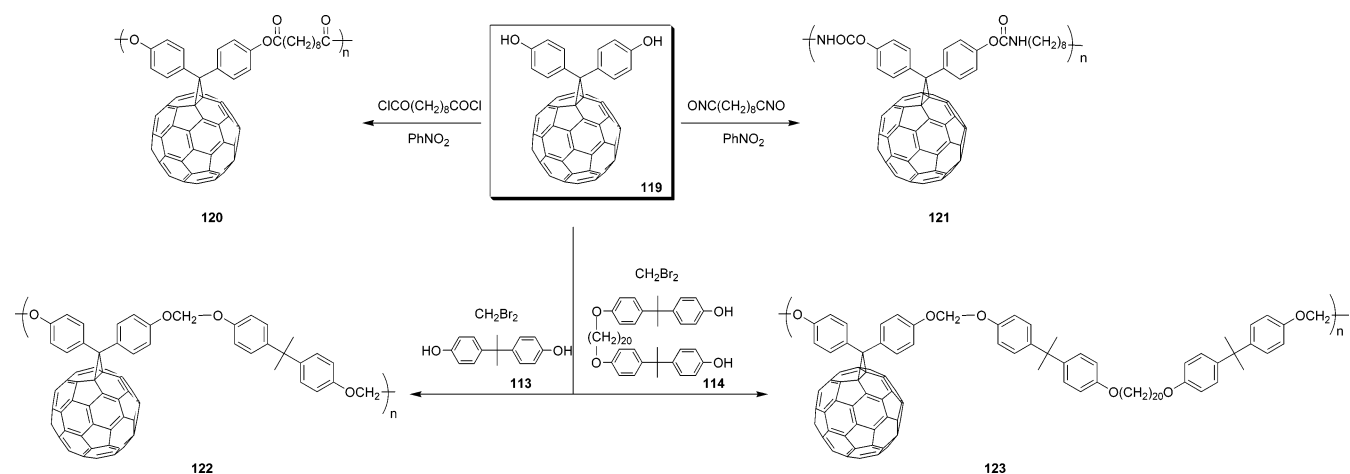


(Scheme 33). These two new materials had a low degree of polymerization and were insoluble in most of the common organic solvents.

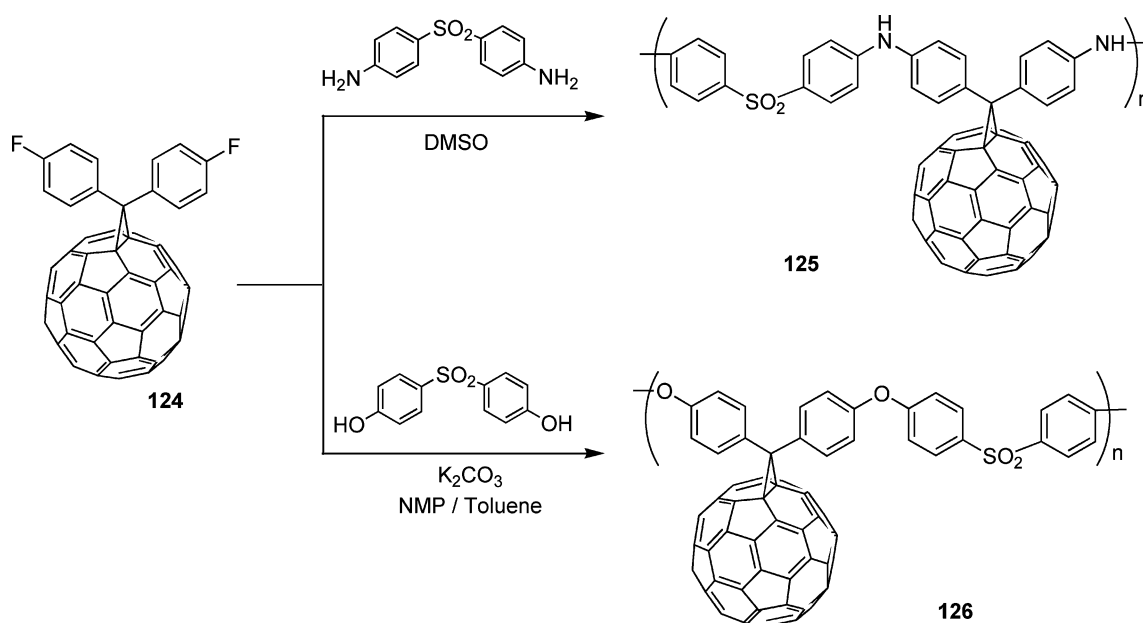
The same C<sub>60</sub> monomer **119** was used by Scamporrino 7 years later to carry out the synthesis of polyethers **122** and

**123** by reacting with dibromomethane and bisphenol A (**113**) or with 1,20-bis(bisphenoxy-A)-eicosane (**114**), respectively (Scheme 33).<sup>178</sup> Such macromolecules were soluble enough to be fully characterized and showed middle *M<sub>w</sub>* values (**122**, ~15 500; **123**, ~27 000).

Scheme 33



Scheme 34



On the other hand, Berrada and co-workers reported the synthesis of poly(4,4'-diphenyl- $C_{60}$  amine) (**125**) and poly(4,4'-diphenyl- $C_{60}$  ether) (**126**) starting from the difluoro-DPM analogue **124** (Scheme 34).<sup>184</sup>

The resulting polymers were soluble in organic solvents such as DMSO or NMP, but low molecular weights were obtained ( $M_w$  between 5000 and 20 000). However, no  $^1\text{H}$  NMR data were reported on the resulting polymers.

One of the first classes of side-chain polymers studied includes the amino- or imino-functionalized ones due to the well-known reaction of amines addition to fullerene double bonds.<sup>185,186</sup> Chart 2 summarizes the different chemical structures for  $C_{60}$ -side-chain polymers derived from the corresponding amino-polymers.

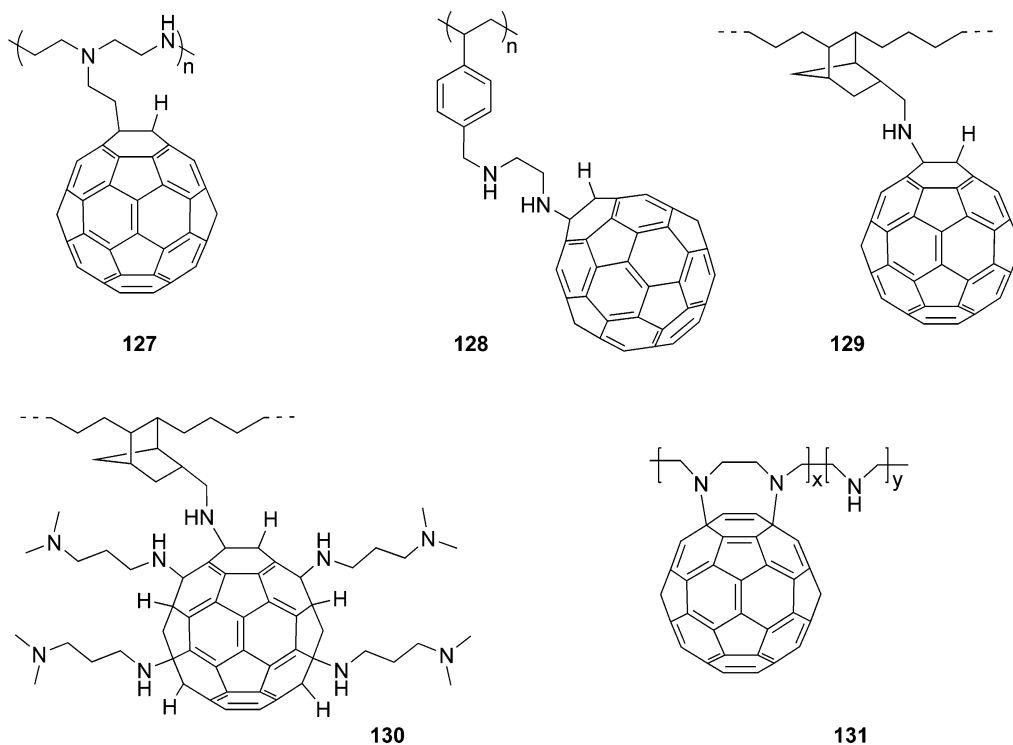
In 1993 Geckeler and Hirsch carried out the synthesis of **127** and **128** by titration of  $C_{60}$  with poly(ethylene imine) and poly{4-[(2-aminoethyl)imino]methyl}styrene, respectively.<sup>187</sup> Polymer **128** was soluble in  $\text{CS}_2$  and toluene, representing the first example of soluble  $C_{60}$ -containing polymer.

Other remarkable examples of  $C_{60}$ -functionalized amino-polymers are **129**,<sup>188</sup> **130**,<sup>189</sup> and **131**.<sup>190,191</sup> The latter was obtained by photochemical reaction between  $C_{60}$  and the

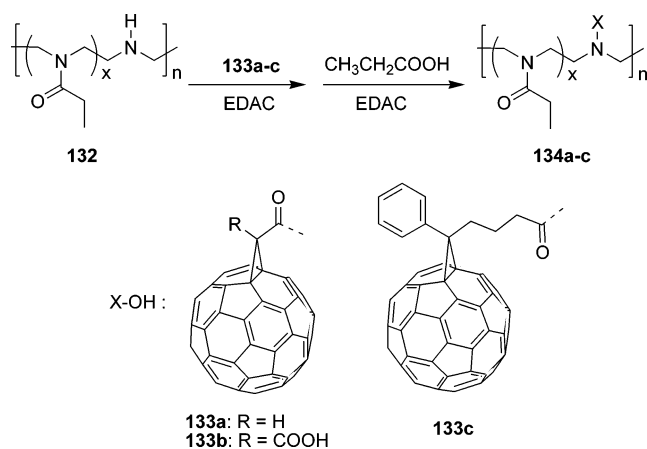
secondary amine of poly(ethyleneimine) following a photoinduced electron-transfer-proton-transfer mechanism. In this way the authors prepared water-soluble materials with a content in  $C_{60}$  of up to 37 wt %, which showed fluorescence quenching via intrapolymer electron transfer. Water-soluble pendant  $C_{60}$  polymers were also prepared following a different approach. Sun and co-workers employed the secondary amino groups of the linear (propionyl-ethyleneimine-*co*-ethyleneimine) (PPEI-EI) as attaching sites for different fullerene pendant groups (Scheme 35).<sup>192,193</sup>

First, the parent poly(propionyl-ethyleneimine) (PPEI) was partially hydrolyzed under acidic conditions, and afterward, the fullerene-containing polymers (**134a-c**) were prepared by condensation with  $C_{60}$  derivatives **133a-c** using 1-ethyl-3-(dimethylaminopropyl) carbodiimide (EDAC) as coupling agent. The obtained polymers displayed  $M_w$  of  $\sim 49\,000$  with a  $C_{60}$  content of  $\sim 11\%$ . Noteworthy, GPC analysis of **134b** did not show significant cross-linking despite possessing two different carboxylic groups. In addition, such materials presented impressive water solubility,  $>90\text{ mg mL}^{-1}$ , representing an effective way to afford water-soluble compounds for biological studies.

Chart 2



Scheme 35



A new example of water-soluble C<sub>60</sub>-containing side-chain polymer was reported by Cousseau and co-workers in 2005.<sup>194</sup> In fact, they synthesized a poly(maleic anhydride-co-vinyl acetate) (MA-VA) by radical copolymerization in which they incorporated successfully a methanofullerene derivative. The resulting material showed a 34% conversion of anhydride groups to ester with an overall 48 wt % of fullerene. Such polymer, after hydrolysis with water followed by reaction of carboxylic groups with NaOH, presented a solubility in water as high as 20 mg mL<sup>-1</sup>.

The ease of access to polystyrene copolymer derivatives made of this class of macromolecules a good candidate for their side functionalization with C<sub>60</sub>. Several approaches have been explored in order to incorporate fullerene moieties both in the aliphatic main chain and in the lateral phenyl groups as depicted in Chart 3.

One approach involves grafting of C<sub>60</sub> via Friedel-Crafts reaction, leading to high molecular weight polymers that in some cases could be due to cross-linking (**137**).<sup>195</sup> The same approach has been used in the side fullereneation of poly(epoxypropylcarbazole) (PEPC) **138**,<sup>196</sup> shown in Chart 4.

On the other hand, Hawker demonstrated the feasibility of modulation of the C<sub>60</sub> content in the final polymer by simply modifying the styrene/*p*-azidomethylstyrene ratio in the precursor copolymer feed.<sup>197</sup> Thus, polymers **136a-d** with fullerene content between 5.5% and 60% have been synthesized, showing very good solubility properties.

In a last example, reaction between fullerene and carbanion intermediates of PS,<sup>198</sup> poly(bromostyrene),<sup>199</sup> or poly(vinylbenzyl chloride)<sup>200</sup> afforded the corresponding polymers fullereneated directly on the main chain **135a-c**. For these polymers stereoelectronic effects as well as steric hindrance of C<sub>60</sub> units affect deeply the structure and physical properties of the polymers. Analogously, the same synthetic strategy applied to poly(vinylcarbazole) (PVK) led to C<sub>60</sub> chemically modified PVK copolymer in which after laser flash photolysis photoinduced electron transfer between C<sub>60</sub> and inter- and intrachain carbazole units take place (polymer **139**, Chart 4).<sup>201</sup>

Reaction between C<sub>60</sub> and polymeric anionic intermediate again allowed direct grafting of C<sub>60</sub> into *cis*-1,4-polyisoprene and *cis*-1,4-polybutadiene,<sup>202-204</sup> affording highly processable materials that could be eventually converted into fully conjugated polymeric backbones by an I<sub>2</sub>-induced conjugation reaction.<sup>205</sup>

An interesting class of C<sub>60</sub>-side-chain polymers includes fullereneated polycarbonates (PC) (Scheme 36). Despite previous attempts to incorporate C<sub>60</sub> into PC by simple irradiation<sup>206</sup> or the more recent direct grafting under microwave irradiation in the presence of AIBN,<sup>207</sup> better results have been obtained using one-pot straightforward Friedel-Crafts experimental procedures.<sup>208,209</sup> C<sub>60</sub> has also been incorporated onto PC chains as its derivative, 61-(*p*-hydroxyphenyl)methano-1,2-[60]fullerene.<sup>210</sup>

These parallel works, in which C<sub>60</sub> or TCNEO-C<sub>60</sub> (TCNEO = 1',1',2',2'-Tetracyanomethanoxymethano) were incorporated into PC, reported very similar results, showing outstanding optical limiting properties and, at the same time,



Chart 3

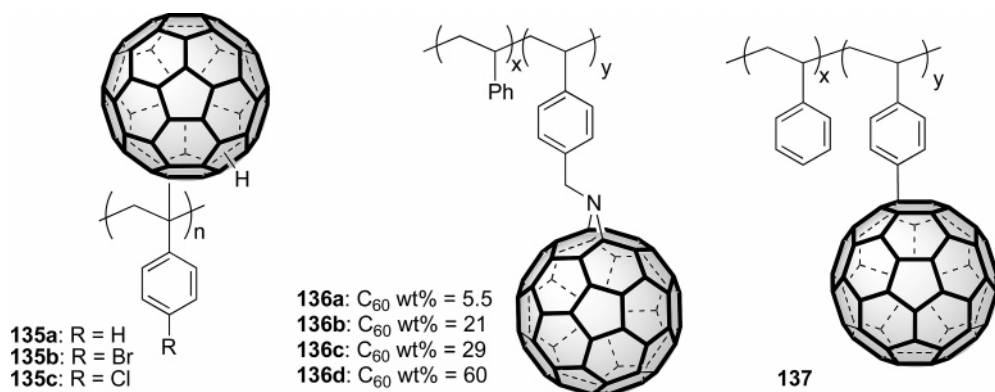
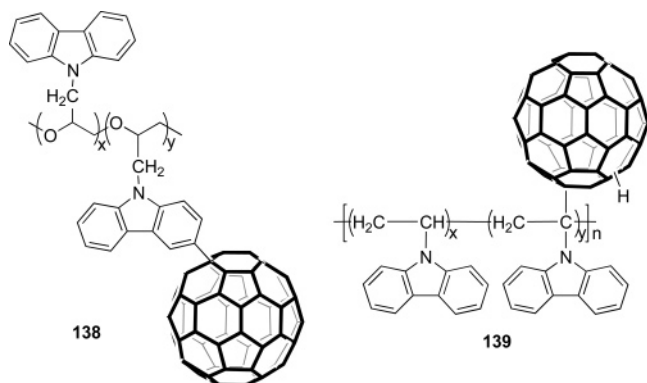
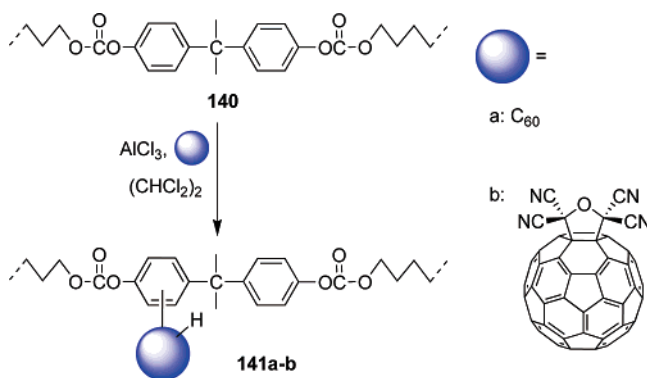


Chart 4



Scheme 36



improving the C<sub>60</sub> processability of such materials. In both cases the calculated  $M_w$ s were lower than that of the starting PC, indicating that some chain cleavage is involved in the fullerene reaction. Comparing these two polymers, the optical limiting properties of TCNEO-C<sub>60</sub>-PC **141b** have a remarkable improvement, suggesting that an increase of the electron-accepting ability of C<sub>60</sub> derivative leads to stronger intermolecular interaction between the C<sub>60</sub> derivative and the PC.

In Chart 5 are summarized the structures for “classical” polymers carrying C<sub>60</sub> as side substituent such as polymethacrylates (**142a,b**),<sup>211</sup> derivatized polyalkyl methacrylates **143a,b**,<sup>212,213</sup> **144a,b**,<sup>214</sup> or poly(hydroxyethyl methacrylate) **145a-f**.<sup>215</sup>

It is interesting to note that for all polymers depicted in Chart 5 the fullerene units have been grafted via the “azido” route<sup>216</sup> as a viable manner to join C<sub>60</sub> and limit bis- and tri-addition and subsequently avoiding cross-linking. In this way, C<sub>60</sub>-containing polyalkyl methacrylates had a very

narrow polydispersity, whereas C<sub>60</sub>-PHEMA (**145a-f**) showed a stronger influence of solubility with the C<sub>60</sub> content. Thus, polymers carrying more than 3.2 wt % of C<sub>60</sub> have a limited solubility. Samples of **145a-f** formed successfully interpolymer complexes when mixed together with poly(4-vinylpyridine) (P4VPy) and poly(1-vinylimidazole) (PVI) as proton-acceptor polymer.<sup>215,217</sup> Interpolymer complexes have also been formed between poly(vinylidene fluoride) (PVDF) and samples of C<sub>60</sub>-containing poly(ethyl methacrylate), poly(methylacrylate), poly(ethylacrylate),<sup>218</sup> or poly(methyl methacrylate).<sup>219</sup> On the other hand, when C<sub>60</sub> is incorporated into poly(ethyl methacrylate), the surface behavior of such polymer suffers a dramatic effect since it becomes more hydrophobic when the C<sub>60</sub> content increases, as shown by an increase in the water contact-angle values.<sup>214</sup>

A good way to graft C<sub>60</sub> to a polymeric backbone is represented by [4+2] cycloaddition reaction between fullerene and side-chain reactive dienes. This strategy was employed by Wang and co-workers, who prepared a number of vinyl polymers with different content in benzocyclobutenone-containing (BCBO) monomer **146** (Scheme 37).<sup>220</sup> This moiety upon thermal activation in *o*-DCB generates a reactive diene, which subsequently undergoes [4+2] cycloaddition with C<sub>60</sub>, leading to soluble macromolecules (**148a-c**) with a 22.5–44 wt % content in fullerene.

On the other hand, good photoconductivities have been measured for styrene/acrylamide copolymers carrying C<sub>60</sub> units directly linked to the hanging amido groups, and the photoconductivity could be enhanced by increasing the fullerene content.<sup>221</sup>

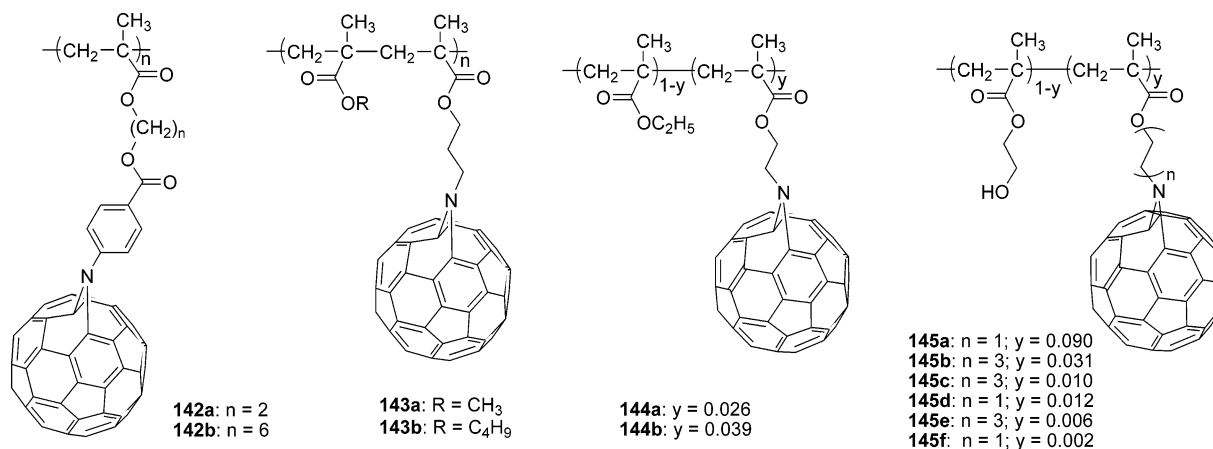
In Scheme 38 is displayed the synthesis of C<sub>60</sub>-containing poly(vinyl alcohol) (PVA-C<sub>60</sub>, **152a-d**).<sup>222</sup>

Treatment of PVA (**149**) with NaH gives rise to formation of PVA anions, which, in situ, react with C<sub>60</sub> to afford the ionized C<sub>60</sub>-PVA (**151a-d**). These C<sub>60</sub>-PVA (**151a-d**) anions were converted to HC<sub>60</sub>-PVA (**152a-d**) by reaction with a cation-exchange resin. Interestingly, after irradiation with a 300 nm light, [2+2] photodimerization occurs. If the cross-linked material is exposed to 254 nm irradiation, photocleavage of the pendant C<sub>60</sub> chromophores takes place and this process can be repeated several times without affecting the material.

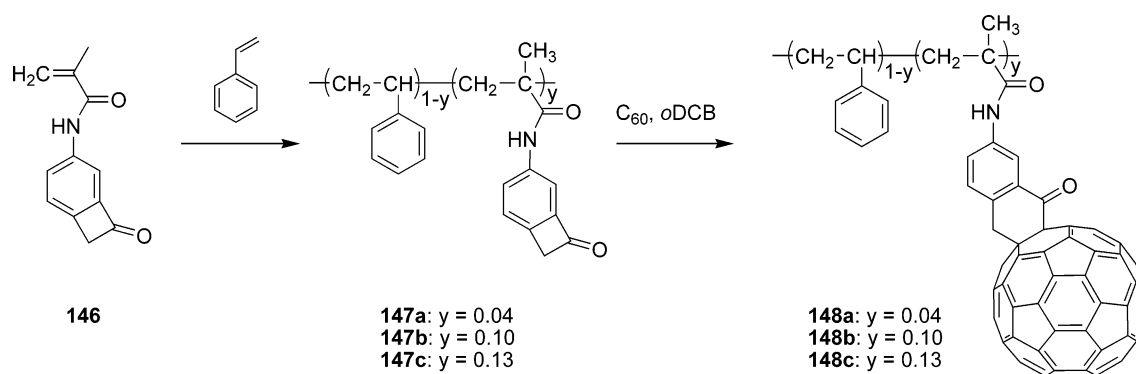
Grafting of C<sub>60</sub> into saturated ethylene-propylene polymer chains has been described to occur via a free-radical route.<sup>223</sup> However, this method does not have a high degree of control and could lead to cross-linked materials.

A more elegant approach to incorporate fullerenes into a saturated alkylic polymer has very recently been reported by Hessen et al.<sup>224</sup> They prepared a polyethene with fullerene

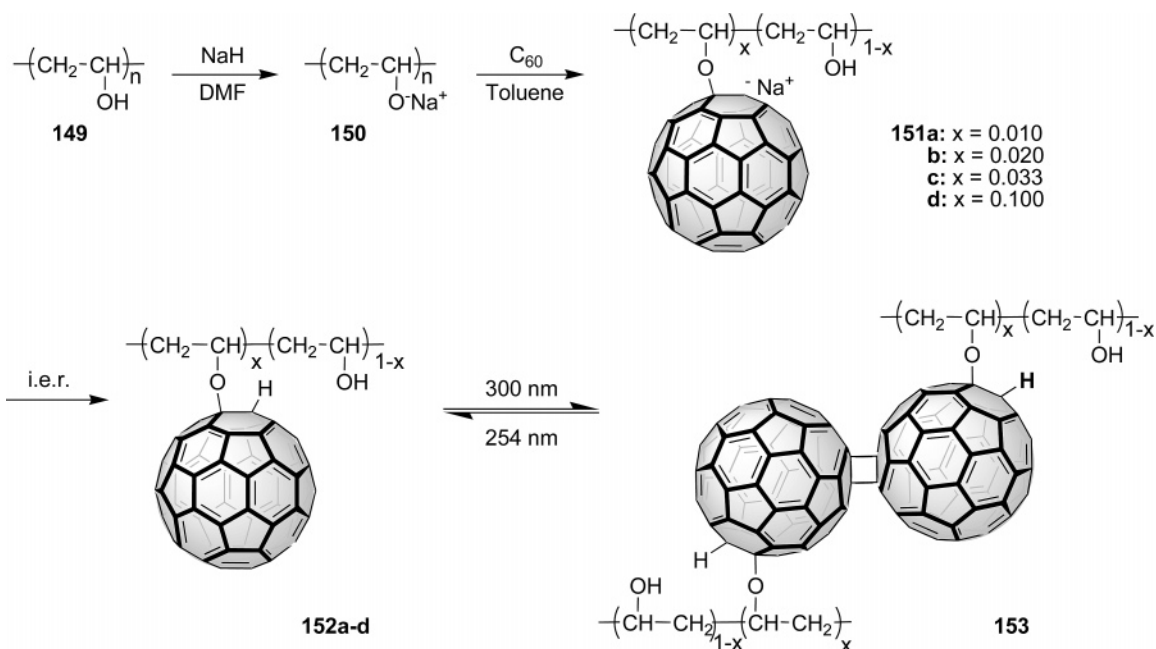
Chart 5



Scheme 37



Scheme 38



moieties pendant on short-chain branches by catalytic polymerization of ethene and a  $\text{C}_{60}$ -containing vinylic monomer **154**, employing  $(\text{C}_5\text{Me}_4\text{SiMe}_2\text{NBu}^t)\text{TiCl}_2$  (**155**)/methylalumoxane (MAO) as catalytic system (Scheme 39).

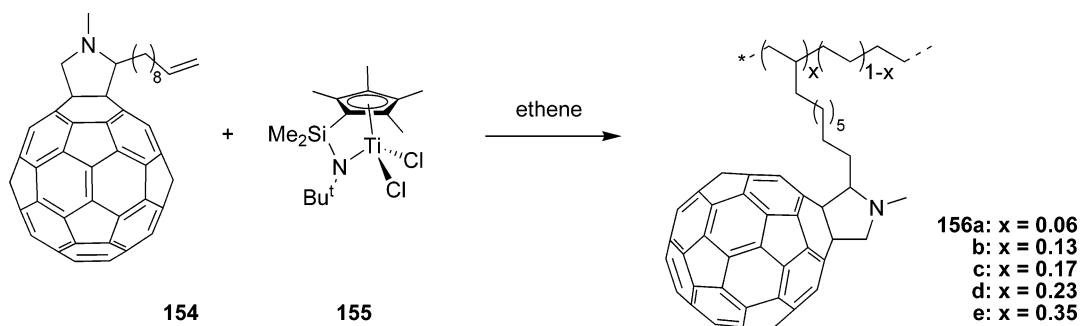
An earlier example of polymerization based on an organometallic catalyst was described in 1995 by Prato and co-workers,<sup>225</sup> who employed  $\text{Mo}(\text{CH}=\text{Bu}^t)(\text{NAr})[\text{OCMe}(\text{CF}_3)_2]_2$  as catalyst for a ring-opening metathesis copolymeriza-

tion (ROMP) between the norbornene-modified  $\text{C}_{60}$  **157** and an excess of norbornene (1 mol % of **157**) (Scheme 40).

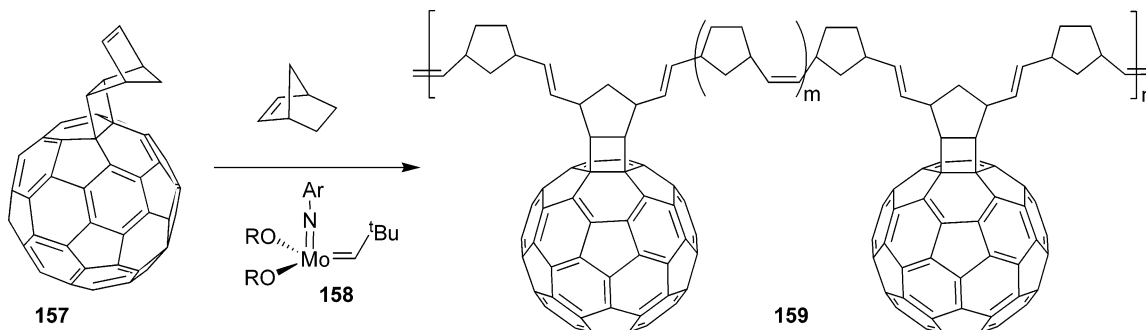
The material so obtained (**159**) showed a cis/trans isomer ratio of 6:2 with a remarkable  $M_w$  as high as  $\sim 103\,000$  and had cross-link processes when heated at  $70^\circ\text{C}$  in the solid state.

Very recently, new examples of ruthenium-catalyzed ROMP have been reported by Fréchet et al.<sup>226</sup> They used

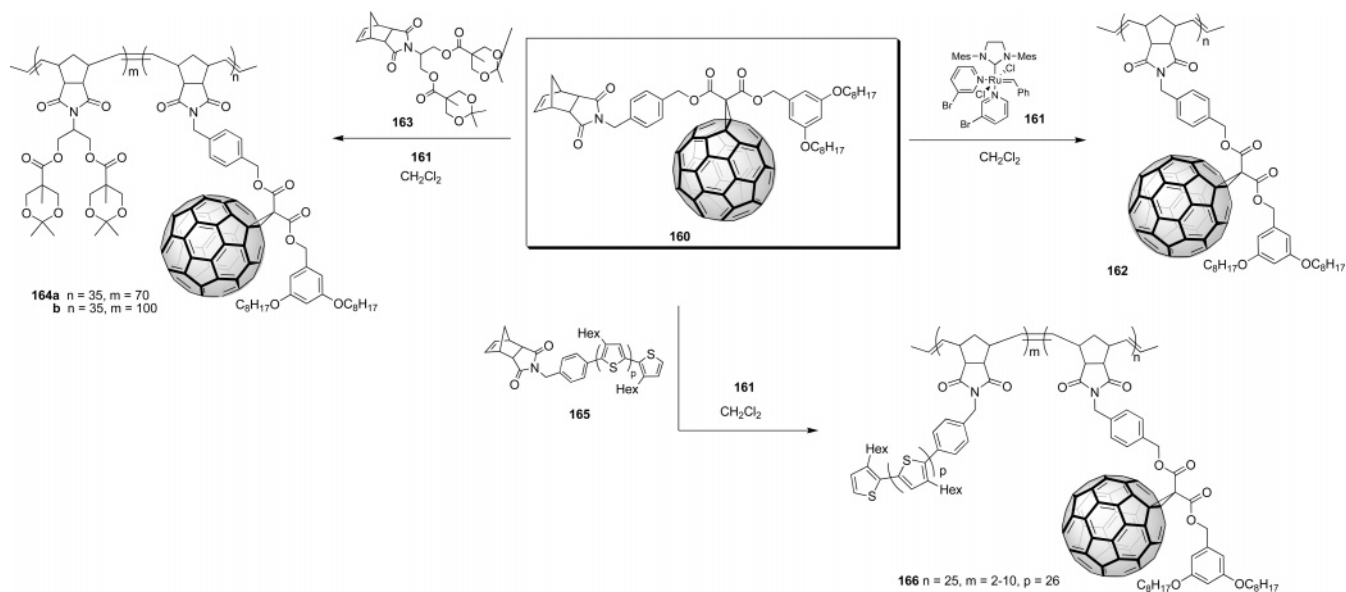
## Scheme 39



## Scheme 40



## Scheme 41

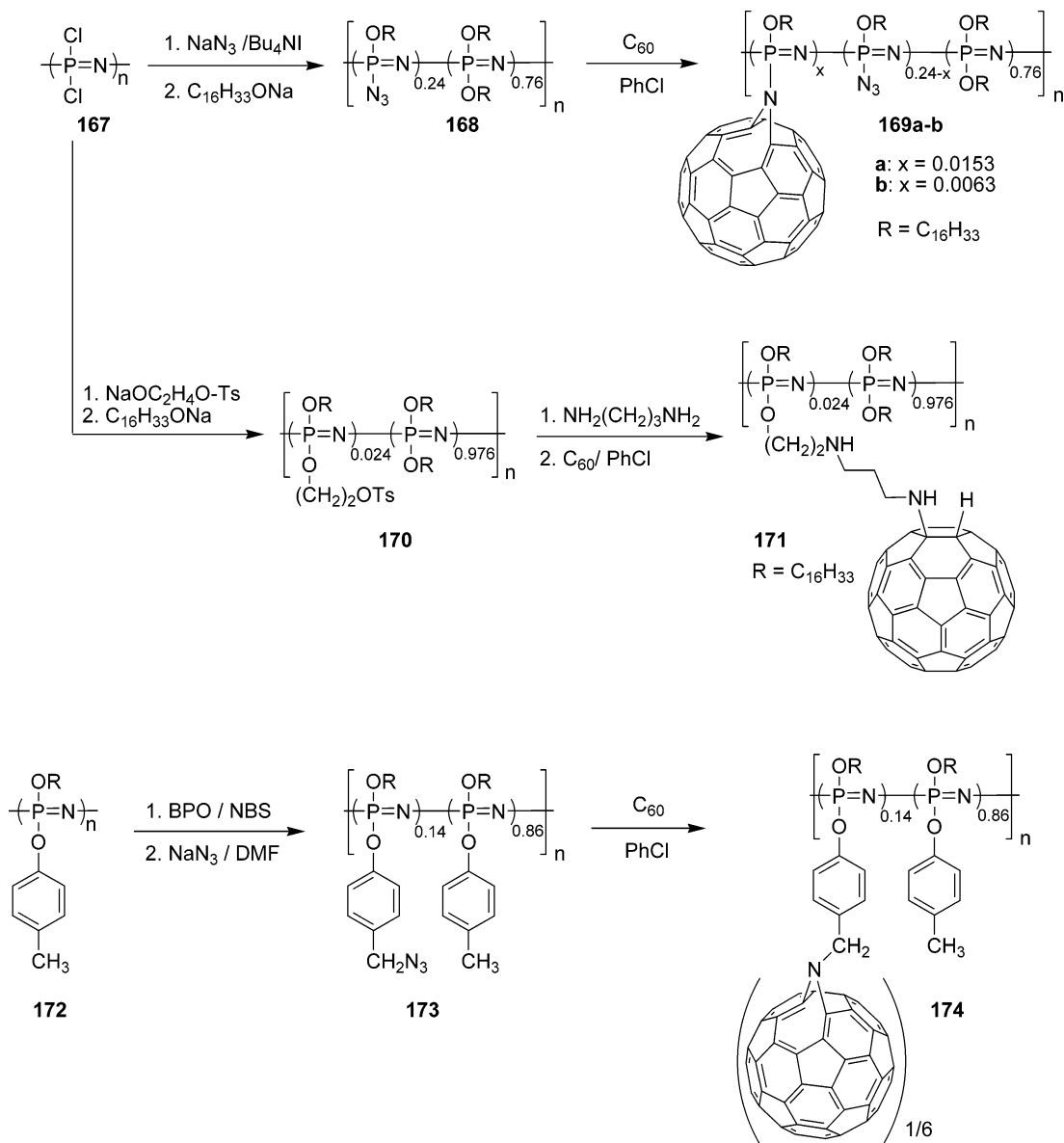


this strategy in order to synthesize a polymer containing 50 wt % of  $C_{60}$  (**162**) as well as the diblock copolymers **164a,b** using the sterically demanding monomer **163** (Scheme 41). In the former case fullerene is incorporated at every repeat of monomer, leading to short inter-fullerene distances in a soluble polymer. On the other hand, copolymer **164a** exhibited micellar aggregation in solution but phase separation with interpenetrating  $C_{60}$  domains in the solid state. They also designed the new amphiphilic diblock copolymer **166** in order to control the blend morphology of the active layer of an organic solar cell (Scheme 41).<sup>227</sup> Incorporation in the polymer backbone of fragments of poly(3-hexylthiophene) (P3HT), which act as compatibilizer between PCBM and P3HT (PCBM = [6,6]-phenyl  $C_{61}$  butyric acid methyl ester), reduces the interfacial energy between the immiscible

components in the solid state. In this way, they observed that once added to a blend of PCBM:P3HT in 17 wt %, polymer **166** leads to photovoltaic devices with comparable performances in terms of efficiency ( $\sim 2.8\%$ ) but enhances the stability of the devices against destructive thermal phase segregation, hence improving the disposal longevity.

To this point we have exclusively shown organic  $C_{60}$ -based polymers, but some examples of  $C_{60}$ -based inorganic polymers are known too, which are of great interest. In the past decades polymers with inorganic backbones have aroused curiosity and interest because of their special properties and some advantages they present over some carbon-chain polymers.<sup>228</sup> Among them, polyphosphazenes and polysiloxanes are noticeable.<sup>229</sup> The former have been used not only as flame-retarding materials<sup>230</sup> but also as liquid

Scheme 42



crystals,<sup>231</sup> photoconductors,<sup>232</sup> and nonlinear optical materials,<sup>233</sup> whereas the latter shows exceptional chain mobility that affords good solubility.<sup>234</sup>

Very recently, Qin and co-workers described the synthesis and characterization of four different C<sub>60</sub>-containing polyphosphazenes (Scheme 42).<sup>235,236</sup>

In Scheme 42 it can be seen that synthesis of polymers **169a–b**, **171**, and **174** is straightforward involving ordinary solvents and reagents. Initially, poly(dichlorophosphazene) was prepared by ring-opening polymerization of phosphonitrile chloride trimer, providing a material with double sites for further functionalization. In this way, two following reactions allow introducing solubilizing chains and reactive sites which, in turn, react with C<sub>60</sub> to give polymers **169a–b**, **171**, and **174**. In all cases, good *M<sub>w</sub>* and narrow polydispersity indexes have been calculated, and C<sub>60</sub> contents between ~2% and ~7% have been calculated for **169b** and **174**, respectively.

On the other hand, attempts to graft C<sub>60</sub> onto a siloxane copolymer using (divinyltetramethyldisiloxane)platinum(0) failed, affording a fullerene cage surrounded by two siloxane chains multiply attached.<sup>237</sup> Better results have been obtained

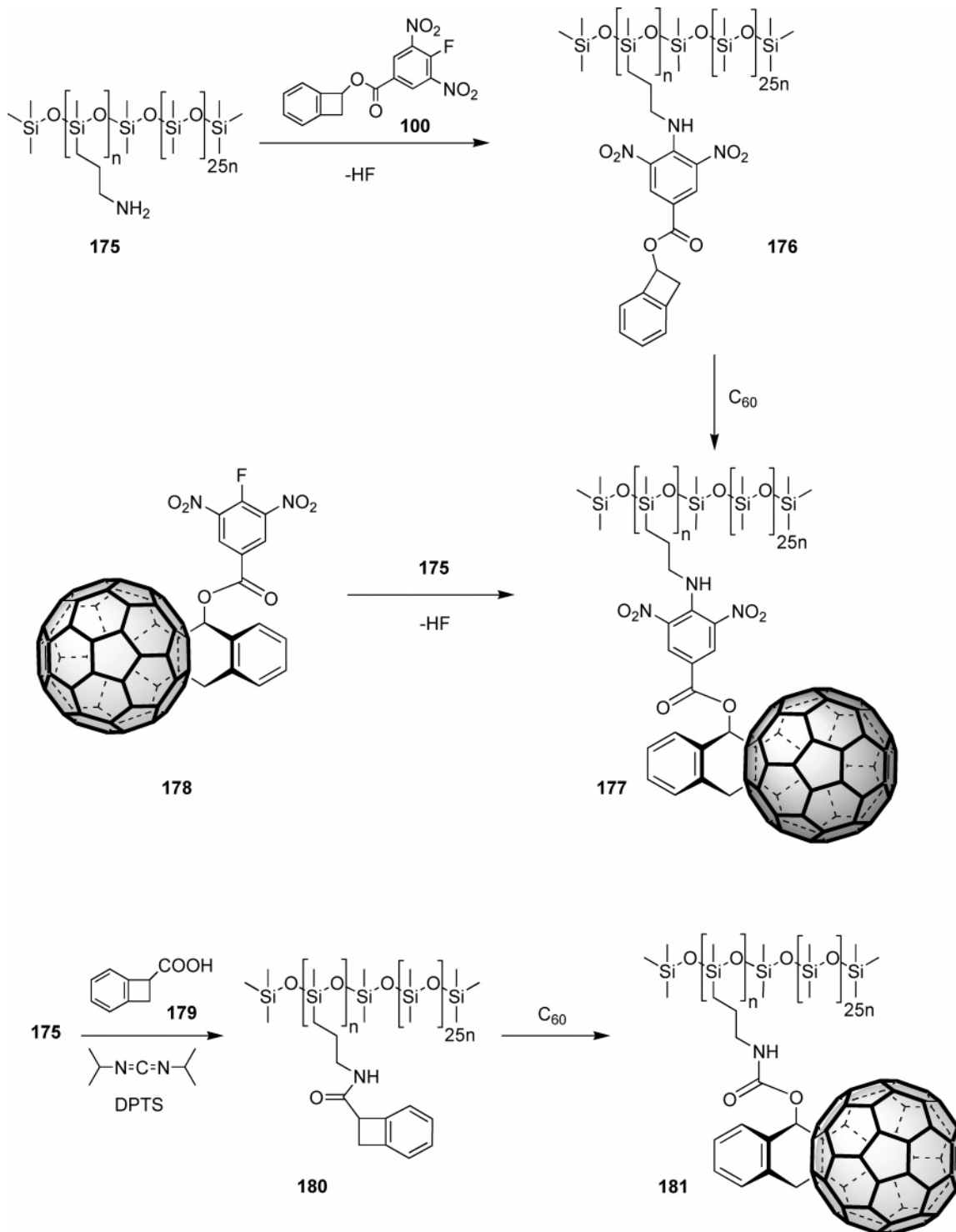
by Kraus and Müllen, who first reported side-chain polysiloxanes with pendant C<sub>60</sub> units (Scheme 43).<sup>172</sup>

Interestingly, polymer **177** was prepared following two different routes: in the first one, C<sub>60</sub> was incorporated directly to a suitably functionalized polymer (**176**) by the *o*-quinodimethane method.<sup>238</sup> The second strategy deals with incorporation of a C<sub>60</sub> derivative directly into an amino-functionalized polysiloxane **175**. Surprisingly, both strategies lead to polymers with identical *M<sub>w</sub>* values and with a remarkable content in [60]fullerene as high as 30 wt %. Once again the authors demonstrate the feasibility of incorporating C<sub>60</sub> to an established polymeric backbone by introducing benzocyclobutene moieties as side chains that readily react with C<sub>60</sub> to afford the new polymer **181** (Scheme 43). This new material displayed a *M<sub>w</sub>* analogue to those of **177** (~35 000) as well as a high thermal stability of up to 435 °C.

In 2003 two new examples of polysiloxanes side-functionalized with fullerene units were described (Scheme 44).<sup>239</sup>

Again, C<sub>60</sub> was loaded into the polymer by means of pendant amino-fishing groups, giving rise to low weight macromolecules with moderate C<sub>60</sub> content (**184a**, 2.5%; **184b**, 3.9%). However, the first example in which a C<sub>60</sub>-

Scheme 43



containing siloxane monomer (**186**) was polymerized to give the corresponding homopolymer **187** was recently reported,<sup>240</sup> as depicted in Scheme 44. Polymerization was carried out using triflic acid as initiator, and GPC revealed a high  $M_n$  value (95 000).

We preserved the final part of this section to report some remarkable side-chain  $C_{60}$  polymers reported in the past few years presenting original structures as well as interesting novel properties.

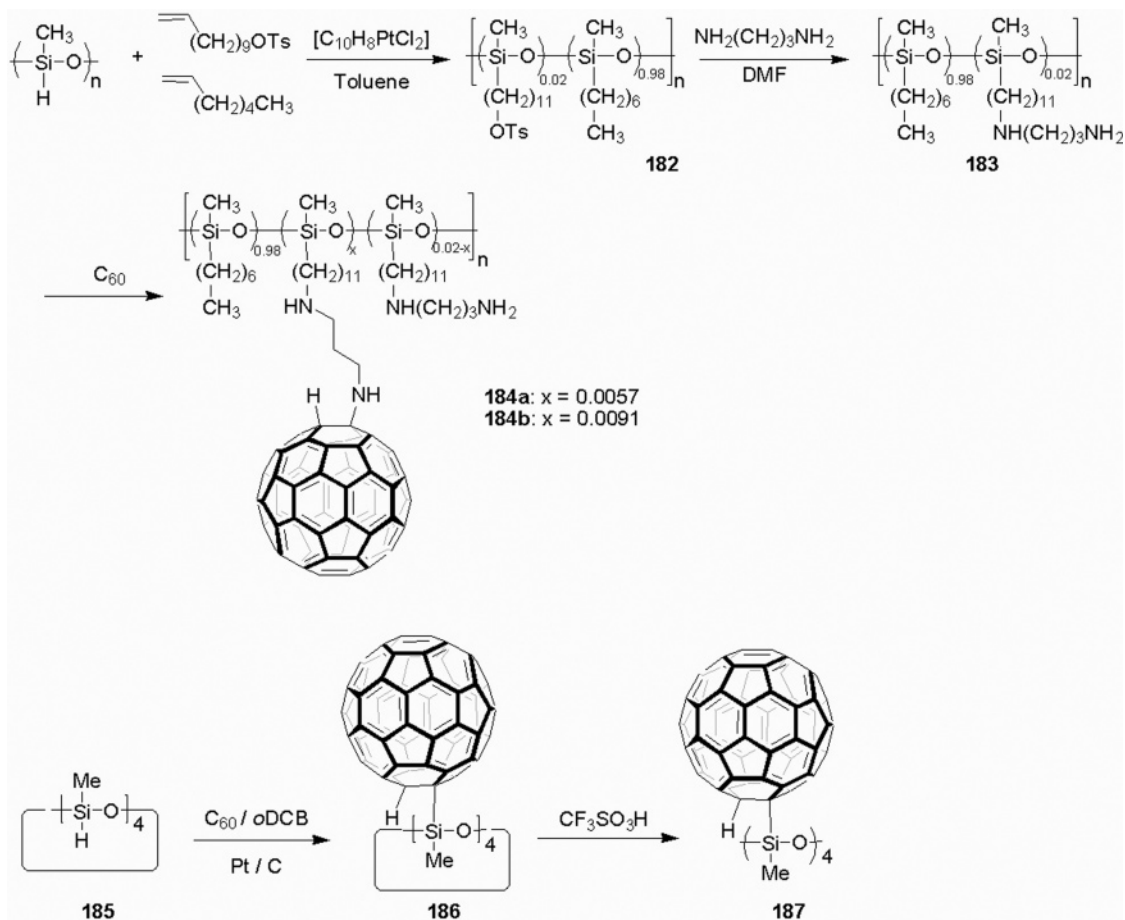
The first example we choose deals with synthesis of water-soluble pullulans bearing pendant fullerene moieties. Pullulan

is a nonionic water-soluble polymer constituted by  $\alpha$ -1,6-linked maltotriose units, produced by the fungus *Aureobasidium pullulans*.<sup>241</sup>

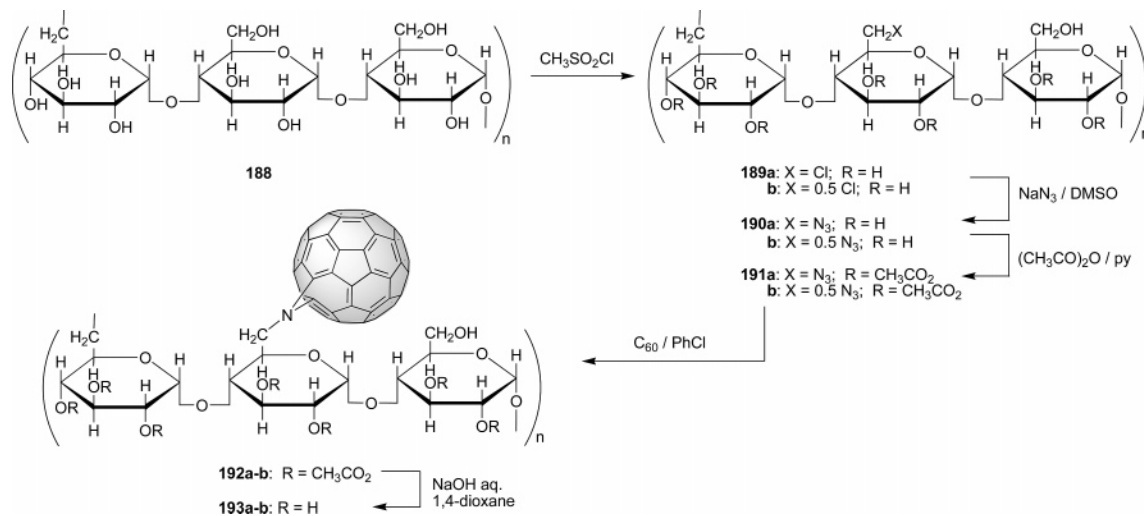
Incorporation of  $C_{60}$  into pullulans was carried out as depicted in Scheme 45 and involves two different degrees of chlorination in order to obtain polymers with different content of  $C_{60}$ .<sup>242</sup>

After reaction of 6-azido-6-deoxypullulans with  $C_{60}$ , in which approximately the 60% of azido groups reacted, pullulans **192a,b** were treated with NaOH to remove acetyl groups to yield the corresponding polymers **193a,b**. These

Scheme 44



Scheme 45

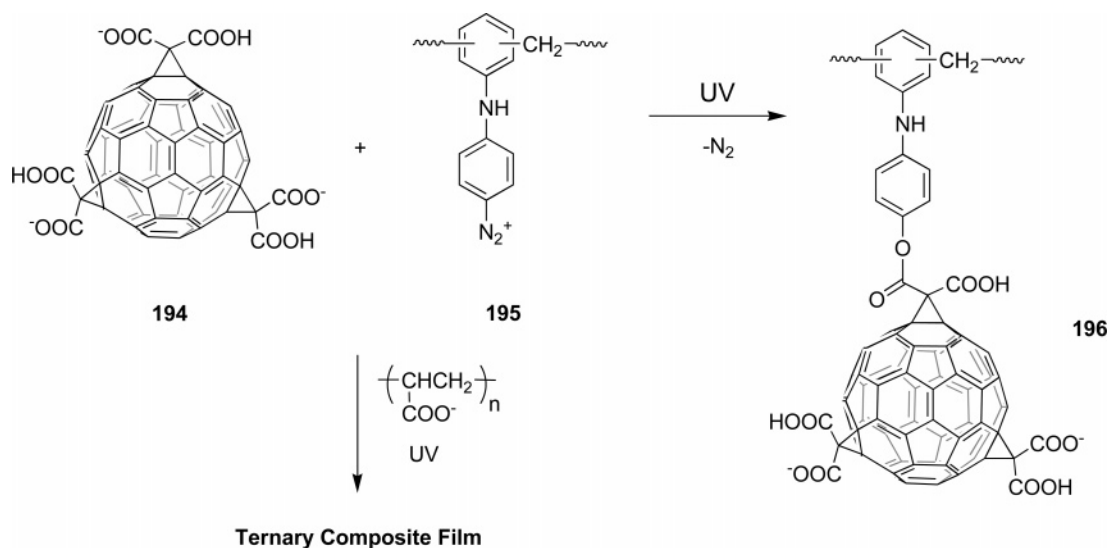


derivatives showed water solubility (**193a**, 216 mg mL<sup>-1</sup>; **193b**, 5.6 mg mL<sup>-1</sup>), and taking into account that the fraction of fullerene in **193a** and **193b** was of 12% and 23%, respectively, a saturation solubility of 26 and 1.3 mg mL<sup>-1</sup> for the C<sub>60</sub> moiety can be estimated.

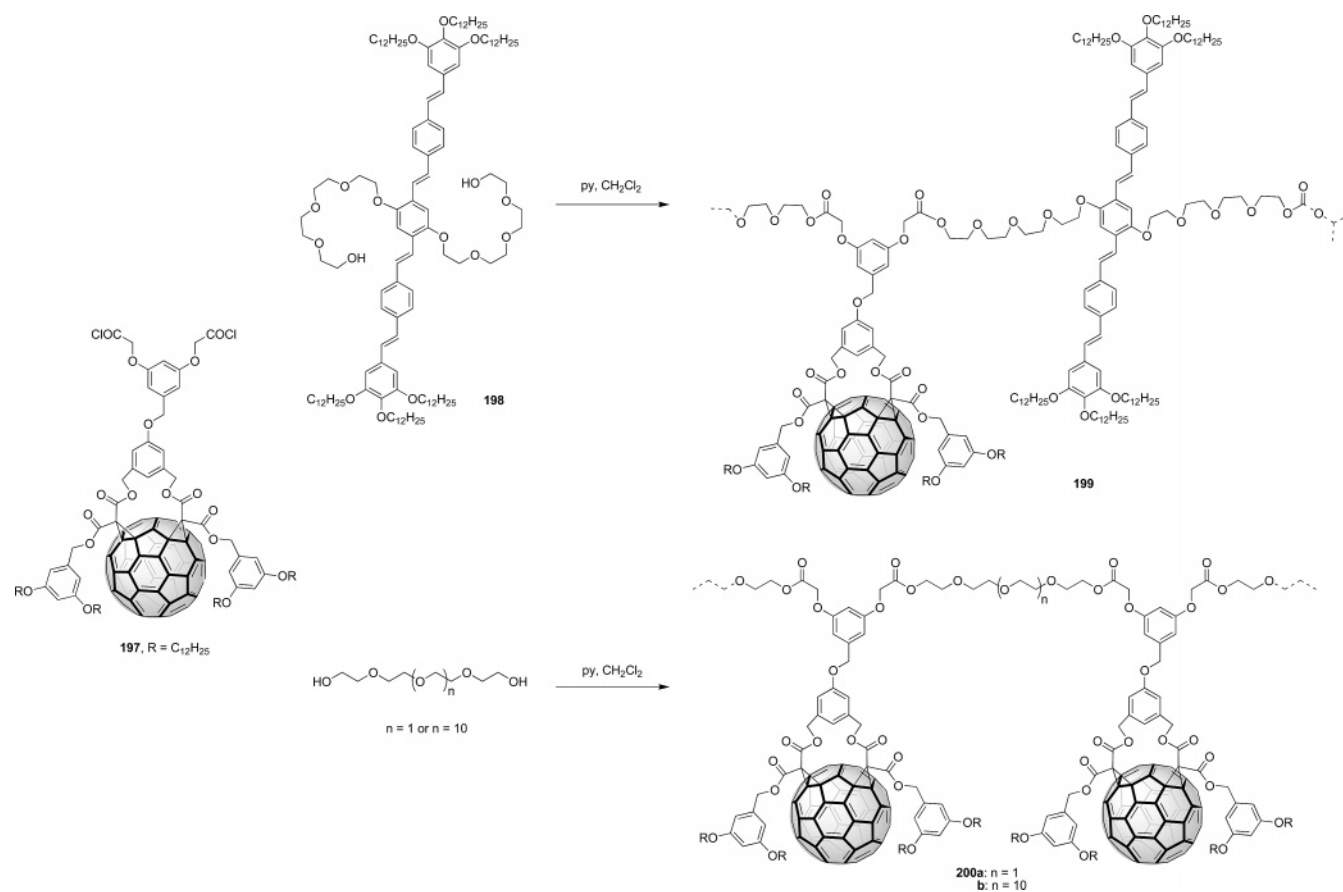
On the other hand, Cao and co-workers reported a very original work in which they first fabricated self-assembly ultrathin films using a C<sub>60</sub>-tricarboxylic acid (**194**) together with a diazoresin (**195**) via electrostatic interaction in aqueous solution.<sup>243</sup> Afterward, the bond nature between the layers changed from ionic to covalent by irradiating with UV light

(Scheme 46). The film so formed was very stable toward polar solvents, and in addition, the microtribological properties have been investigated, revealing that C<sub>60</sub> in the film affords load-bearing capacity. Furthermore, the authors incorporated poly(acrylic acid) with the aim of forming a ternary composite film with enhanced lubricative properties. Such ternary polymer-bound C<sub>60</sub> films displayed very load-bearing as well as low-friction properties. However, one may think that what is really occurring is not simply formation of regularly side-chain polymers but, in some cases, that cross-linking is taking place into the film. In any case, the

Scheme 46



Scheme 47



forementioned approach opens the door to a new way to incorporate fullerene into polymeric chains directly in the solid state.

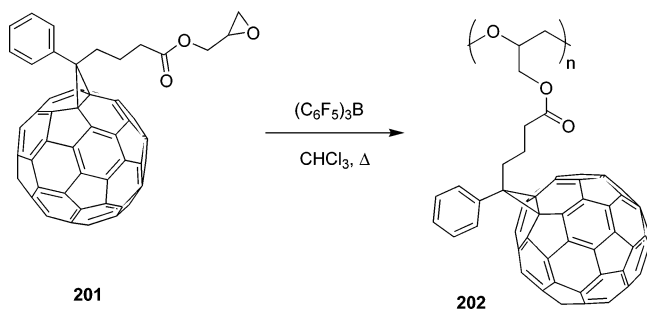
Side-chain polymers containing C<sub>60</sub> have also been employed as donor–acceptor materials for their potential use in photovoltaic devices. In this respect, Nierengarten et al. prepared two different polyesters starting from the suitable diacyl chloride **197**, which was first reacted with the pentamer analogue of PPV endowed with two TEG arms, **198**, (Scheme 47).<sup>244</sup> This interesting material preserved the electrochemical properties of [60]fullerene and showed

a UV spectrum that displayed the characteristic features of both electroactive units. It is worth mentioning that, in this case, a value of 63 000 g mol<sup>-1</sup> ( $M_w/M_n = 1.1$ ) was calculated by analytical SEC coupled with a light-scattering detector, which allows determination of absolute molecular weights.

On the other hand, polycondensation of bisadduct **197** with TEG and PEG ( $M_n = 600$ ) afforded polymers **200a,b** with high yields and high  $M_w$  (66 000 and 70 000, respectively).<sup>245</sup>

Polymer **200a** was blended together with MDMO–PPV and spin-coated in order to prepare organic solar cells.

Scheme 48



However, although some photovoltaic activity has been found, the overall performance was very low.

Improved performances of polyfullerene-containing organic solar cells have been very recently reported by Drees, Sariciftci, and co-workers.<sup>246</sup> They successfully tried a new approach in which first the glycidol ester of [6,6]-phenyl C<sub>61</sub>butyric acid (PCBG, **201**) was prepolymerized in the presence of Lewis acid tris(pentafluorophenyl)borane as the initiator (Scheme 48). Hence, after spin coating the prepolymer in blend with P3HT, ring-opening polymerization was completed by heating the photovoltaic device. In this way a very promising 2% conversion energy efficiency value was obtained, probably due to morphological stabilization of the bulk heterojunction, which prevents its long-term high-temperature instability.

Finally, the last example we present in this section involves the synthesis of C<sub>60</sub>-containing poly(2,6-dimethyl-1,4-phenylenoxide) (PPO) for its use in the fabrication of membranes for gas separation<sup>247</sup> and for blending and miscibility studies with styrenic polymers.<sup>248</sup> Synthesis took place by partial bromination of the methyl groups which, in turn, were substituted for azido groups, as reported in Scheme 49. Thus, by controlling the initial bromine content, it was possible to carry out preparation of a series of C<sub>60</sub>-containing PPO. Gas permeability experiments carried out on pure PPO sample, blend of PPO and C<sub>60</sub>, and C<sub>60</sub> linked to PPO (**206**) showed that the latter exhibited a significantly higher permeability, which in some cases rises 80% without compromising the selectivity.

## 8. Double-Cable Polymers

Since the discovery of an efficient photoinduced electron-transfer (PET) process from nondegenerate ground-state semiconducting  $\pi$ -conjugated polymers to fullerene C<sub>60</sub> in 1992,<sup>249</sup> these materials have received a great deal of attention for fabrication of organic photovoltaic solar cells.<sup>250</sup>

The effective electronic interaction between the electron-donor (p-type component) and the electron-acceptor (n-type

component) molecules of the first p/n photovoltaic cells was limited to the flat geometrical interface existing between them. The new concept of “bulk heterojunction” solar cells in which the interaction occurs in the entire volume by mixing a soluble p-type  $\pi$ -conjugated polymer and the fullerene as the n-type component allowed drastically increasing the efficiency of the new photovoltaic (PV) devices. However, the main drawback in this approach to PV cells is the compatibility between the conjugated polymer and the fullerene components since phase separation and clustering of fullerene can take place, thus decreasing the effective donor–acceptor interaction as well as the charge transport of the photogenerated electrons and holes.<sup>251</sup>

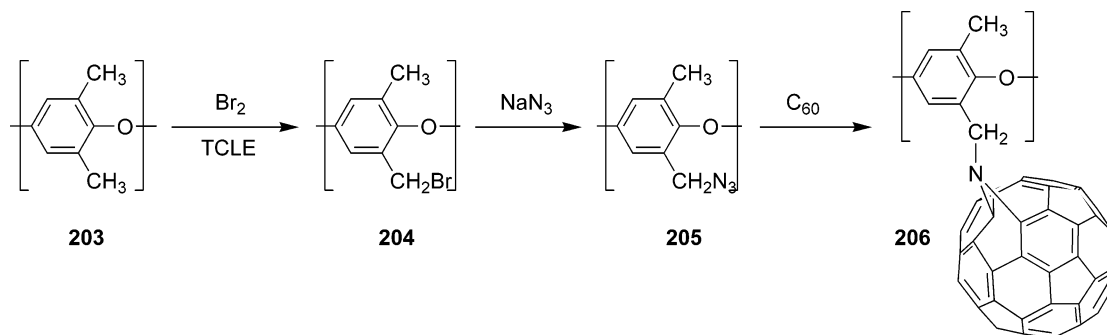
An elegant and new concept to overcome the above problems consists of the use of p-type  $\pi$ -conjugated backbones (donor cable) bearing covalently connected acceptors such as fullerenes (acceptor cable), thus forming the so-called “double-cable” approach.<sup>252</sup> The advantages of this design are (i) a larger donor–acceptor interfacial area, (ii) variation of the chemical nature of the donor and acceptor moieties and length of the spacer connecting them allows tuning the electronic interaction of the double-cable components, and (iii) phase separation and clustering are prevented.

Preparation of photovoltaic cells from organic materials processable as easily as plastics can provide a new hint at both the exploitation of solar energy and the demands for more advanced photodetectors.<sup>253</sup> With respect to silicon technology, organic materials have the advantages of low production costs, environmental impact, and preparation of flexible devices. The materials design at the molecular level leads to the following features: (1) tunability of the electrical and optical properties; (2) easy processability that allows preparation of large surface films with controlled thickness; (3) compatibility with other organic materials for preparation of blends; (4) low cost of both the materials and the technology.

In this section we will discuss the different approaches followed for the design of double cables constituted by a  $\pi$ -conjugated semiconducting polymer and a fullerene derivative as electron-donor and -acceptor components, respectively, focusing on the most significant progress in this field.

Even though several authors indicate the work of Sannicolò and Zotti as the first double-cable polymer reported,<sup>254</sup> the very first example of a C<sub>60</sub> moiety covalently linked to an electroactive conjugated polymer was described in 1994 by Diederich, Gross, and Seiler.<sup>255</sup> They reported a bis-(trimethylsilyl)methanofullerene (**207**) which undergoes reductive electrochemical polymerization to give the corresponding polydiacetylene **208** (Scheme 50).

Scheme 49





Scheme 50

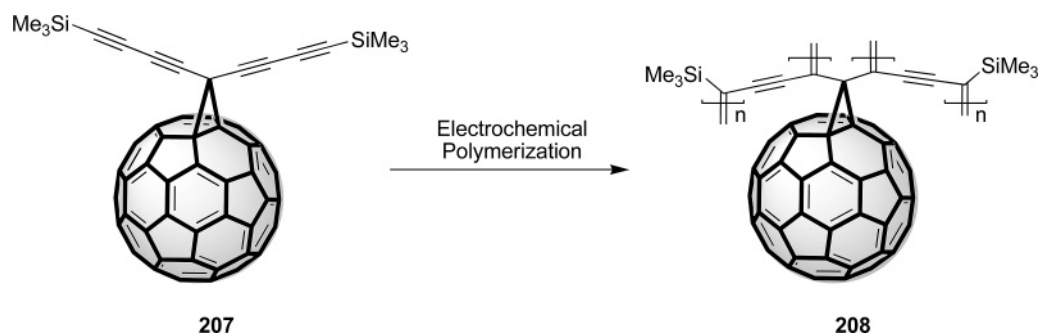
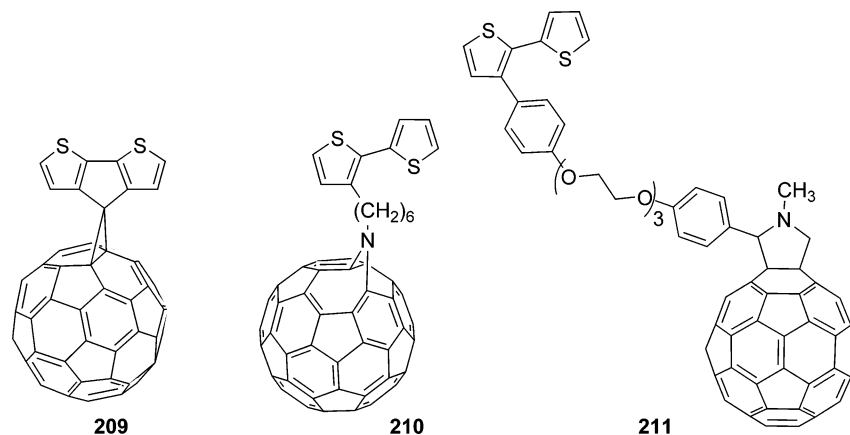


Chart 6. Chemical Structures of Monomers 209–211



This homogeneous film deposits on the platinum cathode surface and continues to build-up during the electropolymerization of **207**, even after it has covered the electrode, implying its electrical conductance. A new proof of conductivity of polymer **208** is given by the fact that film-covered electrodes generate essentially normal electrochemical response with known redox systems if employed as modified electrode.

Electropolymerization of aromatic monomers has been one of the most employed strategies to obtain  $C_{60}$ -containing double-cable polymers. Such a method generally implies electrogeneration of radical cations and their subsequent rearomatization.<sup>256,257</sup> Moreover, this technique represents a useful tool for the synthesis of novel conjugated polymers, allowing growth of these films onto transparent substrates for characterization by spectroscopic techniques.

In this light, in Chart 6 are recompiled the molecular structures of three monomers suitable for electropolymerization.

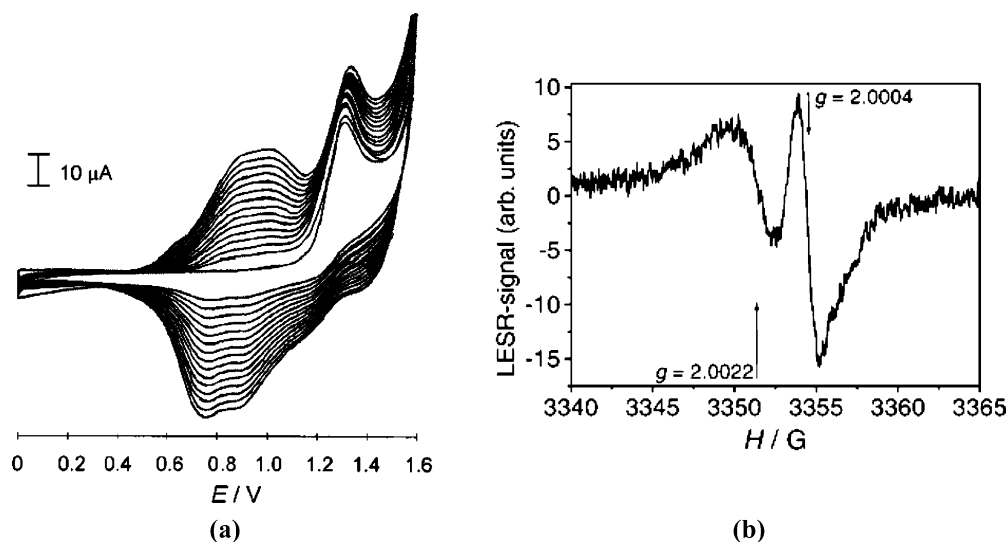
The choice of bithiophene as electropolymerizable unit for **210**<sup>258,259</sup> and **211**<sup>260–262</sup> lies in the lower oxidation potential values that they present as compared to thiophene-based systems, leading to easier and superior degree of polymerization. It is noteworthy how for those polymers (poly-**209**<sup>254–211</sup>) polythiophene backbone and fullerene preserve their own electrochemical behavior, and no interactions have been observed in the ground state. Photoinduced absorption (PIA) and light-induced electron spin resonance (LESER) experiments carried out on poly-**211** revealed that photoinduced electron transfer from the conjugated polymer to the pendant  $C_{60}$  occurs (Figure 9), thus making this material appealing for photovoltaic applications.

Very recently, Komatsu et al. reported electropolymerization of terthiophene monomers (**214** and **215**)<sup>263</sup> and

ethylenedioxy-substituted terthiophene (**217** and **218**)<sup>264</sup> connected to a  $C_{60}$  moiety (Scheme 51).

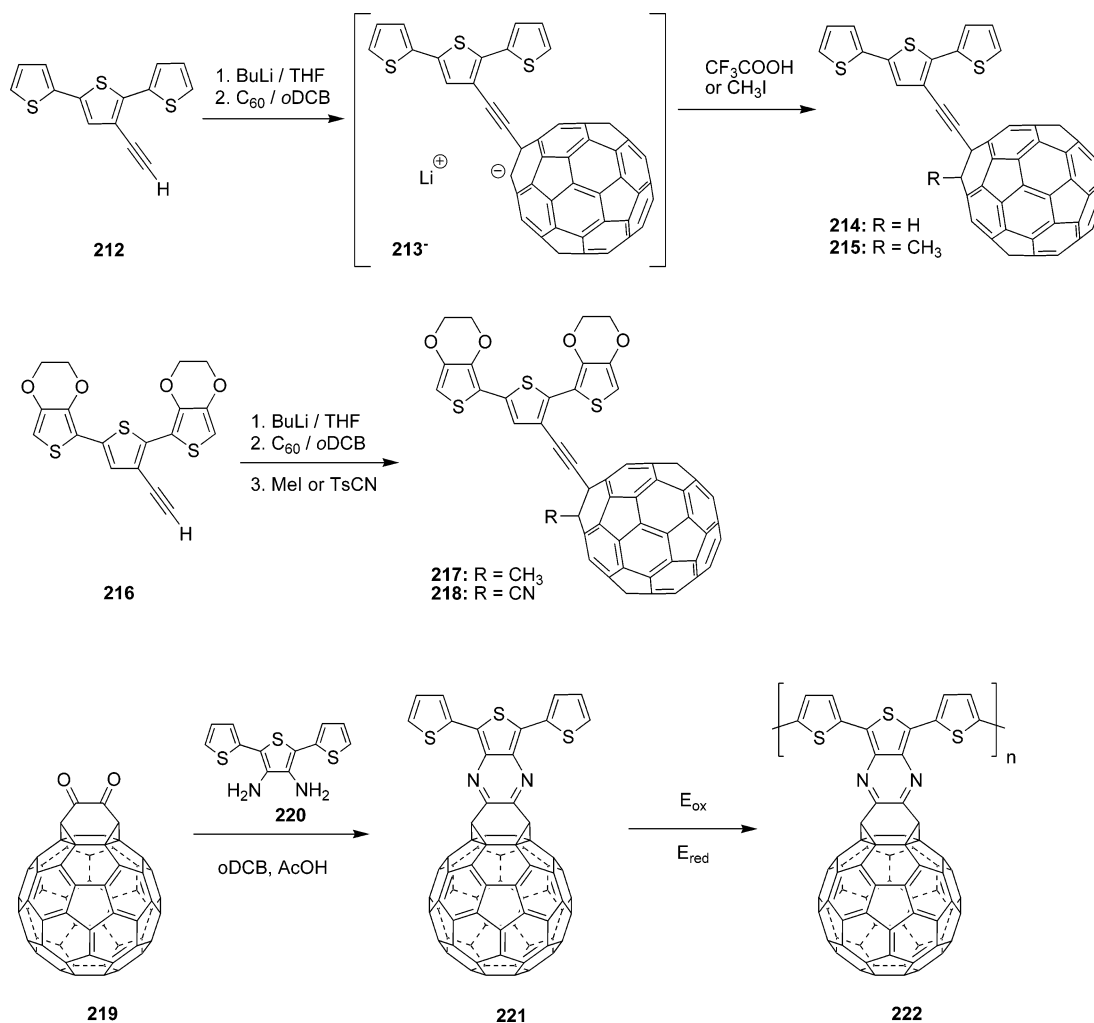
The authors chose the nucleophilic addition of lithium acetylides as a viable method for functionalizing  $C_{60}$ <sup>265</sup> since this strategy allows further incorporation to the fullerene cage of proton or alkyl groups in high yields.<sup>266</sup> However, the presence of a proton in the cage of **214** is harmful since the electropolymerization of such monomer led to a film with a very complex voltammogram due to chemically irreversible processes. This fact has been ascribed to irreversible reactions that take place in the presence of  $C_{60}^{\bullet-}$  that tends to dimerize upon one-electron oxidation.<sup>267,268</sup> On the contrary, poly-**217** was chemically stable and electroactive to both p- and n-doping, showing, in addition, electrochromism as well as poly-**217**. The latter, which is purple in the neutral state, showed a broad absorption band corresponding to the  $\pi-\pi^*$  transition of PEDOT at 580–600 nm when deposited on ITO and maintained at  $-0.6$  V (Figure 10, red line).

On the other hand, when poly-**217** is exposed to a positive potential ( $+0.4$  V) a new broad peak at  $\sim 1500$  nm (cationic or p-doped state of PEDOT)<sup>269</sup> appears and, at the same time, the 600 nm band disappears, resulting in a color change to green (Figure 10, green line). Finally, when the potential is kept at  $-1.6$  V, the 550 nm centered band grew up and the color changed to bluish purple, as already reported for another  $C_{60}$ -charm-bracelet-type polythiophene.<sup>258</sup> The voltammogram of **217** showed, in the first scan, an irreversible anodic peak and three reversible cathodic waves, corresponding to oxidation of terthiophene unit and the first three reduction processes of the  $C_{60}$  moiety ( $E_{pa} = +0.49$  V and  $E_{1/2} = -1.14, -1.53,$  and  $-2.08$  V vs Fc/Fc<sup>+</sup>). It is worth noting that compared to **214** and **215** ( $E_{pa} = +0.85$  and  $0.82$  V, respectively), the oxidation potential is significantly lower in **217**, thus indicating an enhanced donor ability of the terthiophene system and higher planarity for oligo-EDOTs.<sup>270</sup>



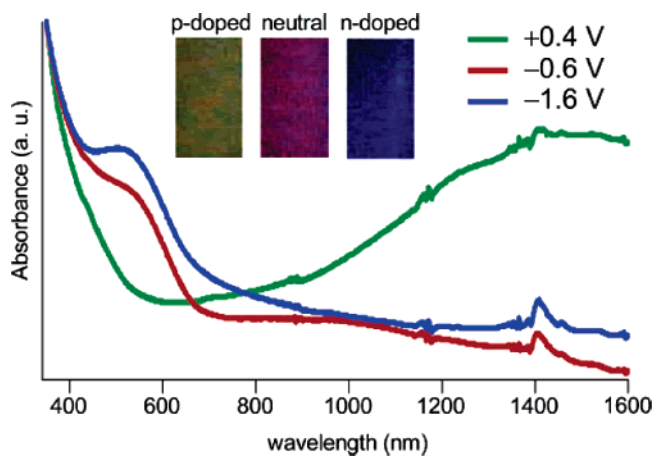
**Figure 9.** (a) Anodic cyclic voltammogram of **211** (0.1 M  $\text{Bu}_4\text{NPF}_6$  in  $\text{CH}_2\text{Cl}_2$ ). Working electrode: Pt foil. Quasi-reference electrode: Ag/AgCl wire ( $-0.44$  V vs ferrocene). Scan rate:  $100 \text{ mV s}^{-1}$ . (b) Integrated LESR (light-on minus light-off) spectrum of poly-**211** on ITO-coated plastic foils. Excitation at  $488 \text{ nm}$  ( $20 \text{ mW cm}^{-2}$ ).  $T \approx 77 \text{ K}$ . The higher  $g$  factor ( $g = 2.0022$ ) is due to the presence of positive polarons on the polythiophene backbone, while the signal at  $g = 2.0004$  is typical of  $\text{C}_{60}^{\bullet-}$ . (Reprinted with permission from ref 262. Copyright 2002 American Chemical Society.)

### Scheme 51



Very recently, Wudl et al. described a most interesting example of electropolymerized double-cable polymer (**222**) in which the  $\text{C}_{60}$  was joined to the terthiophene by means of a thieno[3,4-*b*]pyrazine bridge as a bisfulleroid (**221**, Scheme

51).<sup>271</sup> It is worth mentioning that the authors determined the polymer band gap by means of three different techniques: cyclic voltammetry (CV), differential pulse voltammetry (DPV), and in-situ spectroelectrochemistry (UV–

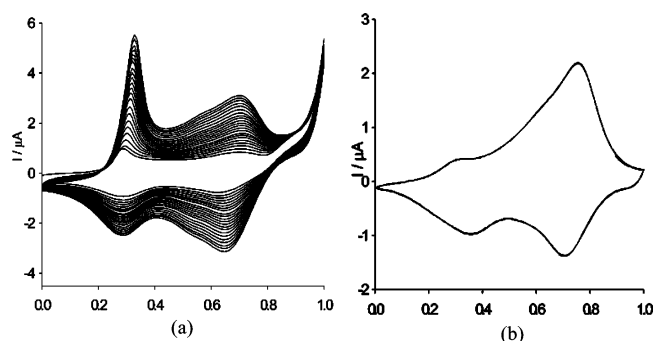


**Figure 10.** Electronic absorption spectra of poly-217 film on an ITO electrode at various applied potentials in MeCN (0.1 M Bu<sub>4</sub>NBF<sub>4</sub>, V vs Fc/Fc<sup>+</sup>). The peak at around 1400 nm is attributed to absorption of the ITO electrode. (Reprinted with permission from ref 264. Copyright 2004 American Chemical Society.)

vis-NIR). The values found were as low as 0.21, 0.18, and 0.30 eV for CV, DPV, and spectroelectrochemistry, respectively. However, they stated that such values could represent a “quasi-gap” due to impurity states in the gap, estimating the real gap on the order of 0.7 eV.

Electropolymerization of precursors containing two or more polymerizable groups can lead to macromolecules with original properties such as faster switching response and strongly improved long-term stability under redox cycling.<sup>272</sup> As an example, Roncali, Blanchard et al. prepared four new bithiophene-based monomers endowed with one or two polymerizable groups attached on C<sub>60</sub>, as depicted in Scheme 52.<sup>273</sup>

As expected, in comparison with 229, bis-adducts 230 and 231 showed a significant cathodic shift of the reduction



**Figure 11.** (a) Potentiodynamic electropolymerization of monomer 231 (10<sup>-3</sup> M) in 0.10 M Bu<sub>4</sub>NPF<sub>6</sub>/1:4 CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub>, 100 mV s<sup>-1</sup>, reference Ag/AgCl. (b) Cyclic voltammogram of poly-231 in potentiostatic conditions at 0.98 V, C = 10<sup>-3</sup> M. Deposition charge Q<sub>d</sub> = 5 mC cm<sup>-2</sup>. Electrolytic medium: 0.10 M Bu<sub>4</sub>NPF<sub>6</sub>/CH<sub>3</sub>CN 100 mV s<sup>-1</sup> reference Ag/AgCl. (Reprinted with permission from ref 273. Copyright 2003 American Chemical Society.)

potential values (~70 mV) due to saturation of a second double bond of the C<sub>60</sub> core which raises the LUMO energy level.<sup>274</sup> The potentiodynamic electropolymerization of 231 led to a strong intensification of the first anodic wave (Figure 11a). The peak potentials shift toward less positive values, suggesting that such electropolymerization of the two-site precursor gives rise to a more extensively conjugated polymer. This hypothesis is also corroborated by the CV analysis of monomer-free CV of poly-231 (Figure 11b) in which the negative shift of the anodic waves indicates that lengthening of the spacer increases the solubility of the precursor, allowing formation of a more extensively conjugated polymer. Moreover, preliminary stability tests performed on poly-229 and poly-231 films revealed that while in the former the amount of charge reversibility exchanged decreases by 44%, in the latter it remains intact, confirming

#### Scheme 52

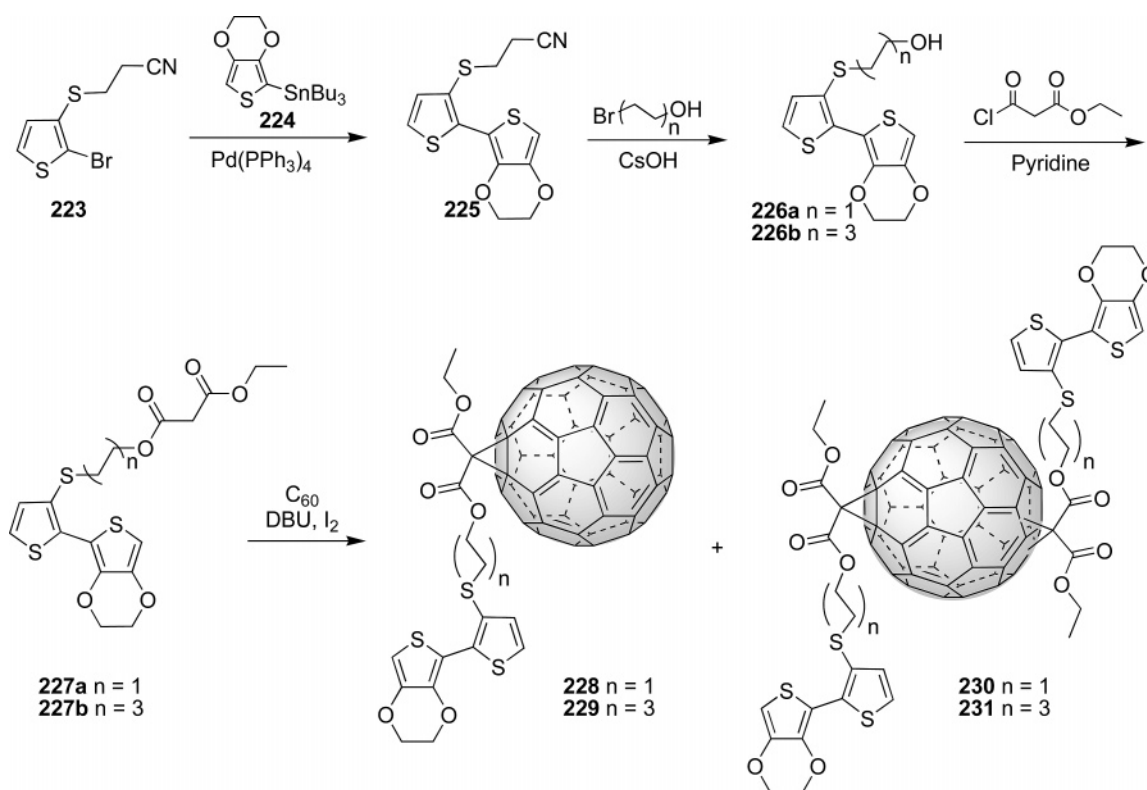
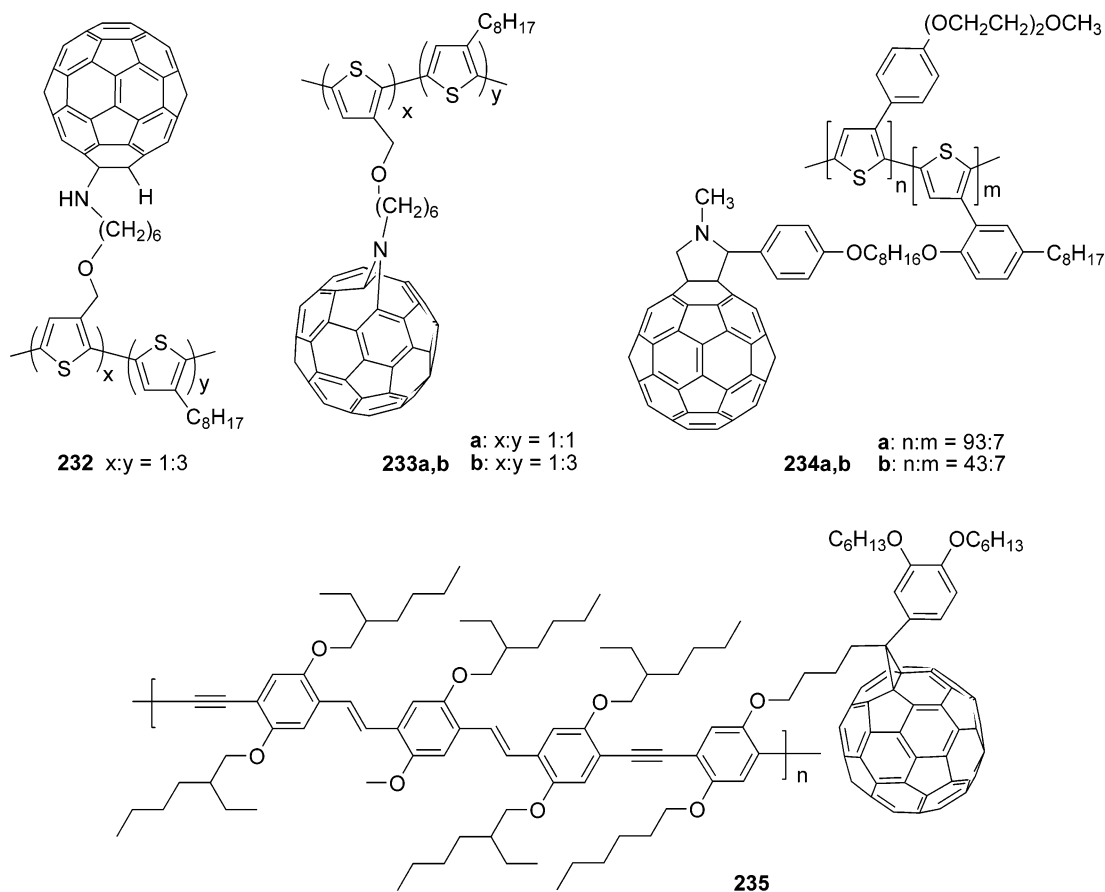


Chart 7. Chemical Structures of Some Representative Chemically Synthesized C<sub>60</sub>-Based Double-Cable Polymers 232–235

a dramatic improvement of the stability for such multisite precursor

Finally, poly-**231** showed a shorter response time in current/time transient measurements than poly-**229** due to the combined effects of higher conductivity and more efficient mass transport in the polymer bulk, making poly-**231** an interesting material for further photovoltaic investigations.

Unfortunately, although all those materials are very appealing for their electrochemical and photophysical studies, the polymers prepared by electropolymerization very often tend to be insoluble and intractable, limiting their use in real applications. To overcome this problem, several chemical strategies have been developed to lead to the preparation of chemically synthesized double-cable polymers. Of course, such strategies involve many synthetic time-consuming steps in order to obtain suitable soluble monomers that can form processable polymers with an adequate load of C<sub>60</sub> for PV or other electronic applications. From an organic chemist point of view, such strategies are more “stimulating” than the electropolymerization one but at the same time are tedious and complexes leading to lower yields and amounts of materials.

The molecular structures of some of the chemically synthesized double-cable polymers prepared so far are presented in Chart 7. It is interesting to note that in all these examples one part of the molecule supports a high solubility to the final product and the rest usually bears the acceptor moiety. However, in this “game of the parts” increasing the number and length of alkyl chains increases the solubility but drastically decreases the percentage of fullerene content in the final polymer and, at the same time, having a negative effect on the electron jumps.

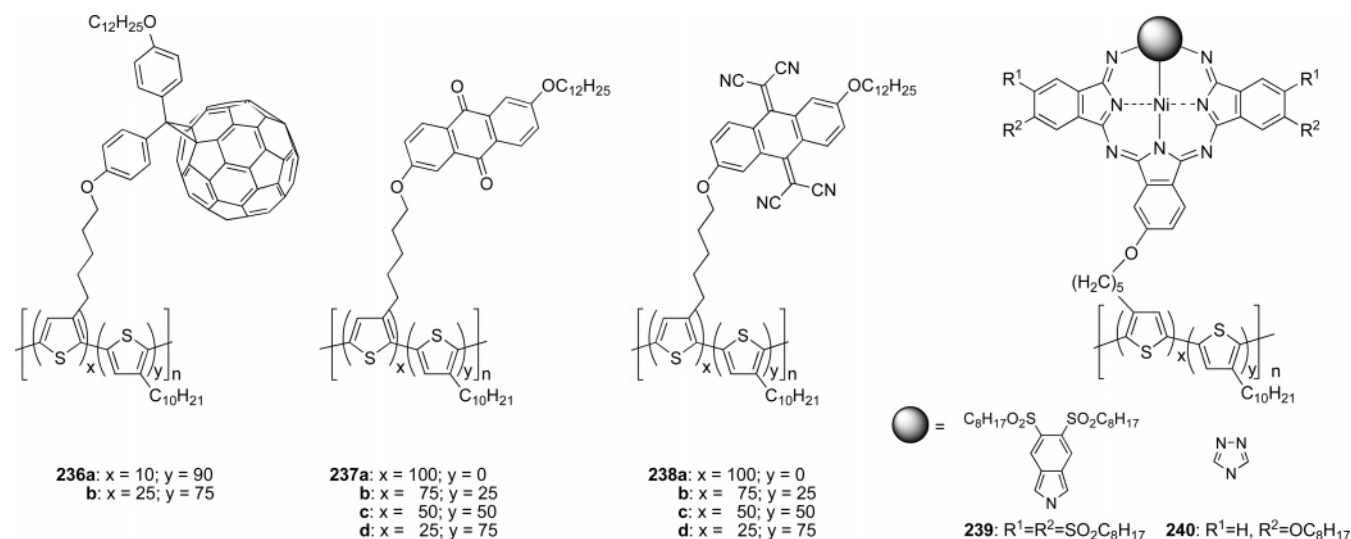
Polymers **232** and **233** prepared by Ferraris et al.<sup>275,276</sup> were solvent-processable conducting polymers with a high C<sub>60</sub> content (**232** and **233b**, ~48%; **233a**, 65%), and although the presence of the acceptor moieties does not perturb the polythiophene backbone, no devices were fabricated.

On the contrary, polymers **234a,b**<sup>277</sup> and **235**<sup>278,279</sup> represent the first examples of C<sub>60</sub>-containing macromolecules used as the sole electroactive layer in photovoltaic cells. Although high and promising open-circuit voltages ( $V_{OC}$ ) were obtained from such devices, they showed low power conversion efficiency values, probably due to their low content in acceptor (**234a,b**, 7–14%; **235**, 38.5%) compared to the usual content of bulk heterojunction devices that can reach up to 80 wt % of fullerene or fullerene derivatives.<sup>250,251</sup>

Many of the double-cable polymers reported so far are based, as we have previously seen, on poly-thiophene derivatives because of their easy functionalization and stability in the presence of C<sub>60</sub>. In this sense, other related examples of thiophene-based double-cable polymers in which the acceptor moiety has been changed to other planar acceptor such as anthraquinone (AQ), tetracyanoanthraquinodimethane (TCAQ), or phthalocyanine have also been reported (Chart 8).

Recently, we reported the ease of tuning the optical properties of double-cable copolymers by modifying the ratio of monomers in the copolymerization process. In fact, by changing the amount of monomer-bearing acceptor moieties in the feed, namely, AQ (**237a–d**)<sup>280–283</sup> or TCAQ (**238a–d**),<sup>282,284</sup> it is possible to change the UV response as well as the photoluminescence of the corresponding polymer in a direct manner (Figure 12a). FTIR photoinduced absorption and light-induced electron spin resonance (LESER) experiments demonstrate the photoinduced electron transfer

Chart 8



from the polythiophene backbone to the anthraquinone moieties. Thus, the LESR spectra show two overlapping lines at a magnetic field of  $\sim 3361$  and  $\sim 3365$  G corresponding, respectively, to  $g = 2.0042$  and  $2.0024$ . The high  $g$ -value signal was assigned to radical anions on the anthraquinone molecule<sup>285</sup> and the low  $g$ -value signal to positive polarons on the polythiophene chain<sup>286</sup> (Figure 12b). By changing the content of acceptor molecules, it is possible to tune the number of photogenerated charges as well as their lifetimes.

The first diode characterizations were carried on **237b** and **237c** using Al or Ca as electrode.<sup>287</sup> In the latter case we found some photovoltaic response (see Figure 13a) and the short-circuit current increases with increasing acceptor content. The photocurrent action spectrum follows the UV-vis absorption spectrum, indicating that charge photo-generation is occurring by either photoexcitation of the conjugated polythiophene backbone or photoexcitation of the anthraquinone substituent (Figure 13b).

On the other hand, use of another acceptor such as Ni(II) phthalocyanine or Ni(II) triazolephthalocyanine covalently linked to the polythiophene backbone (**239** and **240**, respectively) leads to the observation of electron-transfer processes between the donor skeleton and the acceptor moieties.<sup>288</sup>

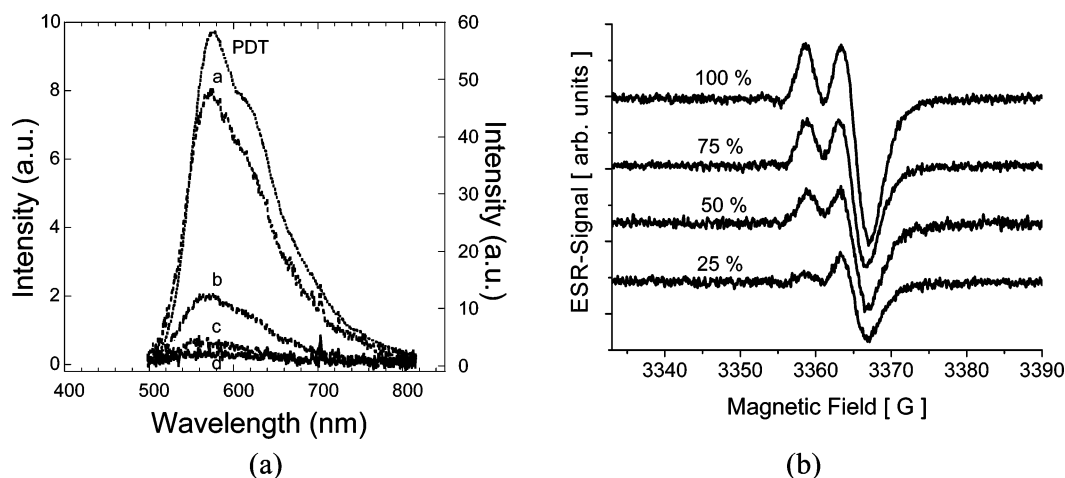
Finally, compounds **236a,b** were synthesized, but due to their low solubility, they could not properly be characterized.

The approach of linking donor and acceptor moieties into a single polymer in order to create a bicontinuous network confined to a molecular scale has also been successfully used employing PPV-based conjugated polymers and copolymers bearing  $\text{C}_{60}$  units in the side chains (Chart 9).

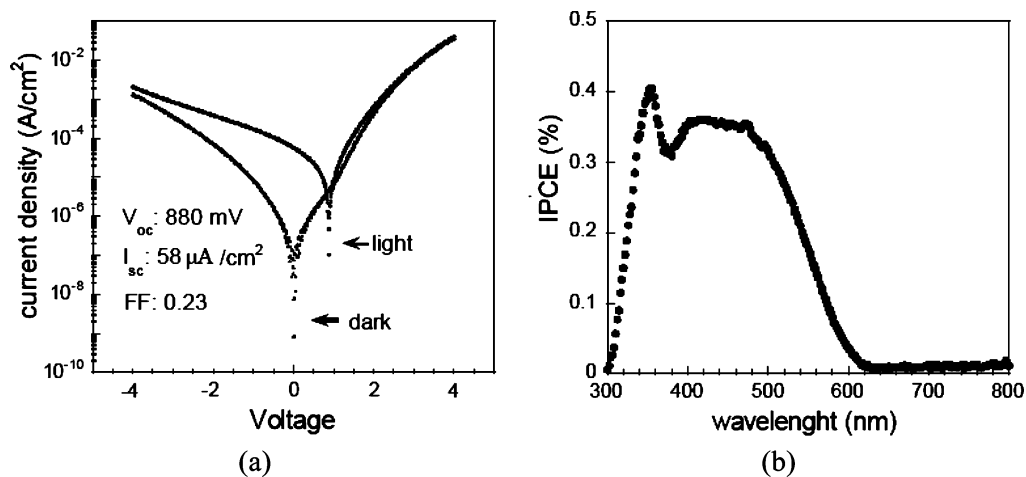
Observing the molecular structures of **240a–c**<sup>289,290</sup> we can see that, in principle, 99–95 1,4-dipentylxy vinylbenzene repeating units are linked with 1–5 units of benzene rings bearing the  $\text{C}_{60}$  cage. This results in a very low percentage of fullerene in the polymer (2–10 wt %), but this value is high enough to produce a strong quenching of the PPV fluorescence.

To improve the electro-/photoactive properties of the final product, carbazole or triphenylamine moieties are good candidates for incorporation in the copolymer main chain, which would result in suitable materials for application in light-emitting diodes or other optoelectronic devices.<sup>291–293</sup>

With this aim, PPV-stop-vinylcarbazole- $\text{C}_{60}$  (**241**),<sup>294–296</sup> (triphenylaminevinylene)-(phenylenevinylene-carbazole- $\text{C}_{60}$ ) (**242**),<sup>294,296</sup> and the copolymer between phenylene-

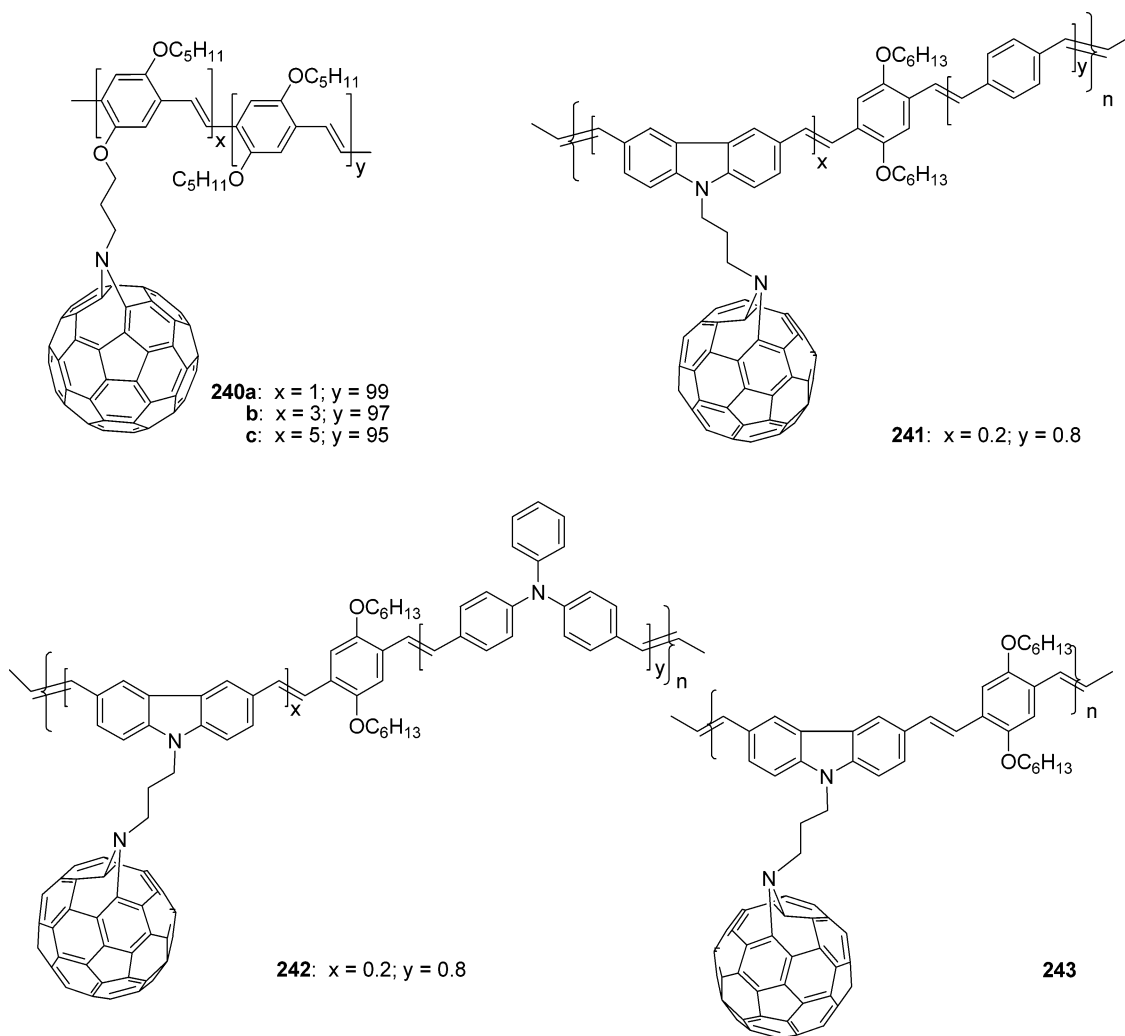


**Figure 12.** (a) PL spectra of poly-AQ **237a–d** and poly-3-decylthiophene (PDT) after photoexcitation at 450 nm in chloroform solutions. (b) LESR spectra of poly-AQ **237a–d**. Measurements were performed at 20 K; microwave power = 20  $\mu\text{W}$ . The spectra shown are corrected for the weak dark signal and shifted on the y axis. (Reprinted with permission from refs 280 and 282. Copyright 2003 and 2004 Elsevier Ltd.)



**Figure 13.** (a) Current–voltage characteristics of a PV device with **237c** as active layer and Ca electrode; solar simulator at 80 mW/cm<sup>2</sup>. (b) External quantum efficiency of a PV device with **237c** as active layer, Ca electrode. (Reprinted with permission from ref 287. Copyright 2003 The International Society for Optical Engineering.)

### Chart 9

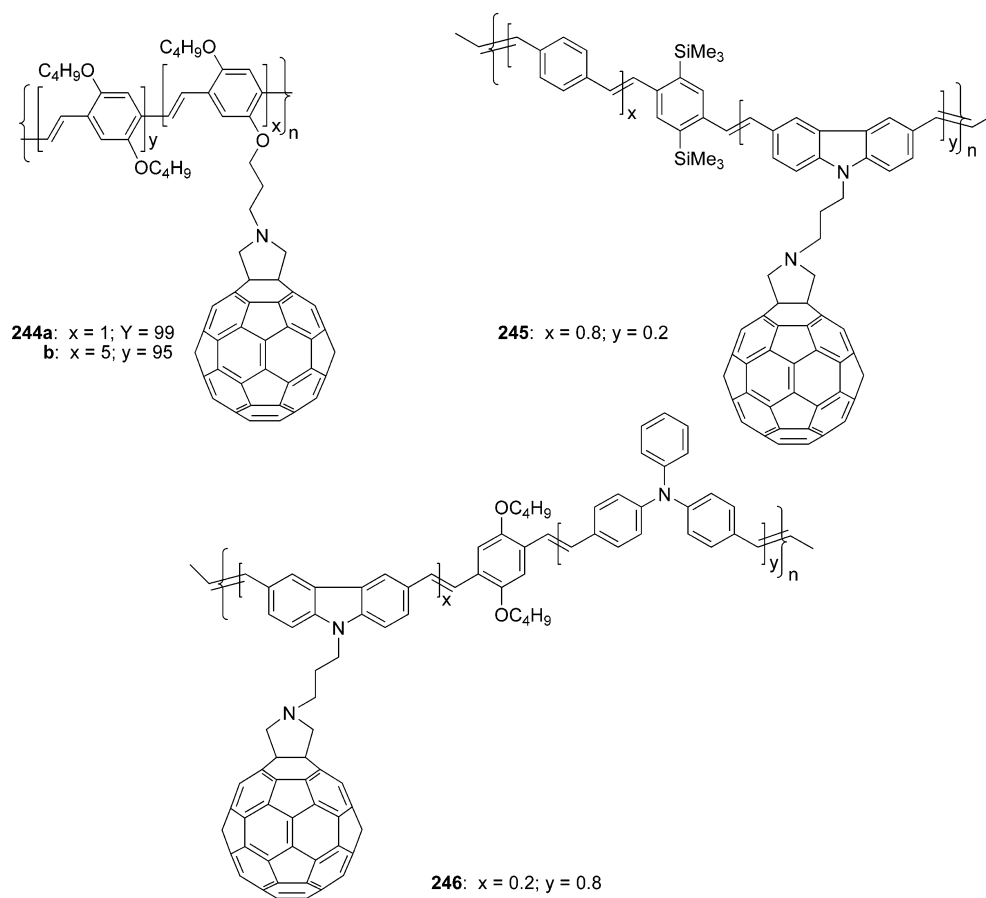


vinylene and vinylcarbazole–C<sub>60</sub> (**243**)<sup>295,297,298</sup> have been prepared (Chart 9). Such polymers showed a low quenching of the fluorescence of the conjugated backbone as well as persistence of the electronic features for both donor and acceptor moieties.

It is worth mentioning that these three copolymers have an interesting increasing C<sub>60</sub> content, that is, 19.9 wt % for

**242**, 21% for **241**, and a remarkable 57% for **243**. The last molecule had very good properties as a dopant for poly{1,4-[2-(3,7-dimethyloctyloxy)-3,5,6-trimethoxyphenylenevinylene]} (POMPV) in polymer oLED.<sup>298</sup> In fact, blending 1 wt % of **243** into conjugated polymer POMPV matrix resulted in an increase of LED luminescence and luminescence effect, making this dopant polymer one of the more

Chart 10



promising hole-trapping candidates in polymer LEDs for further optimization.

However, having a look to the  $M_w$  values of PPV-based polymers **240–243** it seems surprising that they move in the 2307–5838 amu range. Although the authors ascribed this fact to the partial solubility of such polymers in THF, the more soluble polymer precursors showed exactly the same  $M_w$  range.

Chart 10 shows the chemical structures of four novel DC polymers in which the  $C_{60}$  moiety has been connected via Prato's reaction.<sup>299</sup>

Using polymers **244–246** in which the fullerene content varies between  $\sim 3\%$  for **244a** and  $\sim 28\%$  for **245**, photovoltaic cells have been prepared.<sup>300</sup> An ITO/PEDOT:PSS/polymer blend/Al architecture was employed in which the polymers were blended 1:1 by weight with MEH–PPV. However, the most efficient device in which the active layer was constituted solely by **244b** showed an overall conversion efficiency of only 0.01%.

Since polyacetylene derivatives exhibit unique properties such as semiconductivity, high gas permeability, helix inversion, and nonlinear optical properties,<sup>301</sup> they represent an interesting class of macromolecules to be investigated as polymeric backbone in double-cable polymers. In fact, it is expected that attaching side electroactive groups (i.e., fullerenes and porphyrins) to the well-defined  $\pi$ -conjugated system<sup>302</sup> will improve the light-harvesting capacity and charge-separation efficiency for potential applications in solar cells (based on synergistic actions of pendant and main-chain conjugation). In this light, Li, Can, and co-workers prepared a number of polyacetylenes-based DC bearing fullerene and

zinc–porphyrin (ZnP, **249**),<sup>303,304</sup> fullerene and perylene-bisimide (**252**),<sup>305</sup> or only fullerene (**250**) as the pendant groups (Scheme 53).

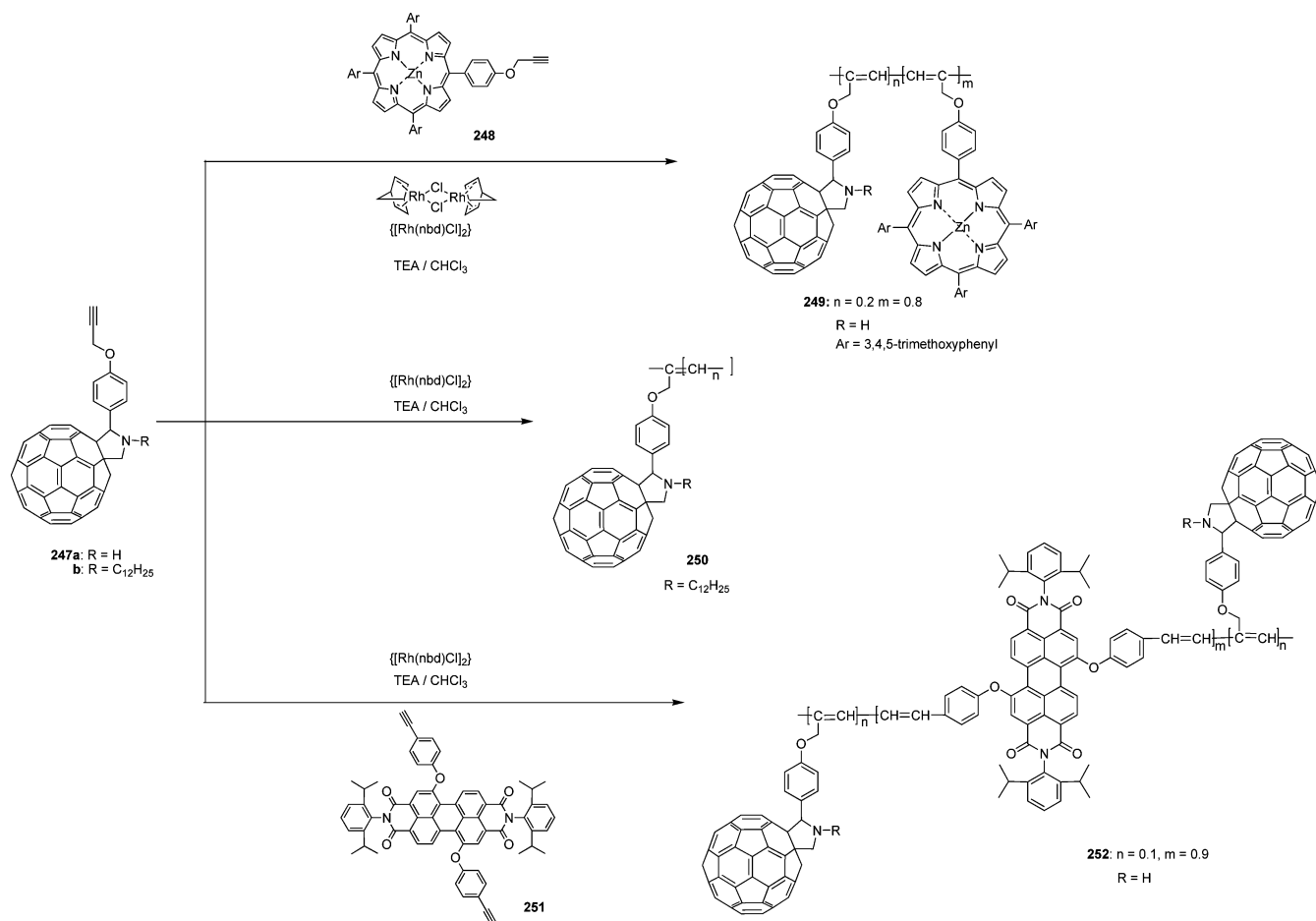
Synthesis of polymers **249**, **250**, and **252** takes place by reacting monomers **247a**, **248**, and **251** in the presence of norbornandienerhodium(I) chloride dimer ( $[\text{Rh}(\text{nbd})\text{Cl}]_2$ ) in dry chloroform (Scheme 53). For polymer **249** a 1:4 (**247**:**248**) stoichiometry has been used, while a 1:9 stoichiometry (**247**:**251**) for **252** has been employed. The  $^1\text{H}$  NMR spectra for all DC polyacetylenes show a signal at 5.3 ppm assignable to the main-chain olefinic protons, indicating a cis–trans structure.<sup>306</sup> However, the broadening of such peaks reveals that the large  $C_{60}$ , ZnP, and perylene units induce distortion of the stereoregularity of the main chain. In Table 1 are reported the cyclic voltammetry data for monomers **247a,b**, **248**, and **251** and polymers **249**, **250**, and **252**.

It is interesting to note that the first reduction potential of fullerene attached to the polyacetylene chain is 90 mV lower than that of the corresponding process for monomer **247a**. The same thing occurs for **250**, indicating a better electron-donating ability influenced by the conjugated backbone. Finally, **249** and **252** showed high capacity to form a photoinduced charge-separated state and produce steady and prompt photocurrent under irradiation of white light, making these materials interesting for further studies in device applications.

Analogously, very recently, Yashima et al. used a similar synthetic strategy in order to obtain new optically active polyacetylene double cables (Scheme 54).<sup>307–309</sup>

In this case they exploited the bulkiness of the  $C_{60}$  cage attached to the phenyl groups of achiral comonomer (**253**)

## Scheme 53



**Table 1. Electrochemical Data for Monomers 247a,b, 248, and 251 and Polymers 249, 250, and 252<sup>a</sup>**

compound	$E_{\text{pa}}^1$	$E_{\text{pa}}^2$	$E_{\text{pa}}^3$	$E_{\text{pc}}^1$	$E_{\text{pc}}^1$	$E_{\text{pc}}^1$	$E_{\text{ZnP}}^1$
<b>247a</b>				-0.98	-1.33	-1.88	
<b>247b</b>				-0.97	-1.35	-1.88	
<b>248</b>	0.80	1.02	1.74				-1.71
<b>249</b>	0.78	1.09	1.68	-0.89	-1.40	-1.81	-1.20
<b>250</b>				-0.90	-1.30	-1.82	
<b>251</b>	1.68			-0.82	-1.07		
<b>252</b>	1.63			-0.81	-1.06	-1.20	

<sup>a</sup> Glassy carbon as working electrode, Pt wire as counter electrode, and Ag wire as quasi-reference electrode; *o*-dichlorobenzene solutions containing 0.04 M TBAPF<sub>6</sub> as a supporting electrolyte were used. Scan rate was 20 mV/s.

to increase the induced circular dichroism (ICD) when copolymerized with optically active phenyleneacetylene (**254a–d**). This is a representative example of chiral amplification of covalent systems in a polymer and originates from the feature of dynamic macromolecular helicity unique to poly(phenylacetylene)s, polyisocyanates, and polysilanes.<sup>310</sup>

The so-obtained polymers exhibited ICD in solution both in the main-chain region and in the achiral fullerene chromophoric region. In this way, the authors demonstrated that such stereoregular polymers form predominantly one-handed helical structures and that the pendant achiral fullerene groups are arranged in helical arrays with a predominant screw sense along the polymer backbone (Figure 14).

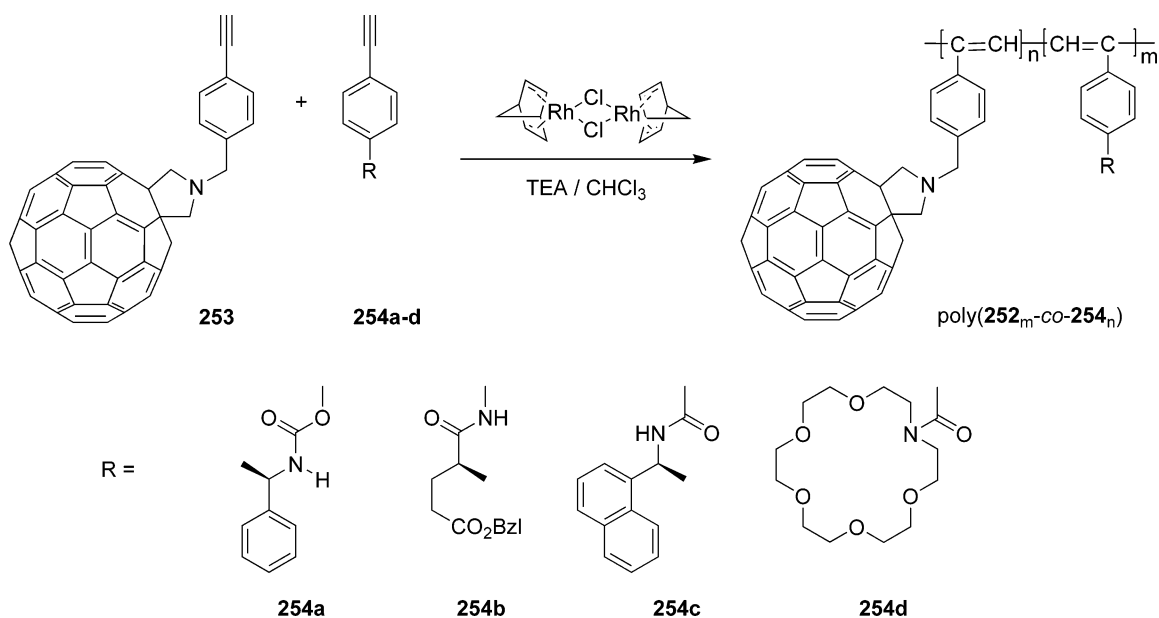
When monomer **254d** is incorporated in the final polymer, interestingly the desired predominantly *E* one-handed helical

conformation is reached by mixing together with *L*- or *D*-alanine perchlorate in acetonitrile. Upon complexation of the optically active amino acid by means of the pendants crown ether units, the achiral C<sub>60</sub> moieties arrange in a helical array with the desired helix sense along the polymer backbone via chiral, noncovalent bonding interactions, amplifying the ICD (see Figure 15).<sup>309</sup>

In Scheme 55 the synthesis of the electroactive block copolymer **259** is shown.<sup>311,312</sup> Although strictly speaking this is not a true example of double-cable polymer, it represents an interesting polymer with continuous and nanometer-scaled interpenetrating phases of electron-donor and -acceptor components, designed to be an efficient photovoltaic material. Hadziioannou and co-workers first prepared the PPV-based block (**256**) via a Siegrist polycondensation.<sup>313</sup> By this method, which uses condensation of para-substituted methylbenzaldimine under basic conditions, oligo-PPVs (oPPVs) of narrow molecular weight with only a formyl group per molecule are obtained. An average degree of polymerization of 10 repeating units was calculated by <sup>1</sup>H NMR analysis. Covalent linking of the ATRA initiator to the oPPV moiety allows the subsequent controlled “living” radical polymerization in the presence of styrene and chloromethylstyrene to form **258**. Finally, the acceptor C<sub>60</sub> is incorporated through a new atom-transfer radical addition to the 4-chloromethylstyrene units to afford the rod-coil polymer **259**. TGA analysis revealed a 46 wt % content of fullerene in the final product, indicating an average of 15 C<sub>60</sub> molecules per chain, revealing also that one for every two chloromethyl moieties reacted with the acceptor. Inter-



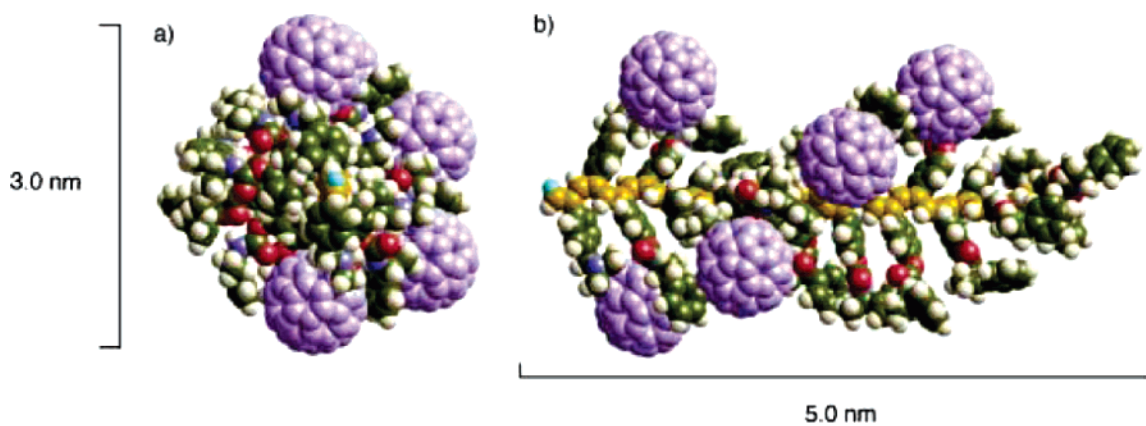
## Scheme 54



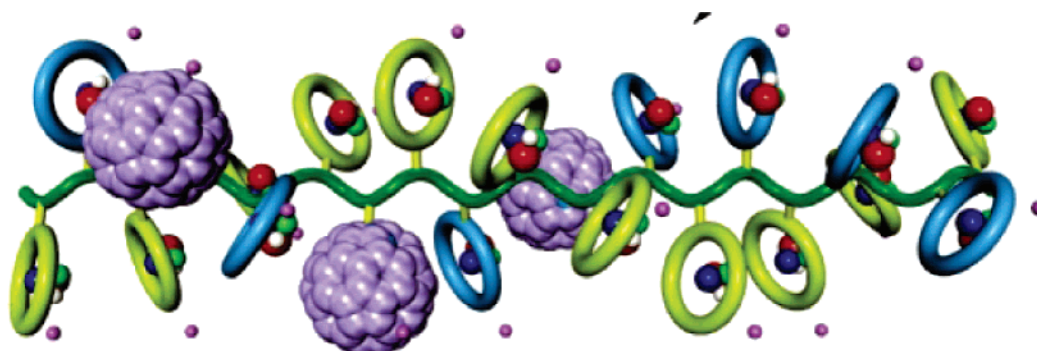
estingly, upon casting films of **259** from CS<sub>2</sub> solutions, formation of honeycomb patterns on a micrometer scale was observed.

The suitability of the type of such block-copolymer for application in photovoltaic devices relies, among other things, on the abilities of the respective blocks to function as electron donor and acceptor as well as a good charge transport media.

When C<sub>60</sub> is incorporated in the final polymer, the photoluminescence intensity in film is reduced by 3 orders of magnitude, evidence for an efficient and very rapid electron transfer from the donor block (PPV) to the acceptor (PS-C<sub>60</sub>). Photovoltaic cells were fabricated using **259** or a blend of PPV homopolymer **256** and a statistical copolymer of styrene incorporating C<sub>60</sub> with comparative purposes. Even

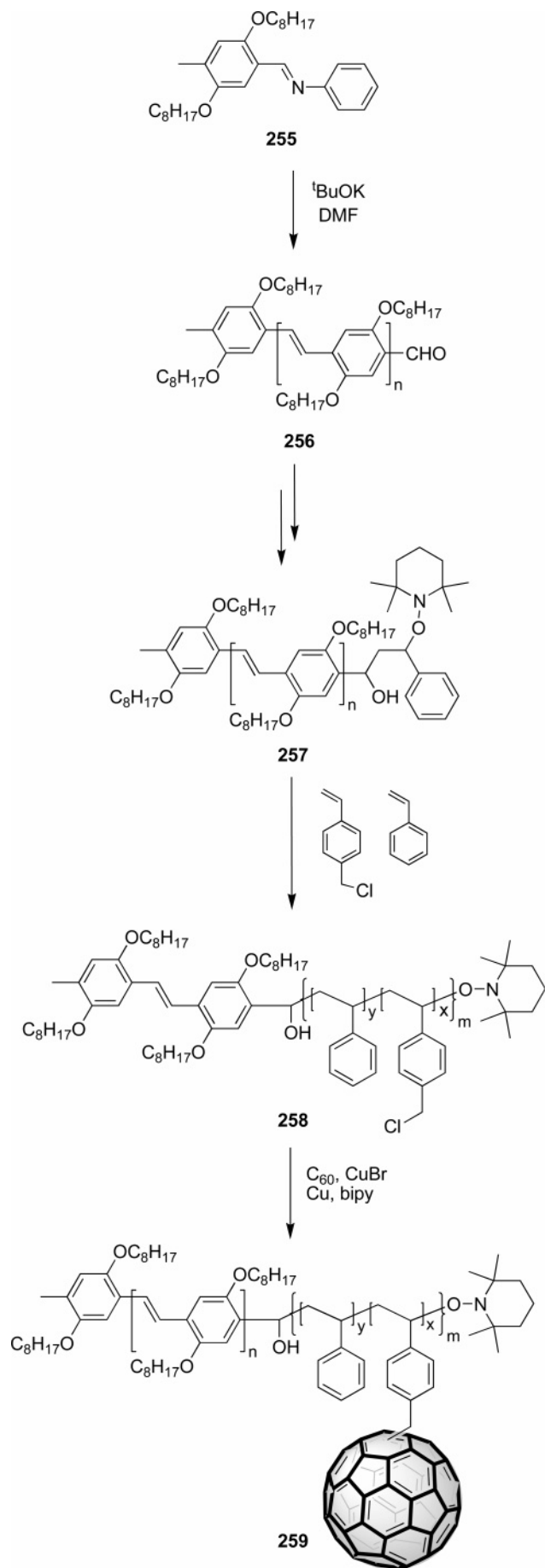


**Figure 14.** Possible helical structure of  $\text{poly}(253_{0.2}\text{-co-}254a_{0.8})$  (20-mer). Space-filling models are shown: (a) top and (b) side views. The fullerene units are assumed to arrange in a left-handed helical array along the right-handed polyacetylene main chain. The helix sense is tentative, but the copolymer should have either a right- or a left-handed helical conformation since it exhibits ICD both in the main chain and in the fullerene chromophoric regions. (Reprinted with permission from ref 307. Copyright 2002 Wiley-VCH.)



**Figure 15.** Cartoon of  $\text{poly}(253_{0.15}\text{-co-}254d_{0.85})$ . The achiral lateral fullerene and crown ether moieties arrange in a helical array along the one-handed helical polymer backbone induced by noncovalent chiral interactions with L-alanine. (Reprinted with permission from ref 309. Copyright 2004 The Royal Chemical Society of Chemistry.)

Scheme 55



though the results were not very sound, the authors clearly demonstrated the superior response of the D–A blocks copolymer over the blend of the two constituent homopolymers, thus evidencing the strength of their approach. Unfortunately, a new attempt to prepare an analogous block polymer, incorporating this time  $\text{C}_{60}$  through azido groups, failed due to the insolubility of the so-obtained material which prevented its full characterization.<sup>314</sup>

As we have seen in the above examples, the fullerene-containing double-cable approach represents a new concept for the preparation of new materials with application in solar energy conversion. However, despite the high number of new double-cable polymers developed so far, the performance of these materials is clearly below of that shown by simply mixing the component photo- and electroactive materials ( $\pi$ -conjugated polymer and fullerene derivatives) without covalent linkage. These results can be accounted for by the high number of factors which must be controlled simultaneously in order to optimize the prepared devices, where factors such as acceptor content, solubility properties, light harvesting, and morphology of the active layer are critical to reach significant energy conversion efficiencies and transport properties. In this regard, a more detailed study of the double-cable approach is compulsory since it represents one of the most rational attempts to have control of the organization of donor and acceptor moieties in the solid state in addition to control of their electronic interaction. Control of both key factors should result in the preparation of significantly better photovoltaic materials in the near future.

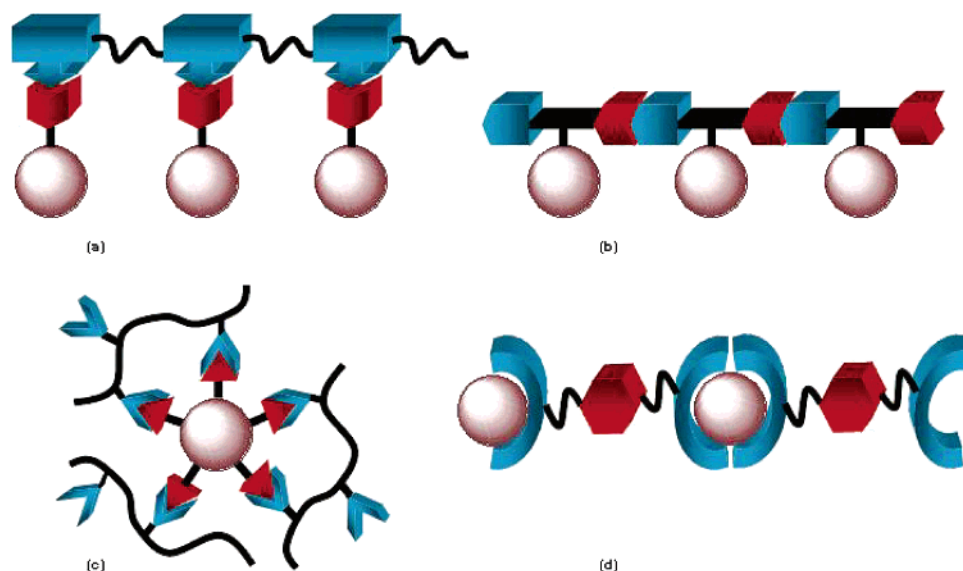
## 9. Supramolecular Polymers

Supramolecular chemistry is experiencing nowadays extensive development in all chemistry fields. Noncovalent interactions play a leading role in determining the secondary and tertiary structure of many natural macromolecules. However, their use in materials science has not been developed in the same extent.<sup>315</sup>

Although a wide variety of supramolecular polymers have been synthesized,<sup>316</sup> fullerene-containing supramolecular polymers have been scarcely studied in comparison with the supramolecular assemblies endowed with  $\text{C}_{60}$  prepared so far.<sup>317</sup>

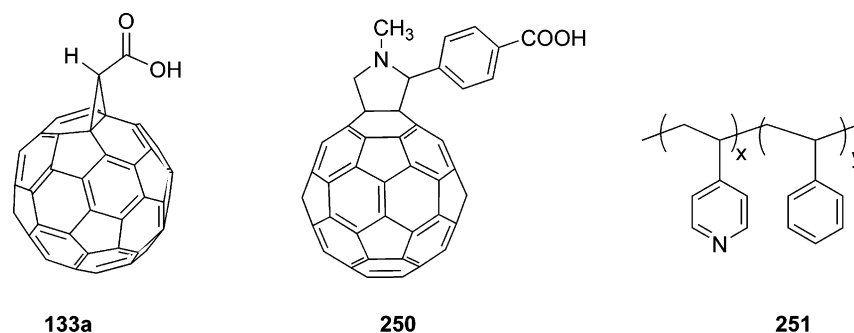
In this section we will show how the scope of  $\text{C}_{60}$ -based polymer chemistry can be developed to a supramolecular level from which unprecedented architectures may be formed.

As stated throughout this text, often linking  $\text{C}_{60}$  directly to a polymeric backbone as well as direct mixing of pristine fullerene with different polymers led to phase segregation with subsequent formation of big  $\text{C}_{60}$  clusters dispersed in the polymeric matrix.<sup>251,318</sup> In this regard, dispersion of a suitably functionalized  $\text{C}_{60}$  derivative into a polymeric matrix through supramolecular interactions seems to be a very appealing approach in order to avoid phase segregation. Furthermore, supramolecular interactions can induce additional order in the solid state, thus being an interesting new approach to achieve control of the structural and electronic properties of the so-prepared materials. However, no studies have been reported in this sense despite the large potential applicability. To date, few examples of supramolecular  $\text{C}_{60}$ -containing polymers are known, and it is possible to collect them in four classes according to the synthetic strategy followed for their preparation, as depicted in Figure 16: (a) interactions between suitably functionalized polymers and  $\text{C}_{60}$  derivatives; (b) self-assembly of  $\text{C}_{60}$  derivatives; (c)



**Figure 16.** Different types of  $C_{60}$ -based supramolecular polymers.

### Chart 11



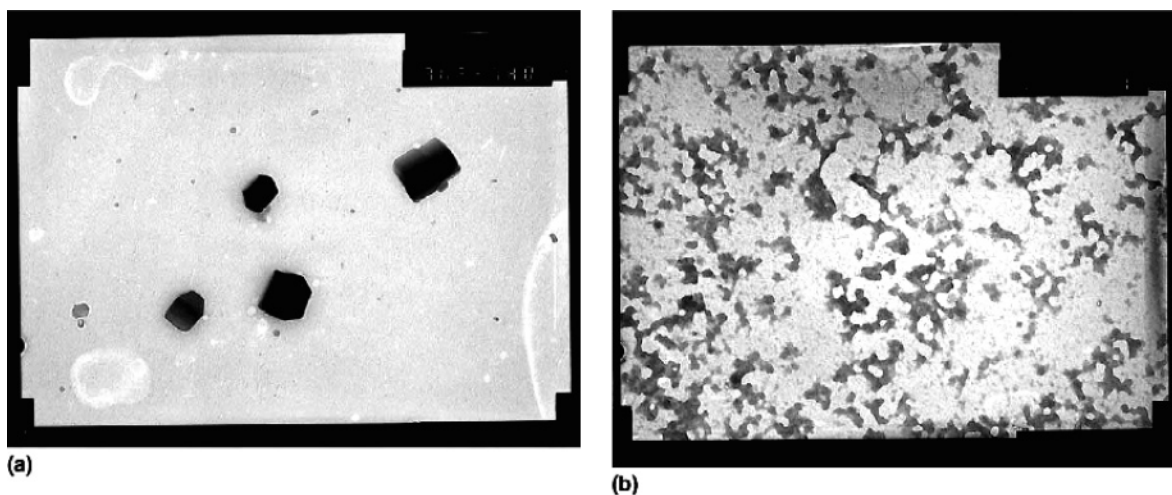
multifunctionalized [60]fullerene and complementary polymeric backbones; (d) complementary interactions between pristine  $C_{60}$  and ditopic concave guests.

In a first approach, very good results have been reported mixing  $C_{60}$  derivatives endowed with a carboxylic group with a proton-accepting polymer, i.e., P4VPy. In this regard, Goh et al. after mixing 1,2-dihydro-1,2-methanofullerene-61-carboxylic acid (**133a**) with PS-*co*-P4VPy (**251**) obtained a material which was processable by solution casting and melt blending<sup>319</sup> (see structures in Chart 11).

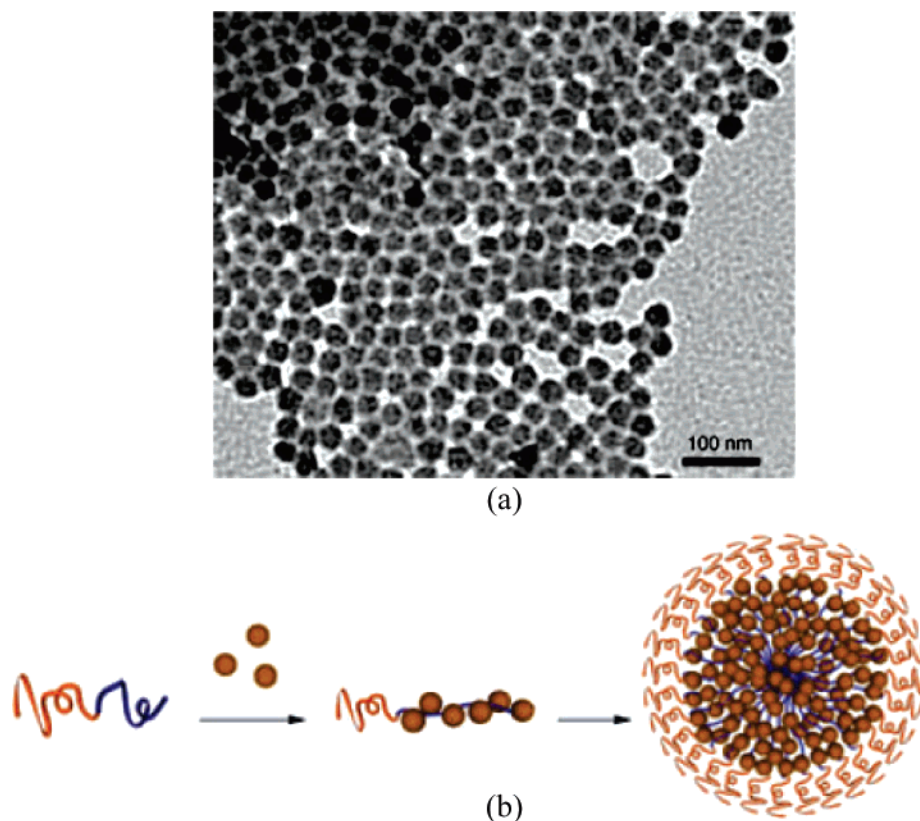
Furthermore, such a blend was soluble in common solvents such as THF or chloroform in which **133a** was not soluble.

In addition, the goodness of this approach has been confirmed by TEM micrographs, in which the better dispersion of **133a** in **251** versus that of pristine  $C_{60}$  was readily demonstrated (Figure 17).

Employing the same copolymer **251**, Shinkai and co-workers were able to form supramolecular aggregates with a determined size and morphology using the carboxylic derivative **250**.<sup>320</sup> They claimed formation of micelle-like superstructures in which the P4VPy blocks of the random-coil structure of **251** adopt a rodlike rigid conformation by interacting with **250**. This P4VPy–**250** complex possesses poor solubility that forces the highly soluble PS blocks to

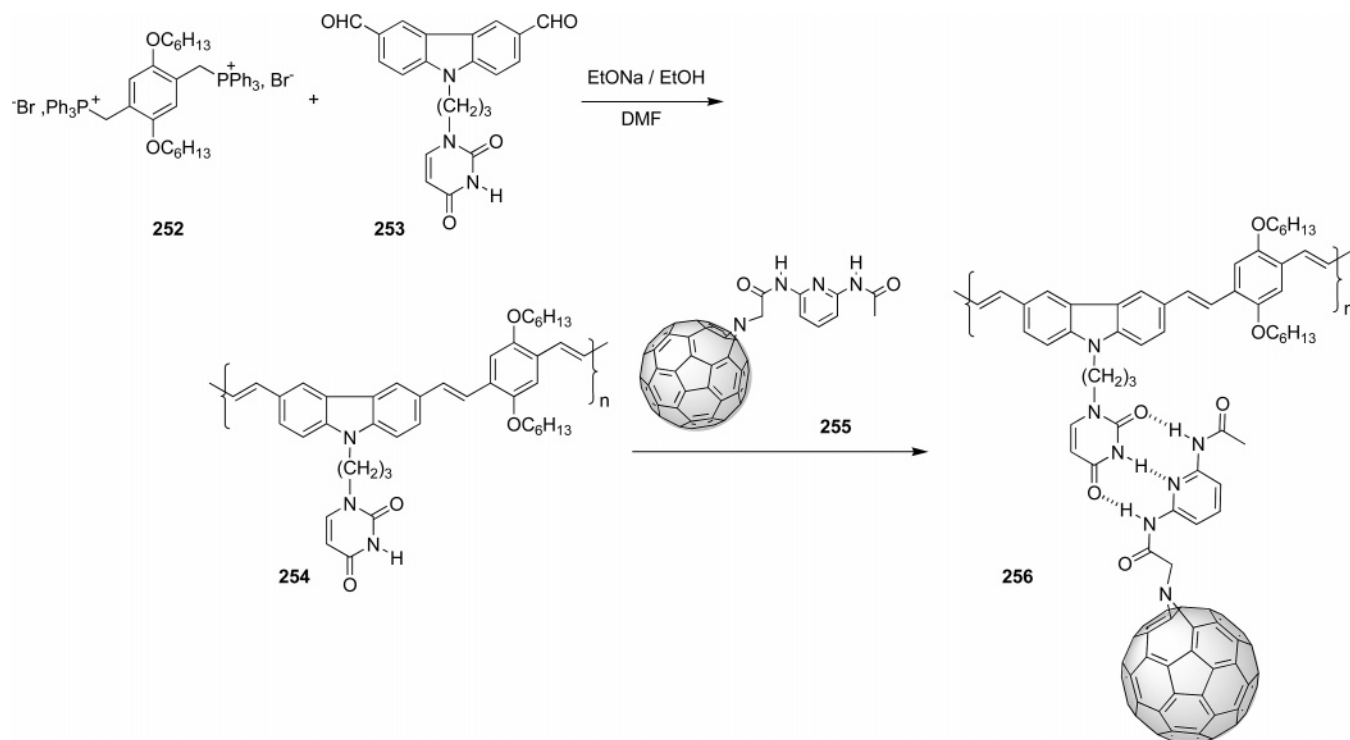


**Figure 17.** TEM micrograph of (a)  $C_{60}/251$  and (b) **133a/251**. (Reprinted with permission from ref 319. Copyright 2001 Elsevier Ltd.)



**Figure 18.** (a) TEM image of polymer **250–251** composite. (b) Schematic representation of the formation of supramolecular rod-coil polymers leading to generation of micelles. (Reprinted with permission from ref 320. Copyright 2005 WILEY-VCH.)

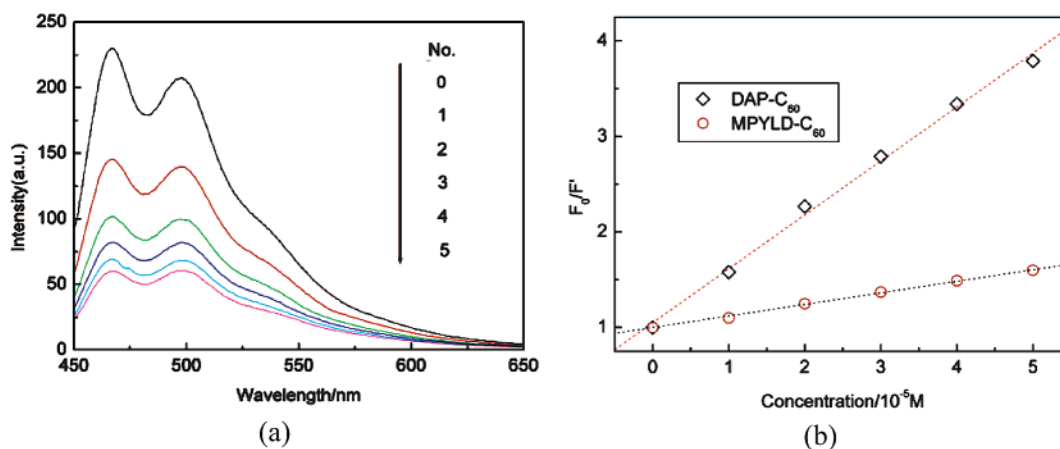
#### Scheme 56



orient outside of the micelle, thus forming the shell, as shown in Figure 18a,b.

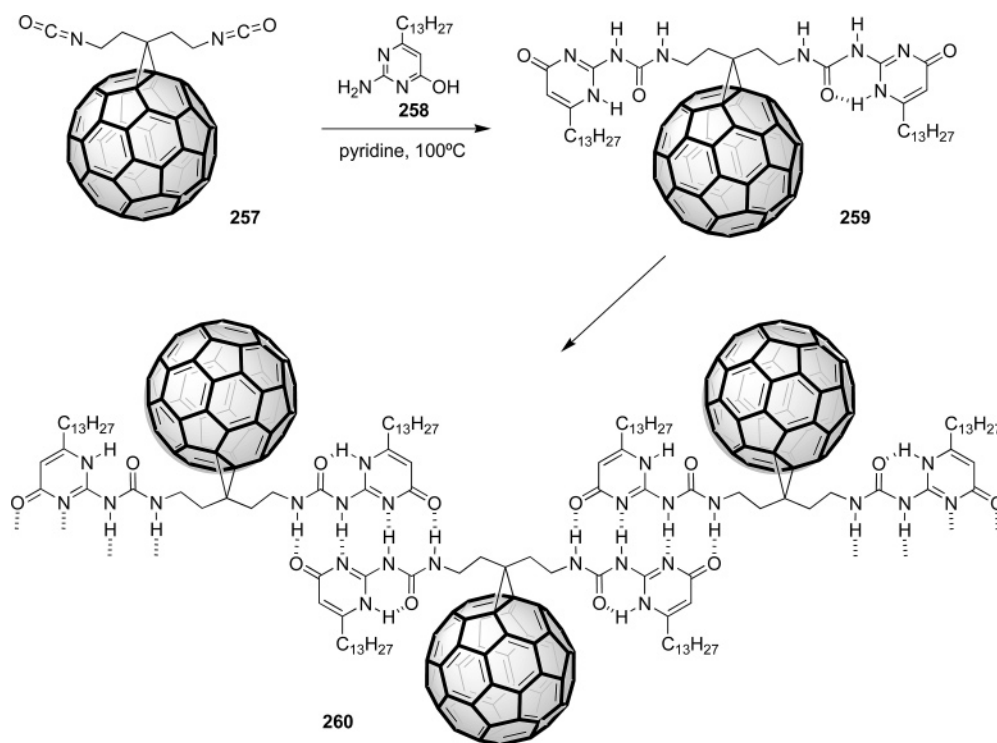
The nanoparticles so obtained, with a diameter of ~20–25 nm, should show interesting redox and photochemical properties, and such methodology could be a milestone for the controlled construction of organic nanoparticles.

Another original way to avoid the high C<sub>60</sub>-content polymers from becoming insoluble or not processable has been recently suggested by Li et al., who first used the supramolecular assemblies approach to obtain heterojunction materials.<sup>321,322</sup> They carried out the synthesis of a poly-*p*-phenylenevinylencarbazole endowed with an uracil moiety



**Figure 19.** (a) Fluorescence of **254** solution ( $1.0 \times 10^{-5}$  M) in  $\text{CHCl}_3$  quenched by **255** solution in  $\text{CHCl}_3$  ( $\lambda_{\text{ex}}$  430 nm). The concentrations of **255** are 0, 0 M; 1,  $1.0 \times 10^{-5}$  M; 2,  $2.0 \times 10^{-5}$  M; 3,  $3.0 \times 10^{-5}$  M; 4,  $4.0 \times 10^{-5}$  M. (b) Dependence of  $F_0/F$  on the concentration of **255** or *N*-methylfulleropyrrolidine. (Reprinted with permission from ref 321. Copyright 2003 American Chemical Society.)

#### Scheme 57



(**254**) able to link a complementary 2,6-diacylaminopyridine- $C_{60}$  derivative (**255**) through a 3-fold hydrogen bonding (Scheme 56).

Fluorescence quenching experiments mixing **254** and **255** were carried out as shown in Figure 19a. For comparison purposes the authors also performed quenching experiments using *N*-methylfulleropyrrolidine (Fp), which does not form H bonds (Figure 19b). The results indicated that the fluorescence of polymer **254** was deactivated by both **255** and Fp, but in the former case the Stern–Volmer constant  $K_{\text{SV}}$  was almost 5-fold larger than that between **255** and Fp ( $5.8 \times 10^4$  vs  $1.2 \times 10^4$  mol  $\text{L}^{-1}$ ), suggesting that the binding force through the hydrogen links was stronger.

A similar approach has been reported by Hummelen and co-workers, but this time they prepared a supramolecular polymer from a self-complementary monomer able to form donor–donor–acceptor–acceptor quadruple hydrogen bonds (**259**)<sup>323</sup> (Scheme 57).

Such a hydrogen-bonded fullerene array was fully characterized, and particularly the  $^1\text{H}$  NMR showed the presence of H bonds. It is worth mentioning that when spin-coated, **260** gave rise to a macroscopically homogeneous film, unlike to the behavior observed for a number of low  $M_w$   $C_{60}$  derivatives.

As stated at the beginning of this paragraph, a third kind of supramolecular binding between  $C_{60}$  derivatives and polymers involves multisubstituted fullerenes which can interact with a properly functionalized polymer. For this purpose, in 1998 Dai described the behavior of polyaniline emeraldine base (PANI-EB) **261** doped with  $C_{60}$  containing an average number of hydrogenosulfated and hydroxylic groups of six (**262**, Scheme 58).<sup>324,325</sup>

The most outstanding results of these studies were that after doping a PANI-EB film with **262**, the conductivity increased by up to 11 orders of magnitude, reaching values of ca. 106 S/cm at 250 K. This value was  $10^6$  times higher

Scheme 58

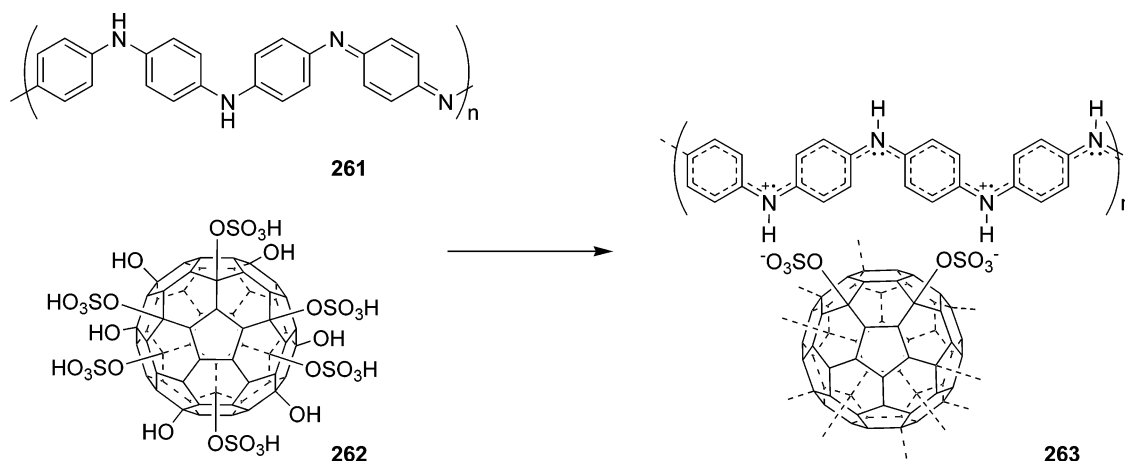
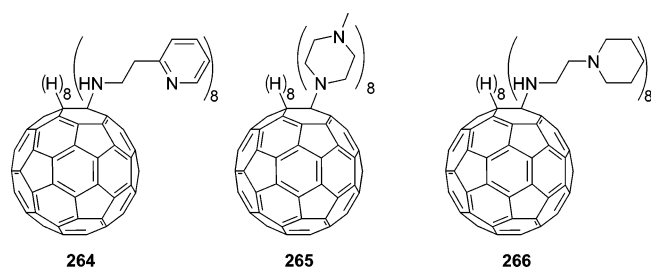


Chart 12

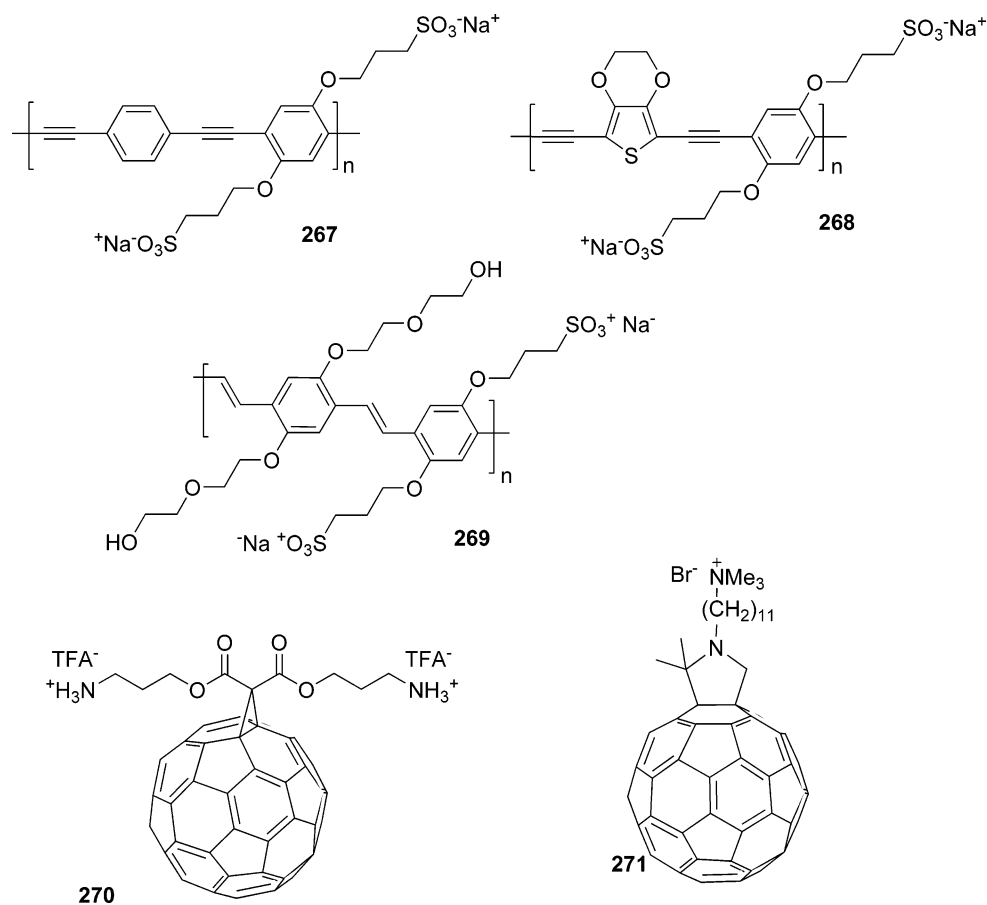


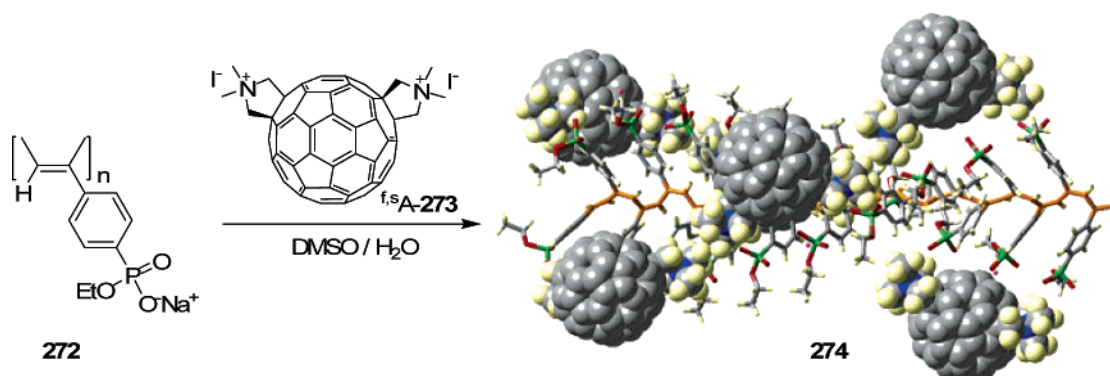
than the typical value for fullerene-doped conducting polymers.<sup>326</sup> Furthermore, dedoping could be achieved after exposure to  $\text{NH}_3$  vapors, recovering both optical and electronic

properties, and these processes could be repeated multiply. The huge enhancement in conductivity has been ascribed to the doping-induced “uncoiling” of the PANI-EB chains when **263** is formed. This unraveling of polymeric chains lead to enhanced intrachain carrier mobility but, at the same time, results in an improvement of interchain ordering, augmenting the final conductance. An analogous attempt to complex **262** with the accepting H-bonding poly-(4-vinylpyridine) (P4VPy) demonstrates the ionic nature of the interactions in the complexes.<sup>327</sup>

The strong ionic interactions between the multifunctional  $\text{C}_{60}$  derivatives **264**,<sup>328</sup> **265**, and **266**,<sup>329</sup> see chemical structures in Chart 12, synthesized by nucleophilic addition of fullerene with amines, led Goh and co-workers to claim

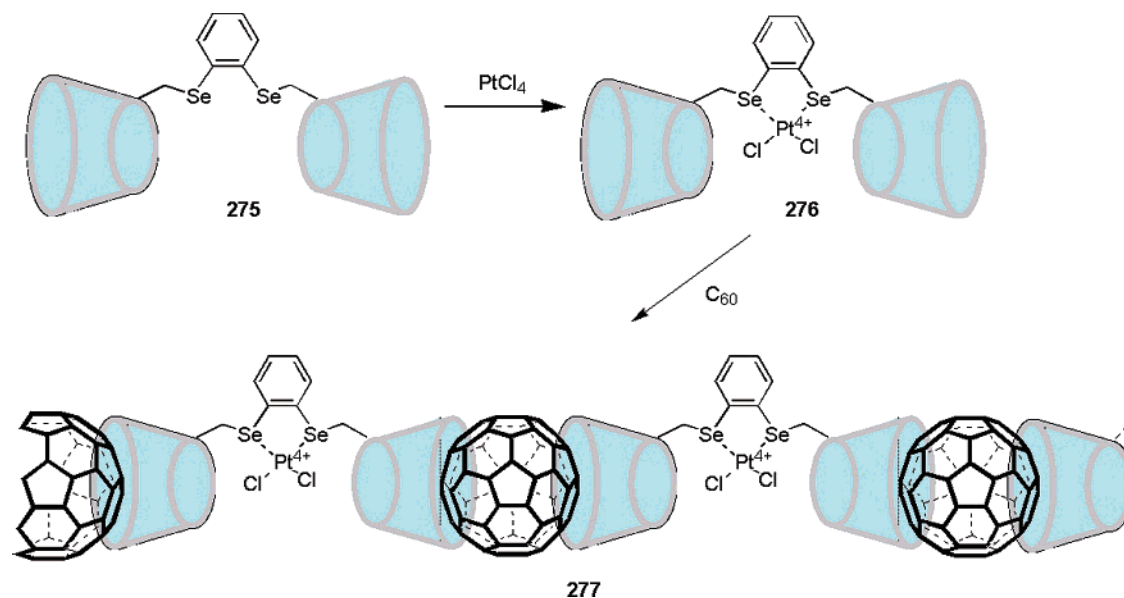
Chart 13



Scheme 59<sup>a</sup>

<sup>a</sup> Reprinted with permission from ref 334. Copyright 2004 American Chemical Society.

Scheme 60



formation of supramolecular complexes with a number of H-donating polymers such as poly(styrenesulfonic acid) (PSSA), poly(vinylphosphonic acid) (PVPA), PAA, or PMA.

FTIR and XPS experiments evidenced strong interaction between the derivatives **264** and **265** and the polymers. In addition, all complexes showed no distinct glass transitions up to the degradation temperatures. In a very recent investigation blends of fullerenols (**3**) with P4VPy and 1-(4-methyl)-piperazinylfullerene **265**/random poly-dimethylsiloxane-*co*-(3-carboxypropyl)methylsiloxane showed poor optical limiting responses.<sup>330</sup> Mixtures of bis(3-aminopropyl)-terminated PDMS and fullereneol lead to very stable complexes as free-standing films due to the strong hydrogen-bonding interactions.<sup>331</sup> Such new nanocomposite materials showed superior thermal and thermal mechanical stability, elastic mechanical response, and attractive dielectric properties.

On the other hand, Reynolds and Schanze described several photovoltaic devices based on an active layer formed by electrostatic layer-by-layer (LBL) deposition bilayers of PPE-SO<sub>3</sub><sup>-</sup> (**267**), PPE-EDOT-SO<sub>3</sub><sup>-</sup> (**268**), and a fullerene modified with two ammonium groups (**270**, Chart 13).<sup>332</sup>

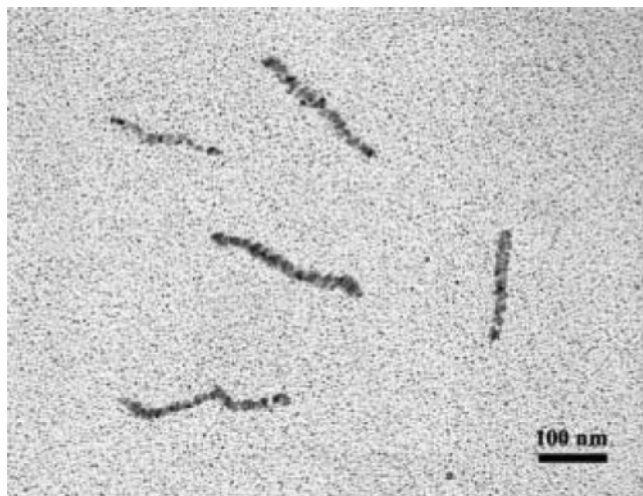
When the bilayers were deposited onto an ITO electrode (50 layers), uniform films were obtained as indicated by the morphology studies. However, the authors claimed that, in

the LBL assemblies, it seems to be likely that there is some interpenetration of the polymer chains within the layers, leading to some kind of bulk heterojunction. After deposition, the active layer showed an absorbance of 0.5–0.7 absorbance units at the  $\lambda_{\max}$ , allowing the capture of 50% of visible light. Afterward, LiF and aluminum layers were vacuum deposited, and the devices irradiated under AM1.5 conditions displayed a good photovoltaic response, although the overall efficiency was rather low (**267/270**,  $\eta = 0.04\%$ ; **268/270**,  $\eta = 0.01\%$ ). However, to date, these values represent the best results obtained with the LBL approach.

In a similar manner, Li and co-workers prepared self-assembled LBL films by alternatively dipping the substrate into solutions of **269** and **271** (see Chart 13 for structures).<sup>333</sup> The resulting film showed a steady, rapid, and reproducible photocurrent response under white light irradiation.

In an analogous approach, cationic C<sub>60</sub>-bisadducts act as macromolecular helicity inducers toward a dynamically racemic helical poly(phenylacetylene) bearing an anionic monoethyl phosphonate group (Scheme 59).<sup>334</sup>

Induction of helicity is highly sensitive to the structure geometry of the C<sub>60</sub>-bisadducts. Thus, *trans*-3 adduct (**273**) induced helicity, while *trans*-2 and *cis*-3 did not. The authors, based on a previous work,<sup>335</sup> claimed a possible “memory effect” in the polymer helicity by substituting chiral C<sub>60</sub>



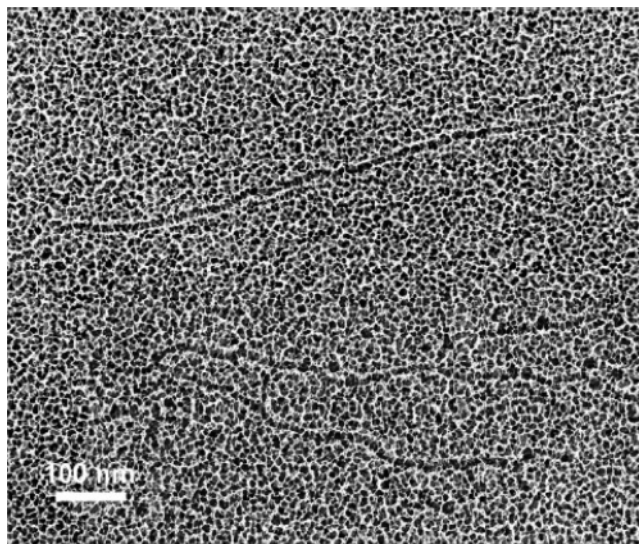
**Figure 20.** TEM image of **277**. (Reprinted with permission from ref 336. Copyright 2004 Wiley-VCH.)

derivatives for achiral ones, even though no experiments in this sense have been done.

Surprisingly, preparation of supramolecular polymer architectures employing pristine  $C_{60}$  has been successfully performed just recently. Three examples have been reported, and all use a concave guest with a 2:1 stoichiometry (guest/ $C_{60}$ ) in order to hold them in a linear array.

In the first example, Liu and co-workers prepared a water-soluble fullerene assembly with a coordinated metal center via end-to-end intermolecular inclusion complexation of fullerene with a cyclodextrin dimer.<sup>336</sup>

In Scheme 60 is shown the synthesis of supramolecular polymer **277**, whose TEM micrographs display the presence of linear structures with a length in the range of 150–250 nm, thus constituted by 60–80 units of complex **276**: $C_{60}$  (Figure 20). Moreover, this complex showed biological activity since it had an effective DNA-cleavage ability under



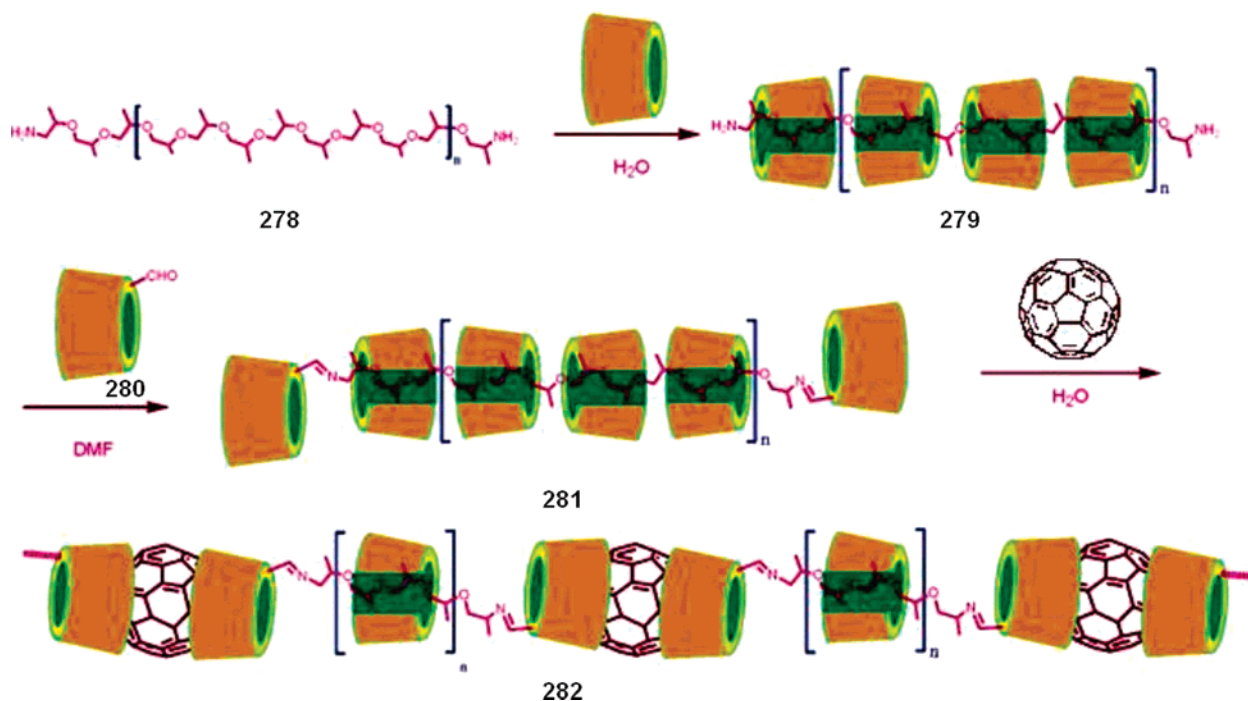
**Figure 21.** TEM image of supramolecular aggregate **282**. (Reprinted with permission from ref 337. Copyright 2005 American Chemical Society.)

light irradiation, representing potential application of **277** in medicinal chemistry.

In a similar way a CD-based polyrotaxane doubly end-capped with  $\beta$ -CD units was employed to form aggregates in the presence of [60]fullerene (Scheme 61).<sup>337</sup>

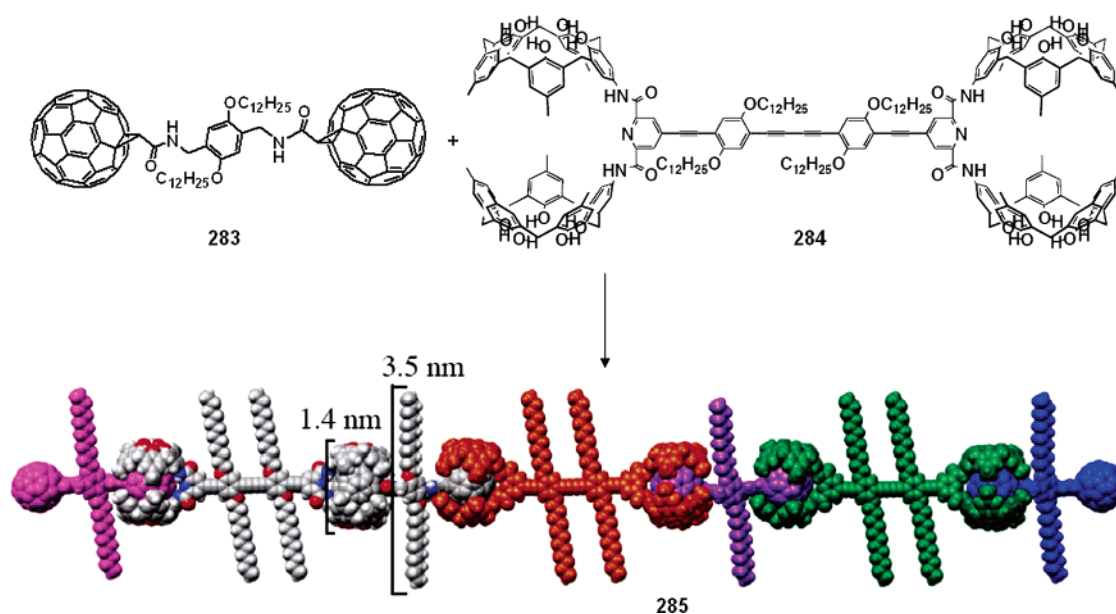
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR data confirmed the structures for the precursor polymers **279** and **281** and, in addition, revealed the presence of 13 and 15 CD units, respectively. SEM and TEM studies on the  $C_{60}$ -containing aggregates showed the presence of linear arrays with alternating white lines and dark dots. In Figure 21 the TEM image of **282** indicates the existence of linear structures that, in some cases, reach 700 nm in length. Surprisingly, GPC measurements on a solution of **282** in water had an extremely narrow polydispersity, 1.07, and a high  $M_w$  (293 000).

#### Scheme 61<sup>a</sup>



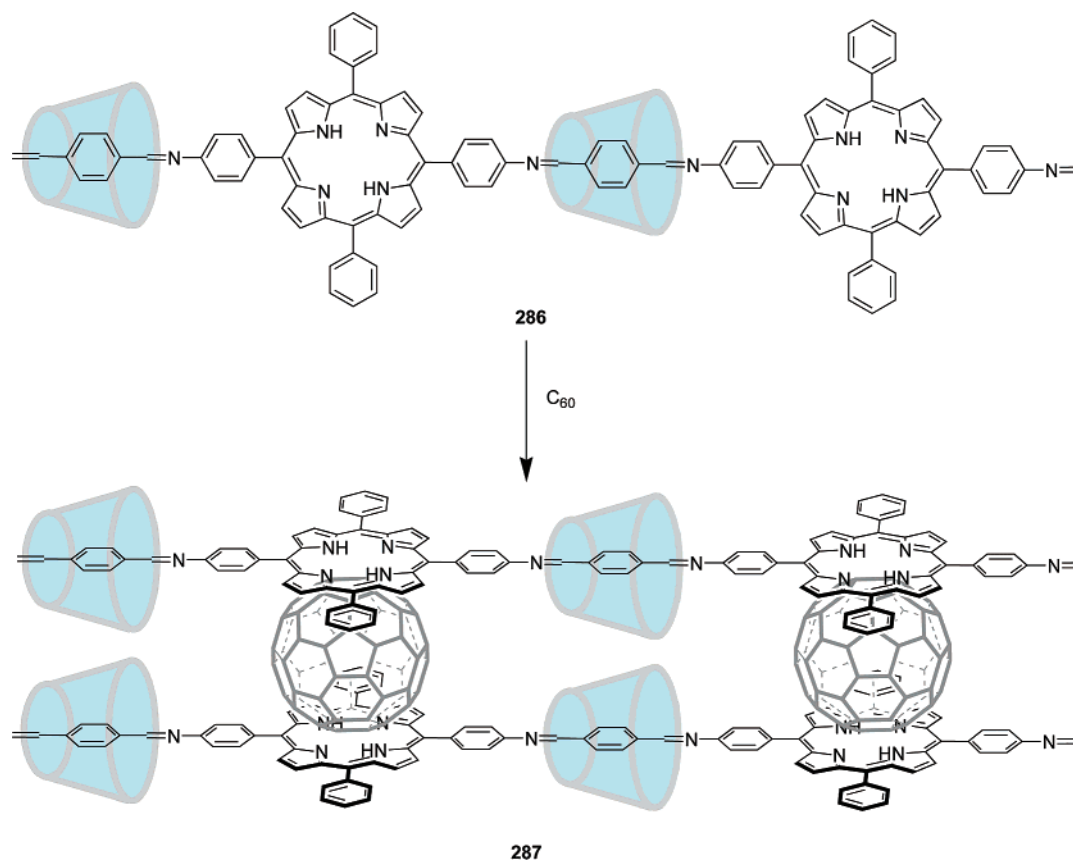
<sup>a</sup> Reprinted with permission from ref 337. Copyright 2005 American Chemical Society.



Scheme 62<sup>a</sup>

<sup>a</sup> Reprinted with permission from ref 338. Copyright 2005 American Chemical Society.

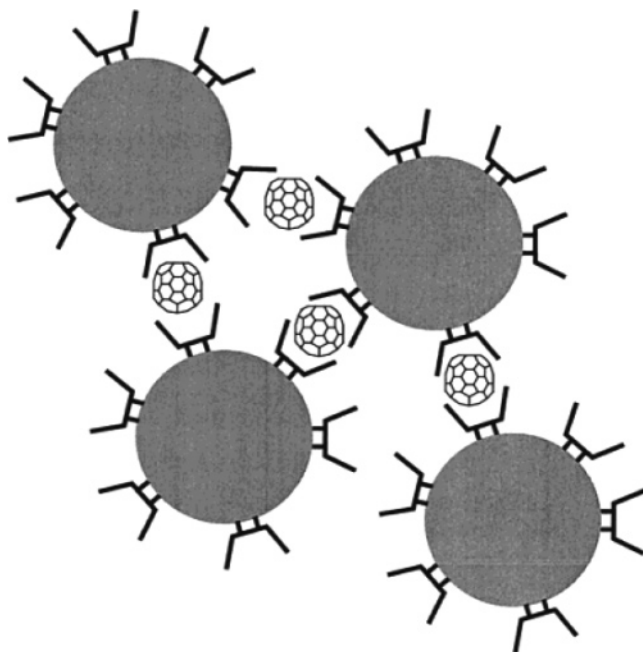
Scheme 63



Finally, the complementary molecular affinity between  $C_{60}$  and calix[5]arenes has been exploited as the driving force for the preparation of self-assembly networks. Thus, mixing of the dumbbell [60]fullerene **283** with the ditopic calix[5]arene host **284** resulted in its self-assembly directed by molecular recognition to afford the formal supramolecular copolymer **285** (Scheme 62).<sup>338</sup> However, diffusion coefficients obtained by pulsed field gradient NMR studies at low concentrations ( $2 \times 10^{-4}$  M) are in

good agreement with a structure composed by a linear trimer.

In the last three examples fullerene and a ditopic host jointly form supramolecular linear arrays. In a different approach, Liu et al. prepared an orthogonal interlocked supramolecular aggregate by complexing  $C_{60}$  molecules between porphyrin moieties of two polyrotaxane chains of the CD-porphyrin system **286** (Scheme 63).<sup>339</sup> Aggregate **287** had significant chiral and electrochemical behavior, and elemental



**Figure 22.** Schematic cartoon of the fullerene-induced network of  $\gamma$ -CD-capped gold nanoparticles in aqueous solution. (Reprinted with permission from ref 340. Copyright 2001 American Chemical Society.)

analysis data demonstrated the CD:porphyrin: $C_{60}$  molar ratio of 2:2:1, with an apparent association constant between **286** and fullerene of  $7800 \text{ M}^{-1}$ .

Finally, a remarkable example of supramolecular organic/inorganic hybrid aggregation is represented by gold nanoparticles and  $C_{60}$  in which fullerene acts as a “molecular glue” in the process of growing up this new material. In a first report, Kaifer prepared water-soluble aggregates as large as 290 nm by mixing  $\gamma$ -CD-capped gold nanoparticles with  $C_{60}$ , thus demonstrating the feasibility of this new kind of 3D assembly by tuning the interparticle chemistry (Figure 22).<sup>340</sup>

By following the same approach, 1-(4-methyl)piperazinyl fullerene derivative **265** and citrate-capped gold nanoparticles have recently been assembled.<sup>341</sup> Finally, polypseudorotaxanes constituted by  $\beta$ -CD or L-tryptophan-modified  $\beta$ -CD treated onto amino-terminated PPG chains were assembled with Au nanoparticles in a netlike form. These aggregates were able to capture  $C_{60}$  from an aqueous solution to form a new assembled species with remarkable DNA cleavage properties under light irradiation.<sup>342</sup>

## 10. Summary and Outlook

The different synthetic strategies to prepare fullerene-containing polymers, either covalently or supramolecularly connected, have been reviewed. Implementing the chemistry of fullerenes into macromolecular chemistry has allowed the preparation of new polymer materials exhibiting outstanding structural, electrochemical, and photophysical properties that might find application, and in some cases are currently under intensive and competitive research, in different fields.

The different  $C_{60}$ -based polymers have been classified according to structural parameters, and consequently, those polymers bearing one or two  $C_{60}$  units at the ends or as the core of the polymer chain have been discussed separately since the presence of the fullerene moieties produce significant modification of the former polymer. Polymers bearing

$C_{60}$  units covalently attached have been presented as cross-linked, main-chain, and side-chain polymers whose preparation has involved a wide variety of synthetic strategies. All- $C_{60}$  and related polymers are a singular class of polymers which have undergone rapid progress from starting work reporting poorly characterized materials to more recent examples involving well-defined synthetic strategies. The so-called “double-cable” approach is an elegant and realistic concept for the preparation of photo- and electroactive polymers for photovoltaic applications which has received a lot of attention during the last years. It represents a rational approach to control structural and electronic parameters in the design of photovoltaic devices in which the morphological aspects play a leading role. It is important to note, however, that this approach has not yet fulfilled the initial expectations, and more work is needed for a better understanding of the key aspects in the fabrication of organic solar cells.

Supramolecular chemistry of fullerenes is a very recent field which has been scarcely studied in assemblies involving macromolecules. The few and significant examples known so far have been discussed and classified according to the different synthetic strategies followed for the assemblies preparation. H bonding, electrostatic interactions, and  $\pi$ - $\pi$  interactions have been mainly used for the preparation of these new photo- and electroactive supramolecular architectures.

This is living interdisciplinary research in which new approaches can be developed with the only limitation being the imagination of the chemists. As a representative example, new fullerene-polyene nanospheres via thermally induced solid-state polymerization have recently been reported, leading to the first preparation of evenly distributed and uniform-sized  $C_{60}$ -based nanospheres.<sup>343</sup> In contrast to previous reports on fullerene nanoaggregates, a remarkable feature in this case is formation of orderly structured nanosphere arrays from amorphous solid thin films, thus opening a new way to different carbon nanostructures.

In summary, we are at the dawn of a new interdisciplinary field in which  $C_{60}$ -based polymers should furnish unprecedented materials in which the integration of fullerenes as a photo- and electroactive building blocks into the polymer structure should result in new properties for development of realistic applications. In this regard, 20 years after the discovery of fullerenes, the scientific community is looking for real applications of the new carbon allotropes. Once more, the ease processability and availability of polymers could be the key for application of fullerenes for practical purposes.

## 11. Acknowledgment

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