

CHAPTER 4

Fullerene-Containing Polymers

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4.1 Introduction

Fullerene is one of the most fascinating classes of carbon clusters¹ and since the preparation in multigram amounts in 1990 of the most abundant member [60]fullerene,² it has attracted great interest due to its unique three-dimensional geometry and its outstanding magnetic,³ superconducting,⁴ electrochemical,⁵ and photophysical⁶ properties. However, because of the low solubility of C₆₀ and subsequently its scarce processability, these unique properties still are not widely employed in real applications. In this regard, the combination of fullerene chemistry and macromolecular chemistry provides an opportunity to create new fullerene-containing polymers, which show promise for an enormously broad scope of real applications since it merges C₆₀ properties with the ease and versatile processability and handling of polymers. This approach has led chemists to design and develop synthetic strategies aimed to obtain even more complex and fascinating novel fullerene-based architectures with unprecedented properties that have been recently reviewed.⁷ Although polymer chemistry was a well-defined and -developed field, fullerene chemistry and properties, especially at the very beginning in the early 1990s, they were not completely disclosed and the combination of both aspects led to uncharacterisable or inutile materials often obtained employing empirical synthetic methods. Fortunately, this experience paved the way for improving and

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enhancing the strategies and nowadays all the reported data is the result of well-known and well-applied chemical methodologies leading in all the cases to processable and easily characterisable smart fullerene-containing polymers. As will be seen in this chapter, chemists are now able to tailor at will a polymeric backbone to C_{60} moieties in such a way as to achieve particular final properties of the macromolecular material. In this way, block-copolymer with well-defined donor–acceptor domains within the diffusion path of electron are created for solar devices,⁸ or water-soluble biocompatible and biodegradable polymers are designed in order to carry fullerene in circulation for photodynamic cancer therapy purposes.⁹ These recent achievements are only the last examples belonging to a growing field in which almost all the materials display outstanding properties such as optical limiting,¹⁰ or photoinduced electron transfer¹¹ just to name a few. In addition, polyfullerenes have been successfully employed as active materials in electroluminescent devices,¹² and in nonvolatile flash devices.¹³

In the present chapter, an extended classification for polymeric fullerene-containing materials will be given including also the most recent hybrid polydisperse materials. Moreover, the general hints and strategies for their preparation will be highlighted with the help of practical examples. Finally, the most recent examples of such polymeric architectures and their properties and applications will be reviewed.

4.2 Classification

The many types of polymeric fullerene derivatives may be classified accordingly on their structural features. As a criterion for the classification, polyfullerenes can be ordered as a function of their increasing chemical complexity and the difficulty to synthesise them (Figure 4.1). In fact, the macromolecular fullerene synthesis may be as simple as the mixing of C_{60} and another reactant without any care, or may require several carefully controlled reaction steps.

As all-fullerene polymers, or C_{60} -intrinsic polymers,¹⁴ are intended, all those structures constituted exclusively by fullerene units covalently linked to each other without any additional linking groups or side groups. Usually, these polymers are prepared by exposing pristine fullerene to a strong external stimulus such as visible light,¹⁵ pressure,¹⁶ but also electron beam¹⁷ and plasma irradiation¹⁸ with no thought for the final structure. Analogously, heterometallic polymers, a family of heteroatom-containing polymers in which metals or elements other than carbon (including oxygen) are present in their structures and are obtained by means of charge-transfer polymerisation mediated by metals¹⁹ but also by electroreduction of fullerene epoxide.²⁰ For these two classes of polymers the synthesis will be not discussed in the next section. Crosslinked fullerene-containing polymers were among the first examples in which the C_{60} moiety has been randomly reacted with a polymeric backbone. Their synthesis often does not require other chemical control but the presence

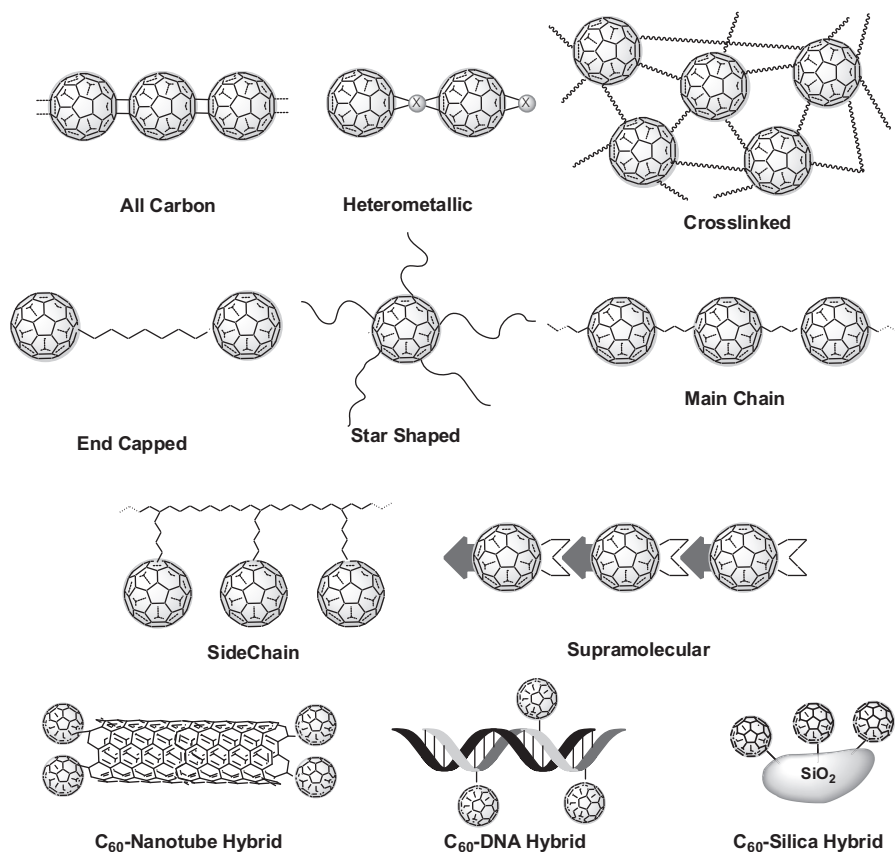


Figure 4.1 Classification of the different types of C₆₀-containing polymers and C₆₀-hybrid materials.

of several orthogonal organic functional groups. One or two spheres of fullerene are present in the structures of end-capped, or telechelic, and star-shaped, or flagellenes, polymers and are allocated at the edge or in the centre, respectively. In the main-chain polymers, also-called *in-chain* or *pearl necklace*, the fullerene units are located in the polymer backbone forming a necklace-type structure, while in the side-chain family the C₆₀ moieties are pending from the repeating units of the polymeric structure. In this latter class are also included the double-cable polymers, which possess a π -conjugated backbone. Unlike all the other classes, the more recent supramolecular polymers, in which aggregation and organisation stems from reversible interactions of one or more types of complementary components properly designed for self-assembly. Finally, just recently the synthesis of some interesting hybrid systems such as those containing nanotubes, DNA or silica have been reported and their promising properties studied.

4.3 Synthetic Strategies

For each family of fullerene-containing polymers, in the two decades since their birth, different strategies have been developed that exclusively led to the synthesis of one particular polymer. Herein are collected the strategies so far employed in the synthesis of each family of polymers, highlighting the corresponding practical examples reported in the literature.

4.3.1 Crosslinked Polymers

The synthesis of crosslinked polymers takes place from random and quick reactions that proceed in three dimensions with the help of the C_{60} sphere. However, some extent of control of the addition reactions to the 30 fullerene double bonds is required in order to avoid a drastic intractability of the final products. Crosslinked C_{60} -containing polymers can be prepared by three main pathways (Figure 4.2):

- C_{60} or a C_{60} derivative and a monomer are mixed together and allowed to react randomly;
- a preformed polymer properly functionalised at the end termini is allowed to react with C_{60} or a multisubstituted C_{60} derivative;
- polymers endowed with pending reacting moieties are allowed to react with C_{60} .

Most of the first examples of crosslinked C_{60} polymers have been prepared by means of free-radical and “living” anionic polymerisation.

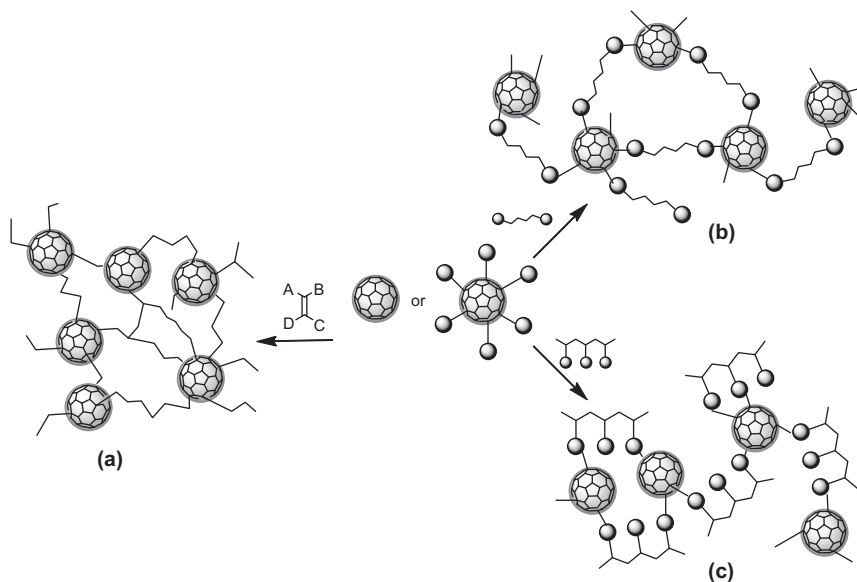
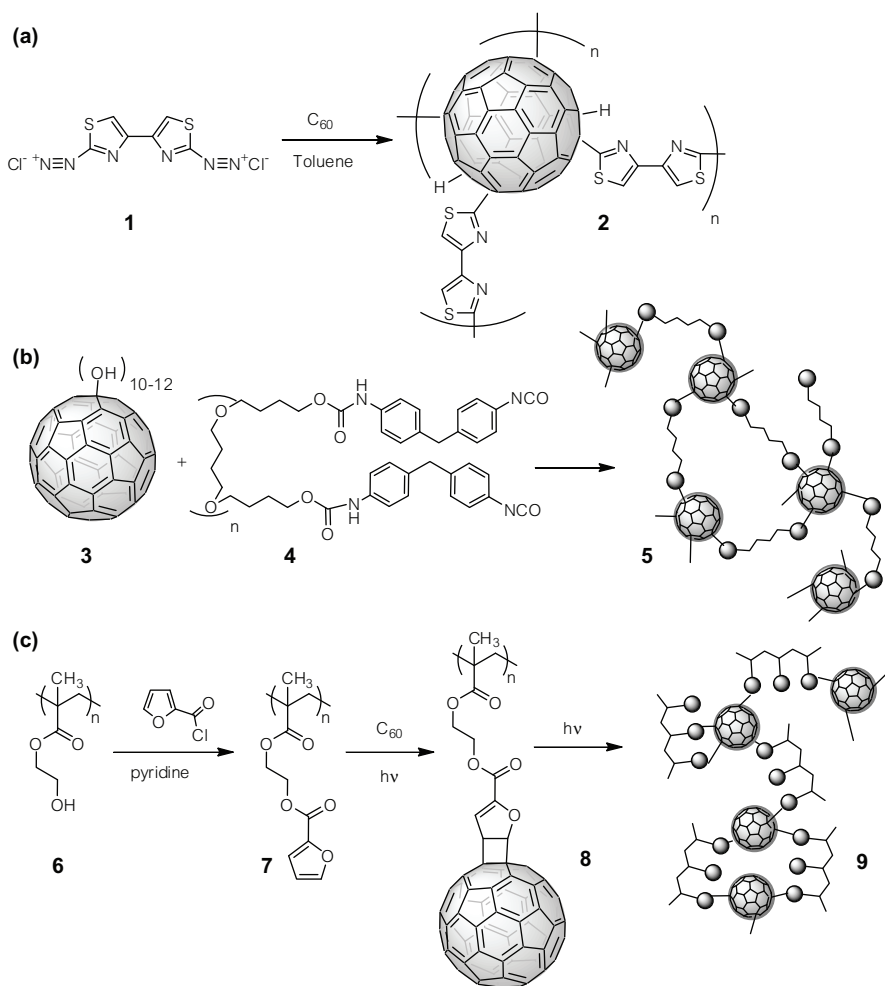


Figure 4.2 Synthetic pathways leading to crosslinked fullerene polymers.

In this regard, the first pathway includes both the uncontrolled radical or anionic polymerisation of a vinylic monomer in the presence of fullerene, as in the case of styrene,²¹ or the random linking of a AA monomer to the double-bond system of C₆₀. This latter case has been exploited by Sun and coworkers who synthesised the crosslinked copolymer **2** reacting the bis-diazonium salt derived from bithiazole (**1**) with C₆₀ (Scheme 4.2a).²² Interestingly, such a polymer behaves as an antiferromagnetic material, while its corresponding ferro-complexes, prepared by treating **2** with FeSO₄ (not shown here), exhibited soft magnetic behaviour.

The polyurethane protocol has been the most widely used in order to obtain functional C₆₀-based crosslinked polymers. In doing so, fulleranol



Scheme 4.1

C₆₀(OH)_{10–12} or other fullerenes endowed with multiple OH groups have been chosen as the crosslinkers mixed with suitable di- and tri-isocyanate prepolymers. In 1995 Chiang and coworkers polymerised fulleranol **3** with di-isocyanate polymer **4** in DMF/THF (Scheme 4.1b).²³ The hyperbranched polyurethane showed improvement in the thermal and mechanical stability of the resulting material.

On the other hand, prolonged irradiation with visible light on a poly(2-hydroxyethyl methacrylate) endowed with pending furane moieties (**7**) in the presence of C₆₀ allowed the corresponding crosslinked polymer **18** (Scheme 4.1c) to be obtained.²⁴

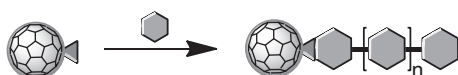
4.3.2 End-Capped Polymers

The capping of polymeric backbone terminal positions with C₆₀ often strongly influences both the molecular and bulk behaviour of well-known and established polymers. In fact, the presence of fullerene moieties at the end of the polymeric chain can modify the hydrophobicity of the parent polymer and, subsequently, its properties. Just two different synthetic strategies have been followed so far to prepare this class of polymers (Figure 4.3):

- the “*grafting from*” method, namely the growth of the polymeric chain from a C₆₀ derivative employed as starting material;
- the “*grafting to*” method, namely the incorporation of fullerenes onto presynthesised polymer.

In the first case, falls the example reported in 2000 by Li and coworkers, who used the C₆₀-monoadduct initiator (**10**) in a copper-mediated atom-transfer radical polymerisation (ATRA) (Scheme 4.2) thus avoiding the risk for multiple additions to the fullerene cage.²⁵ For the “*grafting to*” method, until a few years ago cycloaddition of an azido-ended polymer to fullerene has been the reaction of choice for the covalent linking.²⁶ However, more recently ATRA reactions have also been employed,²⁷ 1,3dipolar azomethine ylides

(a) *Grafting from*



(b) *Grafting to*

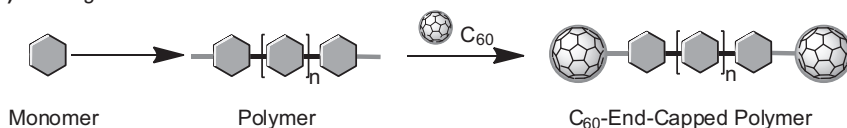
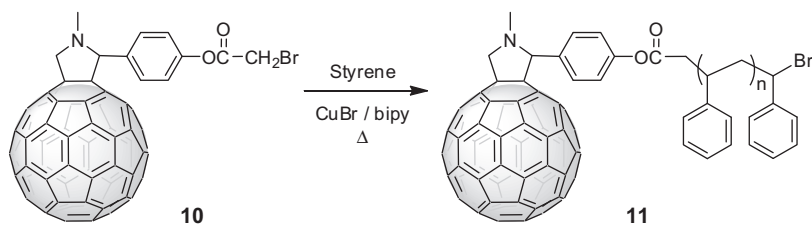
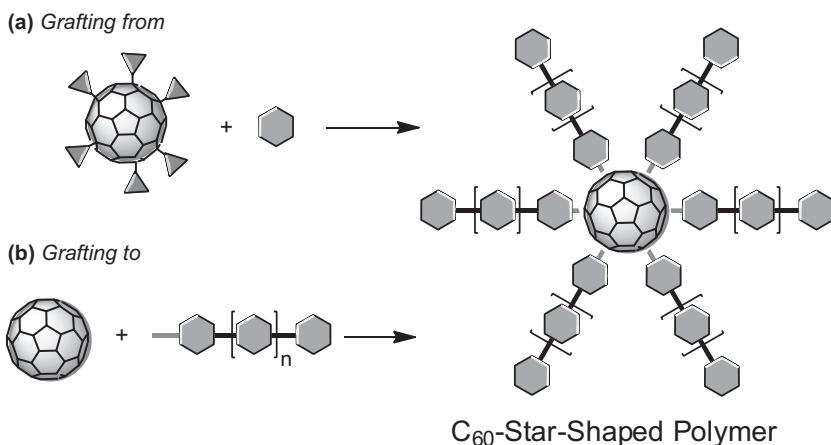


Figure 4.3 Synthetic strategies for the synthesis of C₆₀-end-capped polymers.



Scheme 4.2

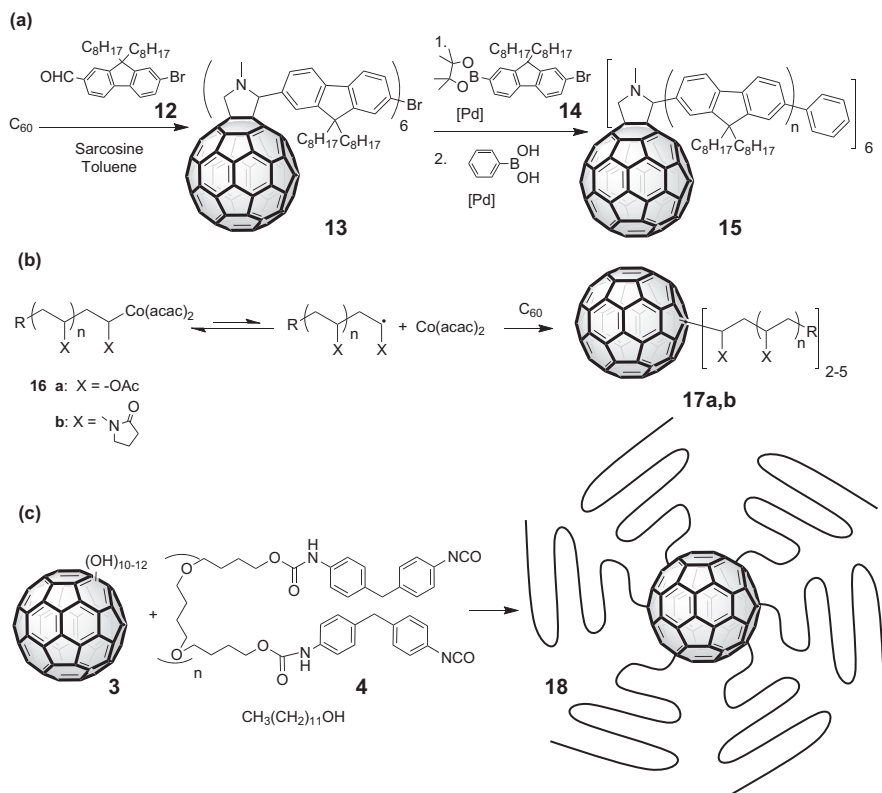
Figure 4.4 Synthetic strategies for the synthesis of C_{60} -star-shaped polymers.

cycloadditions²⁸ as well as Huisgen “click” reactions²⁹ in the synthesis of fullerene-end capped polymers.

4.3.3 Star-Shaped Polymers

In this class, a fullerene unit (or two) is covalently linked with two to twelve long and flexible polymer chains, giving rise to topologies resembling that of sea-stars. Samulski called such macromolecules “flagellenes”, in the first example reported in 1992, since its shape is similar to that of Flagellated-unicellular protozoa.³⁰ Analogously to end-capped polymers, star-shaped one have been prepared by means of “grafting from” and “grafting to” methods (Figure 4.4). This latter may take place both on pristine fullerene and on C_{60} multiadducts.

A real and recent example regarding the “grafting from” method has been reported by Bo *et al.* in 2007. They efficiently synthesised the hexakis-adduct of C_{60} with 7-bromo-9,9-dioctyl-9H-fluorene-2-carboxyaldehyde **12** by means of



Scheme 4.3

Prato's protocol (Scheme 4.3a).³¹ The mixture of hexa-adducts has been in turn polymerised *via* Suzuki polycondensation reactions in order to afford the C₆₀-cored star polyfluorene **15**. The three-dimensional structure effectively reduces the aggregation of the polyfluorene chains, and this blue-emitting material exhibited very good luminescent stability upon annealing in air. On the other hand, the cobalt-mediated radical polymerisation (CMRP) technique, has been used to prepare well-defined poly(vinyl acetate) chains end capped by the metallic species which has been grafted onto the fullerene (Scheme 4.3b). Afterwards, the hemolytic cleavage of the cobalt–carbon bond released the radical species that, in the presence of C₆₀, led to radical addition yielding star-poly(vinyl acetate) **17a** and star-poly-(*N*-vinylpyrrolidone) **17b**. The former has been subsequently methanolised to afford the corresponding water-soluble polyvinyl alcohol.

Fullerenol **3** has been also employed for the “grafting to” synthesis of star-shaped polymers. Reaction with di-isocyanate polymer **4**, but this time in the presence of dodecanol in order to prevent crosslinking, gave rise to the soluble star polymer **18**.³²

4.3.4 Main-Chain Polymers

Probably, this is the less exploited class of fullerene polymers due to the few examples reported to date. Here, C_{60} moieties are directly allocated in the polymer backbone forming a necklace-type structure. Unfortunately, double addition on the C_{60} sphere affords a complex regioisomeric mixtures (up to 8 isomers) beside the formation of crosslinking products by multiple additions. Main-chain polymers are prepared by following three different synthetic strategies:

- a direct reaction between the C_{60} cage and a suitable symmetrically difunctionalised monomer;
- a polycondensation between a fullerene bis-adduct (or a mixture) and a difunctionalised monomer;
- reaction between C_{60} or a fullerene bis-adduct and a linear polymer difunctionalised at both ends (see Figure 4.5).

Very recently, Hiorns exploited the ATRA protocol in order to synthesise 1,4-connected in-chain polymers, reacting 1,4-bis(methylcyclohexyl ether)-2,5-dibromomethyl benzene **19** and fullerene in the presence of CuBr (Scheme 4.4a).³³ The so-obtained polymer **20** worked well in nonoptimised photovoltaic devices showing the remarkable conversion of light efficiency of 1.6%. The method (b) has instead employed for the preparation of two pearl-necklace polyiminofullerenes (*e*-**23** and *cis*-3-**24** in Scheme 4.4b).³⁴ Starting from enantiopure *equatorial* bis(formyl-methano)[60]fullerenes (*e*-**21**) or alternatively from the corresponding *cis*-3 isomer (*cis*-3-**22**) and the aromatic diamine 4,4''-diamino-2',5'-bis(dodecyloxy)-*p*-terphenyl **22**, it has been possible to carry out the synthesis of title main-chain polymers. These macromolecular products showed excellent processability. Finally, route (c) has been followed by Hiorns and coworkers, who prepared in-chain polymer **26** by alternatively linking fullerene with the conjugated poly(3-hexylthiophene) by means of 1,3dipolar cycloadditions of azomethine ylides (Scheme 4.4c).³⁵

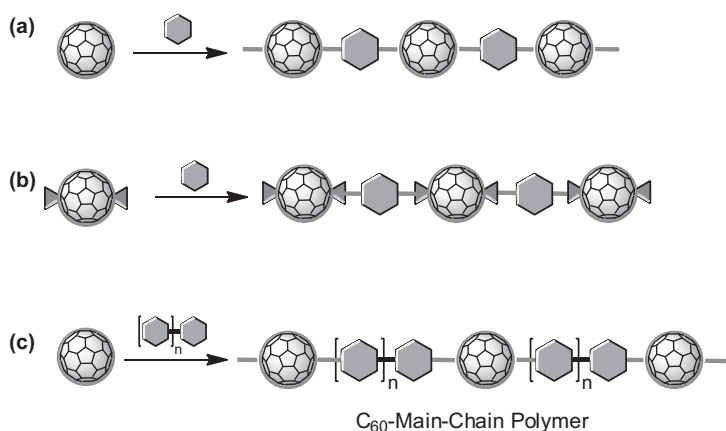
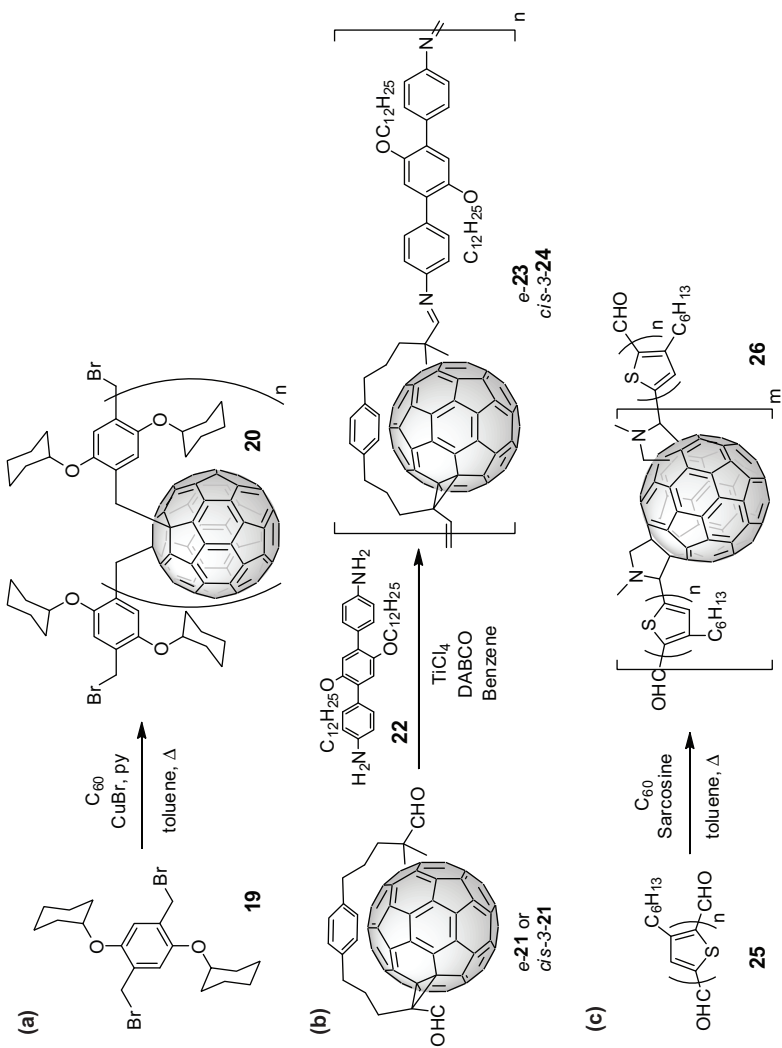


Figure 4.5 Synthetic strategies for the synthesis of C_{60} -main-chain polymers.



Scheme 4.4

4.3.5 Side-Chain Polymers

Contrary to the previous class, this is the most widely studied family of C_{60} polymers, having the fullerenes pendant from the main polymer chain, sometimes called *on-chain* or “*charm-bracelet*”. Here chemists have exploited the knowledge collected during a century of studies on polymers and have then bonded C_{60} to all of the “classic” families of polymers such as polystyrenes,³⁶ polyacrylates,³⁷ polyethers,³⁸ polycarbonates,³⁹ polysiloxanes,⁴⁰ polyvinylcarbazoles,⁴¹ and polysaccharides⁴² in the search for improved processability and enhanced properties, with a wide range of potential applications. In this family are also included the “double-cable” polymers,⁴³ in which the π -conjugated semiconducting polymer (p-type cable) with electron-donating characteristics is endowed with covalently connected electron-accepting 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.

Despite the large number of examples reported so far in the literature, the synthetic strategies followed for the preparation of side-chain polymers can be summarised as only two different approaches (Figure 4.6):

- direct introduction of fullerene itself or a C_{60} derivative into a preformed polymer;
- synthesis of a C_{60} derivative that can be, in turn, directly homopolymerised or copolymerised together with other monomer(s). In the case of double-cable polymers electropolymerisation is also possible.

Undoubtedly the most widely method for the direct introduction of fullerene on a polymeric chain has been by means of a 1,3dipolar cycloaddition with azido pending groups, however, other methods have also been employed such as [4 + 2] cycloaddition, nucleophile attach, atom-transfer radical addition (ATRA), hydrosilation and Friedel–Craft reactions.⁴⁴

[4 + 2] cycloaddition reaction between fullerene and side chain “*in situ*” generated reactive dienes has been employed by Wang.⁴⁵ Thermal activation in *o*DCB of benzocyclobutenone moieties in polymer **27** provokes the [4 + 2] cycloaddition with C_{60} , leading to soluble macromolecules **28** with high fullerene content (Scheme 4.5). On the other hand, a well-known protocol for the

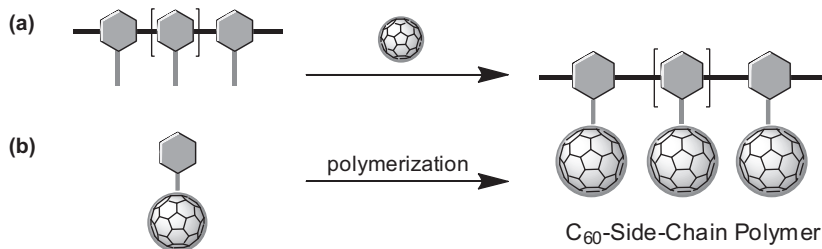
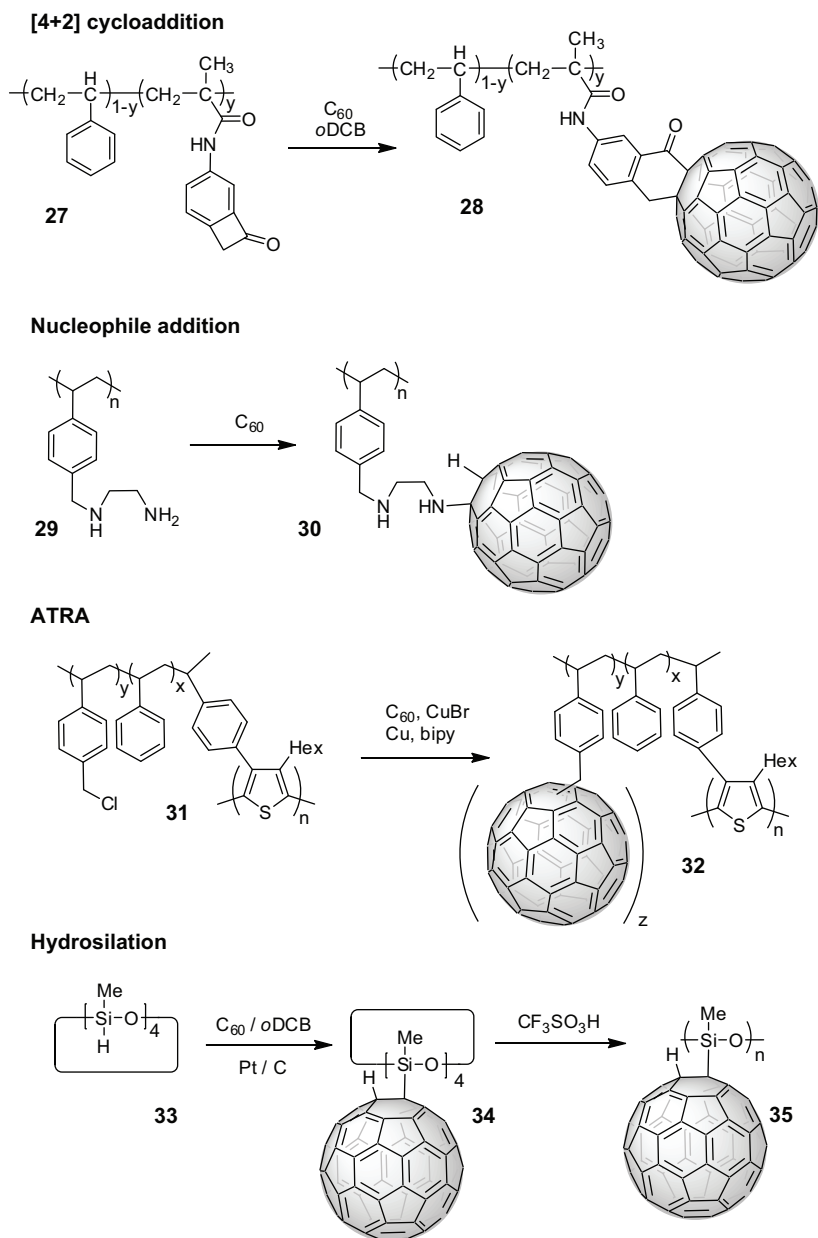


Figure 4.6 Synthetic strategies for the synthesis of side-chain C_{60} polymers.

incorporation of C_{60} on the pendings is the nucleophile attack of amino groups to fullerene, as shown in Scheme 4.5 for polymer **30**.⁴⁶ This reaction has been mainly used for the first examples of fullerene-containing polymers. Next, the ATRA reaction has been chosen especially when in the presence of easily



Scheme 4.5

available choromethyl-functionalised polystyrenes, as in the case of polymer **32**.⁴⁷ Finally, Pt-catalysed hydrosilation has been used to link fullerene to 2,4,6,8-tetramethylcyclotetrasiloxane **33**.⁴⁸ The subsequent polymerisation of **34** took place by means of triflic acid affording polymer **35**.

On the other hand, Hessen *et al.* prepared a polyethene endowed with fullerene moieties pendant on short-chain branches (**38**) by catalytic polymerisation of ethene and the C₆₀-containing vinylic monomer **36**, using (C₅Me₄SiMe₂NBu^t)TiCl₂ (**37**)/methylalumoxane (MAO) as the catalytic system (Scheme 4.6).⁴⁹ Wudl, Prato, and Maggini in 1995 employed the Schrock's catalyst Mo(CH-Bu^t)(NAr)[OCMe(CF₃)₂]₂ (**40**) in the preparation of C₆₀ polymer **41** achieved reacting norbornene modified-C₆₀ **39** and an excess of norbornene by means of the ring-opening metathesis copolymerisation (ROMP) technique.⁵⁰ Since then, several other fullerene polymers have been prepared in the same manner mediated by Grubb's catalyst.⁵¹

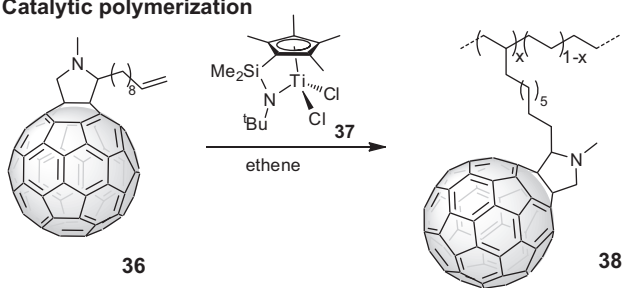
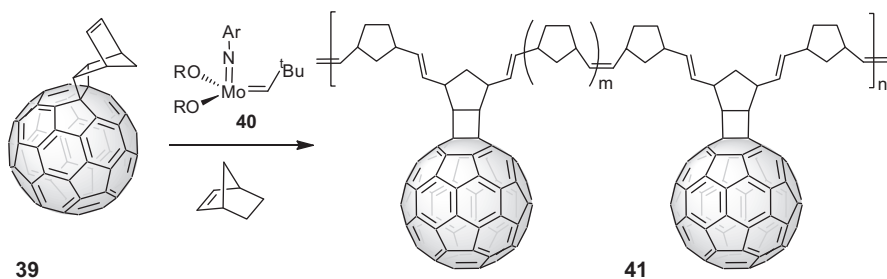
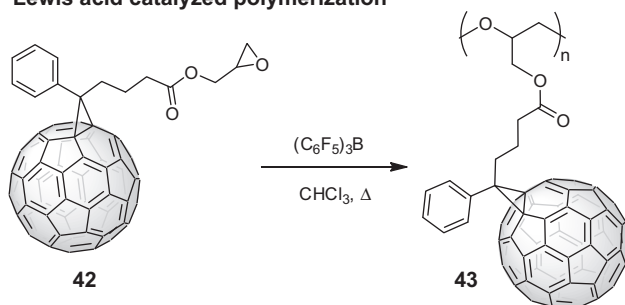
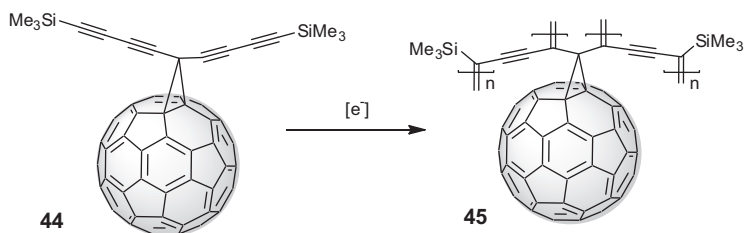
Drees, Sariciftci and coworkers succeeded in a new approach regarding both the synthesis and the performances in organic solar cells of epoxidic polymer **43** (Scheme 4.6).⁵² The glycidol ester of [6,6]-phenyl C₆₁butyric acid (**90**) was prepolymerised in the presence of Lewis acid tris(pentafluorophenyl)borane as the initiator and, after spin coating, blended with poly(3-hexylthiophene) (P3HT). The ring-opening polymerisation was completed by heating the photovoltaic device, obtaining an interesting 2% conversion energy efficiency. Electropolymerisation of thiophene, bithiophene and terthiophene monomers has been one of the most employed strategies to obtain C₆₀-containing double-cable polymers. Such a method generally implies electrogeneration of radical cations and their subsequent rearomatisation.⁵³ Moreover, this technique represents a useful tool for the synthesis of novel conjugated polymers, allowing growth of these films onto transparent substrates for characterisation by spectroscopic techniques. In this regard, Diederich *et al.* in 1994 reported the first example of electropolymerised double-cable polymer.⁵⁴ Monomer **54** undergoes reductive electrochemical polymerisation to give a homogeneous polydiacetylene film deposited on the platinum electrode.⁵⁵

4.3.6 Supramolecular Polymers

This family can be considered the most recently explored among all the other polyfullerenes, however, in recent years, an ever-growing interest has been devoted to the assembly of supramolecular C₆₀ polymers, gaining momentum as an effective method to prepare functional, novel carbon-based materials.

Accordingly, with supramolecular complementary interactions, to date four strategies have been used in the assembling of C₆₀ supramolecular polymers (Figure 4.7):

- interactions between functionalised polymers and fullerene derivatives or C₆₀ itself;
- assembling of self-complementary C₆₀ derivatives;

Catalytic polymerization**Ring opening metathesis polymerization****Lewis acid catalyzed polymerization****Electropolymerization**

Scheme 4.6

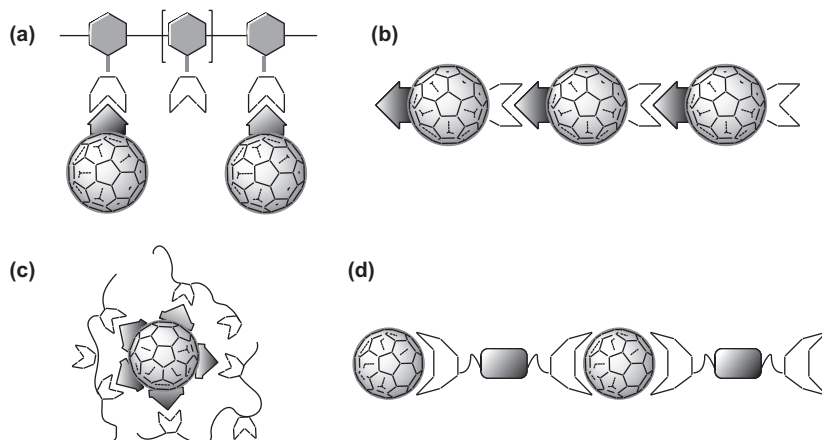


Figure 4.7 Strategies for the assembling of supramolecular C_{60} polymers.

- c) fullerene multiadducts and polymers endowed of complementary functionalities; and
- d) AA–BB complementary interactions between ditopic hosts and C_{60} .

In Figure 4.8 are collected four examples representing supramolecular polymers belonging to the different synthetic strategies. In 2005 Shinkai and coworkers, exploited electrostatic acid–base interactions by mixing a full-eropyrrolidine carboxylic acid with the polystyrene-poly-4-vinylpyrrolidone copolymer (PS-*co*-P4VPy), obtaining the assembly **46** with a micelle-like superstructure. Here, the P4VPy blocks interact with the fullerene derivative and form the core, while the highly soluble PS blocks are oriented outside of the micelle forming the shell.⁵⁶ A self-complementary monomer able to form donor–donor–acceptor–acceptor quadruple hydrogen bonds has been used by Hummelen and coworkers, in the synthesis of the supramolecular polymer **48**.⁵⁷ On the other hand, when polyaniline emeraldine base (PANI-EB) is doped with a C_{60} -multiadduct containing several hydrogenosulfated and hydroxylic groups, the corresponding supramolecular crosslinked polymer **47** an 11 orders of magnitude increase in conductivity.⁵⁸ Finally, Liu and coworkers prepared the water-soluble fullerene assembly **49** with a coordinated metal centre *via* end-to-end intermolecular inclusion complexation of fullerene with a cyclodextrin dimer.⁵⁹ Assemblies of 60–80 units have been so obtained with length in the range of 150–250 nm, as observed in TEM images, showing an effective DNA-cleavage ability under light irradiation.

Recently, other interesting examples of supramolecular assemblies have been reported, including helical polymers,⁶⁰ one of them able to selectively complexate and separate higher fullerenes from C_{60} and C_{70} from carbon soot,⁶¹ as well as head-to-tail donor–acceptor supramolecular polymers based in π,π concave–convex interactions.⁶²

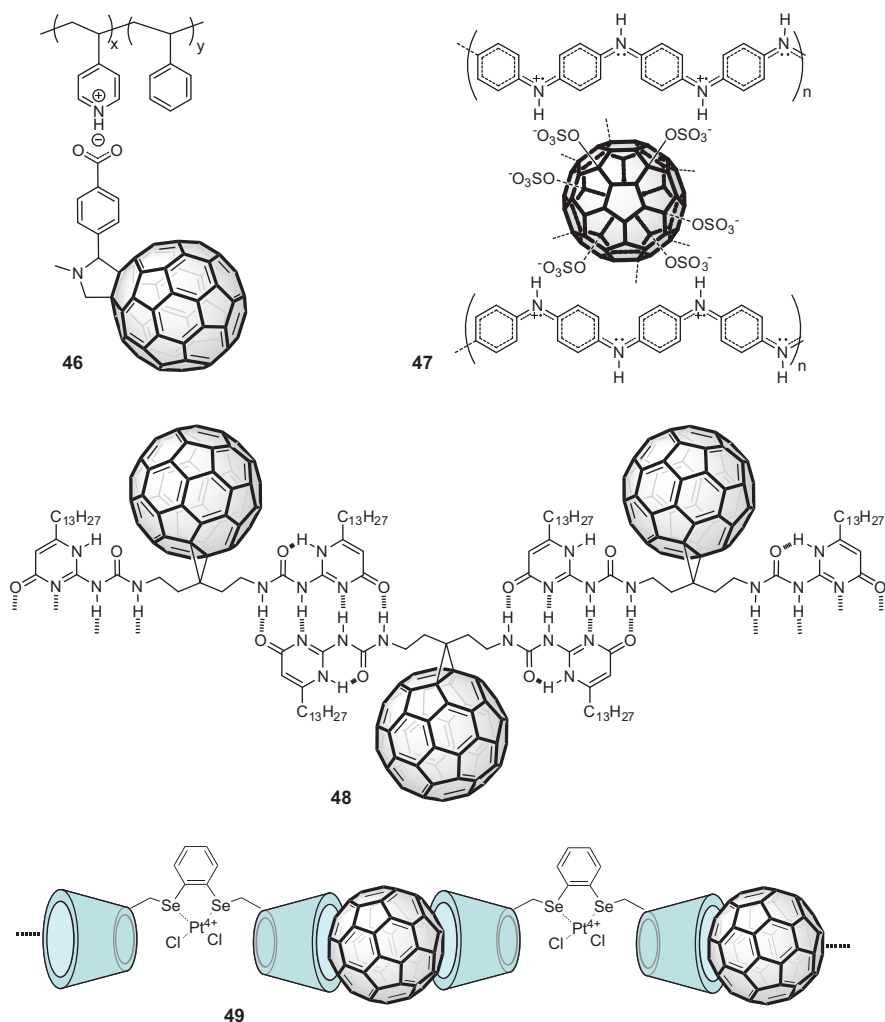


Figure 4.8 Examples of C_{60} supramolecular polymers.

4.3.7 Carbon-Nanotube–Fullerene Hybrids

In 1998 Luzzi serendipitously discovered that several C_{60} units, byproduct in the synthesis of single-walled NTs (SWNTs), were trapped inside of open-ended nanotubes, forming quasi-1D arrays.⁶³ The high geometrical matching between C_{60} and SWNTs is responsible for the very intensive van der Waals forces present in such peapods (as they have commonly been called) with a strong interaction of 3 eV between the two carbon allotropes, making encapsulation a spontaneous and irreversible process.⁶⁴ Since then, this kind of aggregate has been extensively studied and a series of endohedral and

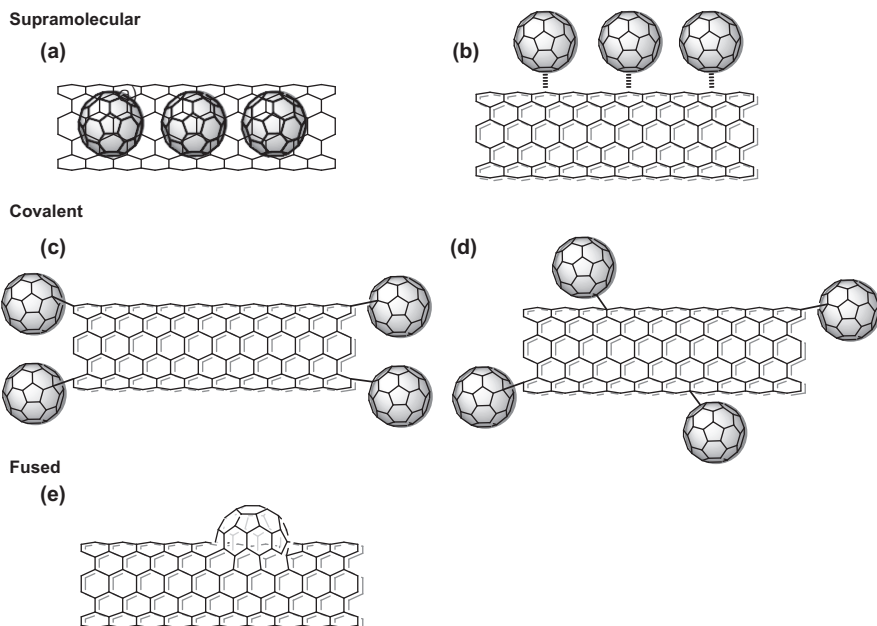


Figure 4.9 Strategies for the assembling of C_{60} -NTs hybrids.

functionalised hollow fullerenes have been introduced in the inner space of nanotubes and have been investigated.⁶⁵

Fullerene-NTs hybrids have been prepared both *via* supramolecular or covalent methods. To date, five strategies has been disclosed for the combination of the two allotropes:

- the supramolecular filling of the void space of NTs with hollow fullerene or endohedral derivatives both pristine or functionalised;
- supramolecular interaction between C_{60} , or its derivatives, and the side wall of NTs;
- the covalent derivatisation of the external rims of NTs;
- the covalent random derivatisation of the sidewall and rims of NTs;
- the covalent fusion of C_{60} onto the NTs surface.

There are three different approaches in which SWNT and C_{60} interact to form supramolecular assemblies (Figure 4.10). In 2006 Prato, Guldi and Maggini succeeded in the preparation of **50** in which a pyrene–fullerene conjugate interacts with the outer wall of HiPCO single-walled NTs *via* π – π interactions.⁶⁶ The effective direct interaction of pyrene and the nanotube was definitively confirmed by electrochemical studies. Next, D’Souza and Ito prepared the similar assembly **51** but with the help of two different supramolecular interactions: a pyrene-alkyl ammonium entity was first used to functionalise SWNT, then a complex with benzo-18-crown-6 functionalised

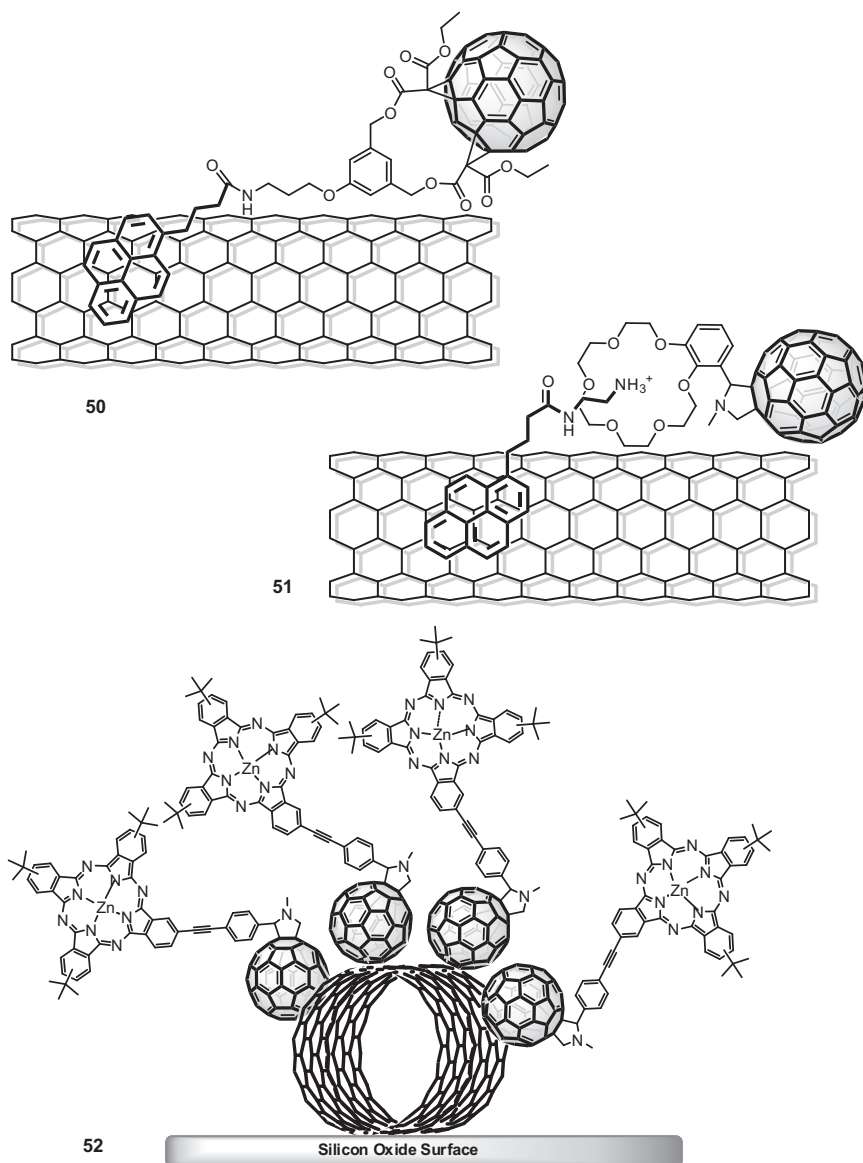


Figure 4.10 Examples of supramolecular NT–fullerene assemblies.

fullerene *via* ammonium–crown ether interactions has been formed.⁶⁷ Very recently, Torres and coworkers reported the organisation properties of a covalently linked phthalocyanine–C₆₀ fullerene conjugate which is able to self-organise by means of noncovalent interactions on the outer wall of SWNTs grown by catalyst-assisted vapour deposition on silicon oxide surfaces (**52**, Figure 4.10).⁶⁸

In 2007, Langa and coworkers reported the first example of SWNTs chemically modified at the ending rims by means of amidation reactions between the carboxylic groups of NTs and an amine-functionalised C_{60} derivative (**53**, Figure 4.11).⁶⁹ Bonifazi, Prato *et al.* anchored D–A diads in which the acceptor was C_{60} and the donors were ferrocene, porphyrin and N,N-dimethylaniline moieties (**54a–c**, Figure 4.11).⁷⁰ Confirmation of linking was furnished by a series spectroscopies and, in addition, HR-TEM images showed that, besides ending functionalisation, some wall functionalisation also occurred due to the likely amidification of $-COOH$ groups present in wall defects.

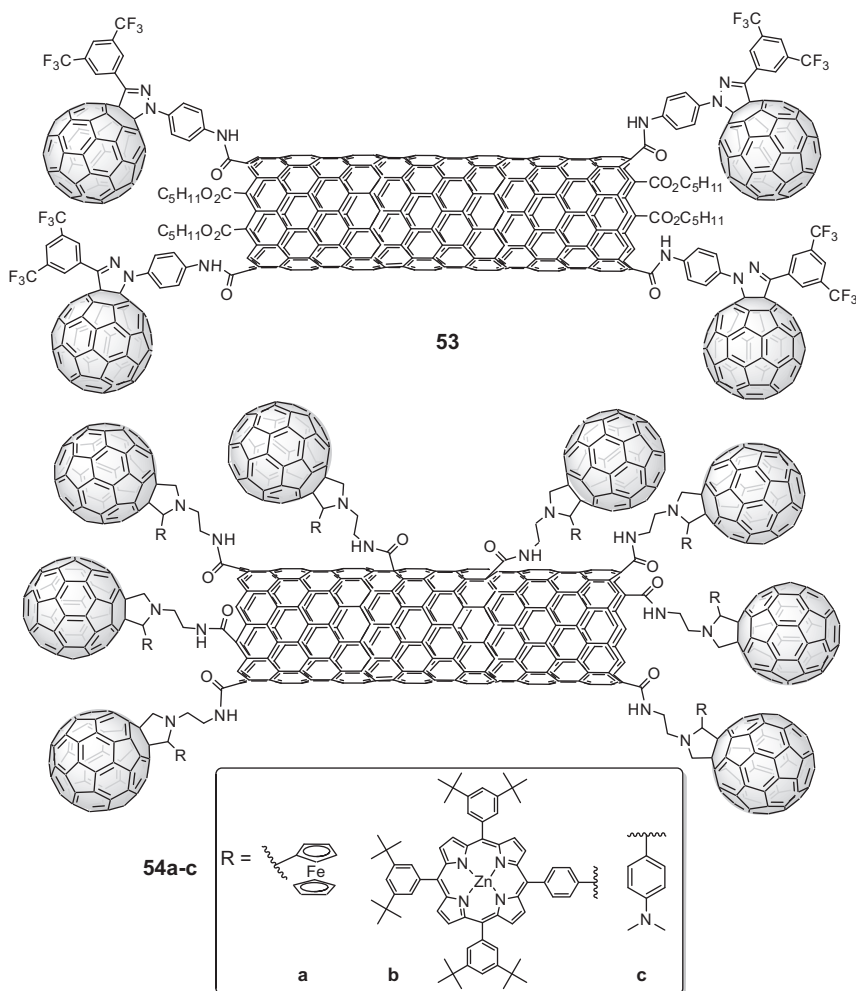


Figure 4.11 Structures of fullerene–NT conjugates.

In 2009 Fang reported a three-step chemical functionalisation of multiwalled NTs (MWNTs) with C_{60} ,⁷¹ whilst in 2010 Liao covalently linked double-walled NT and C_{60} by amination reaction with a polyethylenimine spacer.⁷² In this latter work, optical limiting performance of DWNT–fullerene hybrids was found to be superior to those of fullerene and SWNTs at the same level of transmission. The authors claim that charge transfer between the DWNT and fullerene moieties probably plays an important role of optical limiting.

Finally, the last strategy devoted to the synthesis of C_{60} -NT hybrids has been very recently discovered and regards the synthesis of nanobuds, carbon nanostructures in which fullerene moieties are fused on the outer wall of the nanotube. These carbon hybrid were discovered by Kauppinen, Nasibulin *et al.* in 2007, who suggested that both fullerenes and SWNTs originate from graphitic carbon precipitated on the surface of Fe nanoparticles catalysing CO disproportionation in the presence of etching agents such as H_2O and CO_2 .⁷³ Due to the highly curved nature of the fullerene fragment fused, these moieties represent selective and reactive sites for the exclusive functionalisation of nanobuds.⁷⁴

Beside fullerene–nanotubes, just recently other covalent hybrid between two different allotropes of carbon have also been reported. In this regard, in 2008 a C_{60} –diamond hybrid has been prepared by deposition of evaporated fullerene onto the bare-diamond surface,⁷⁵ whereas hydroxylated diamonds have been used for the covalent linking of $C_{60}F_{48}$ molecules, although they decompose by annealing over $200^\circ C$.⁷⁶ Finally, in the same year the synthesis and characterisation of a graphene–fullerene hybrid was reported.⁷⁷

4.3.8 DNA–Fullerene Hybrids

Interactions of functionalised fullerenes and DNA have attracted much interest since the discovery in 1993 that a water-soluble fullerene cleaves DNA upon irradiation with visible light.⁷⁸ Since then two different strategies have been mainly followed in order to decorate DNA with fullerenes: 1) the supramolecular complexation, since DNA may be regarded as an anionic polyelectrolyte, it can form polyelectrolyte-surfactant complexes with positively charged fullerene derivatives; 2) the covalent binding of C_{60} at the end of a polynucleotide chain (Figure 4.12).

Nakamura and its group were pioneers in this field, especially exploiting the first approach.⁷⁹ They prepared the tetracationic C_{60} derivative **55** capable of tightly interacting with DNA thanks to the perfect matching of the diammonium–fullerene side chains with two parallel phosphate backbones along the major groove of a DNA duplex (Figure 4.13).⁸⁰ This compound acted as an effective transfection reagent for gene transfer causing the folding of a supercoiled DNA molecule to form disk-like condensates that are composed of one to a few DNA double strands.⁸¹ They also disclosed the complexation⁸² as well as the cell-uptake mechanisms.⁸³

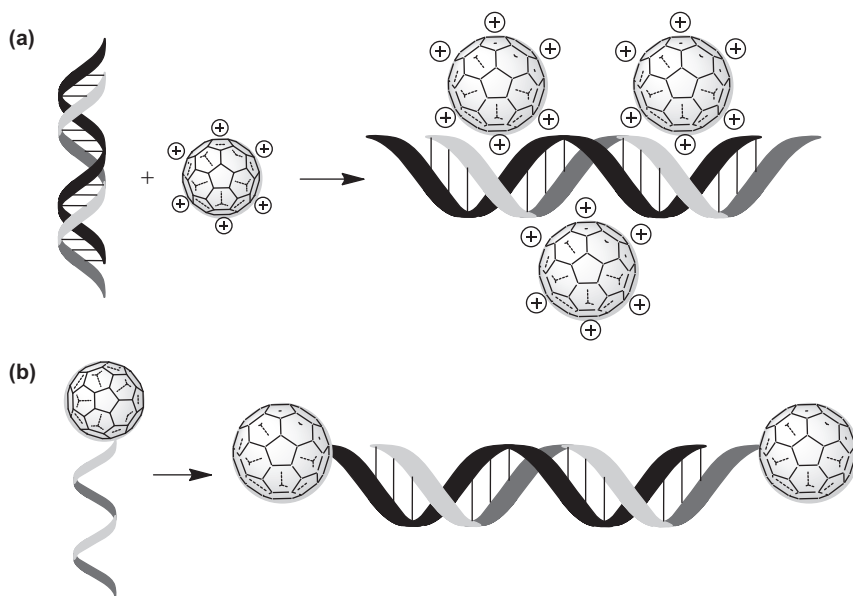


Figure 4.12 Strategies for the preparation of DNA- C_{60} hybrids.

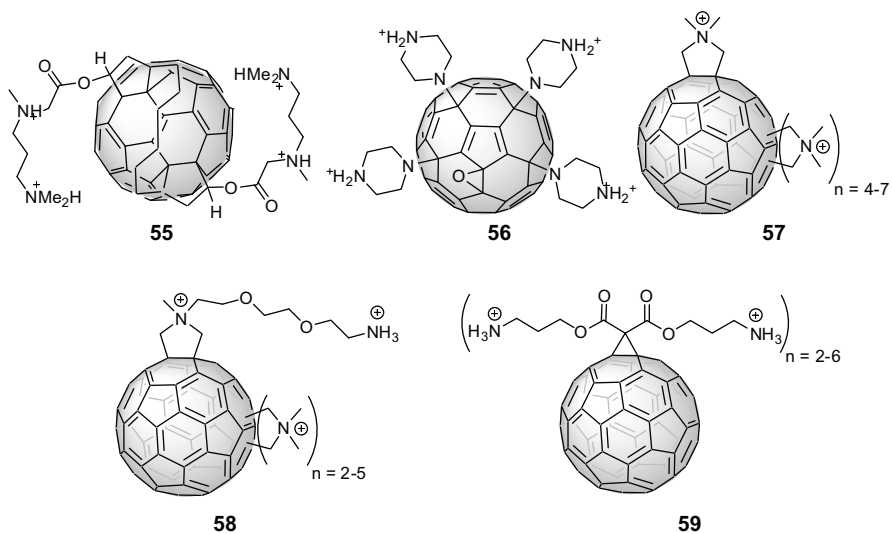


Figure 4.13 Cationic fullerene derivatives used in DNA complexes.

The same group successfully prepared and tested the gene-delivering aminofullerene **56**, giving the general rules for future chemical design of other effective C₆₀-based gene-delivering reagents.⁸⁴

Other fullerene derivatives have been tested as vectors for gene transfer (Figure 4.9). In 2007 Prato *et al.* investigated DNA complexation and plasmid delivery ability of multicationic multi-*N,N*-dimethylfullerenopyrrolidinium derivatives **57** and **58** able to strongly bind plasmid DNA through several electrostatic interactions.⁸⁵ Also, Engler and coworkers studied a series of cationic Bingel-type C₆₀-multiadducts (**59**) as nonviral gene-delivery vectors.⁸⁶

On the other hand, fewer examples have so far been reported on covalently modified oligonucleotides and plasmids. Hélène first reported in 1994 the C₆₀-linked deoxynucleotide **60** (16-mer) able to form double and triple helices with complementary single-stranded DNA, duplex DNA and DNA duplex with hairpin structure (Figure 4.14).⁸⁷ Moreover, they found that, after irradiation with light, occurs. Rubin, employed C₆₀-oligonucleotide conjugate **61** (38-mer) to shed light on the mechanism of the exclusive cleavage at guanine bases that involved a single electron-transfer process between ³C₆₀ and guanine.⁸⁸ In 2009, Ree described a pH-driven enthalpic molecular nanomachine with two fullerene moieties covalently bounded at 3' and 5' ends of i-motif DNA, (Figure 4.14).⁸⁹ This DNA-fullerene hybrid changes its conformation from "closed" to "open" by varying the pH value from 5 to 8 probably exploiting the strong hydrophobic C₆₀-C₆₀ interactions in aqueous media.

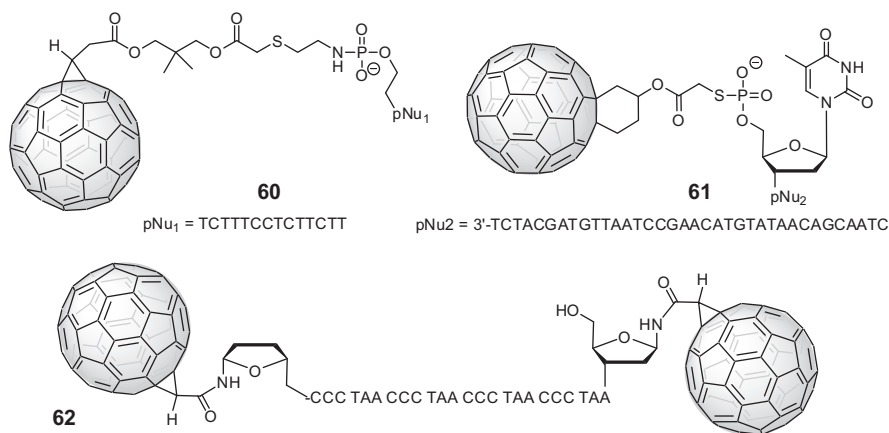


Figure 4.14 Structures of some fullerene-containing oligonucleotides.

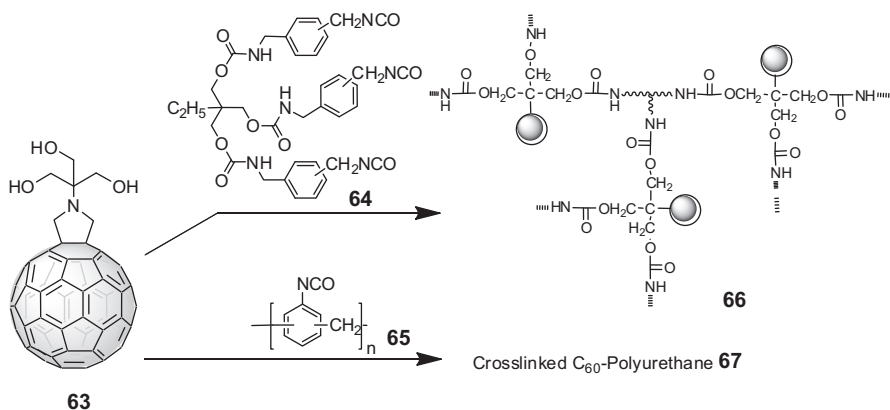
4.4 Properties and Applications

Although fullerene polymers have been extensively studied over the last two decades, to date this class of smart material has not been used for real applications. However, their investigation reveals, year by year, new potential applications and improved properties with respect to early examples, as will be

shown in the case of photovoltaic applications. In this section, in order to give the reader an idea, some of the most promising applications for C_{60} polymers are collected. In the last two decades fullerene polymers have been tested in membranes both for gas separation⁹⁰ and for proton-exchange fuel cells,⁹¹ but also as active materials in electroluminescent devices⁹² and in nonvolatile flash devices,⁹³ among others. Herein, optical limiting, photodynamic cancer therapy and DNA-cleaving and photovoltaic properties of C_{60} -containing polymers will be overviewed, focusing on the very latest examples reported in the literature.

4.4.1 Optical Limiting

Optical limiting is a nonlinear optical (NLO) process in which the transmittance of a material decreases with increased incident light intensity. In this regard, optical limiters are systems that permit the transmission of ambient light levels but that strongly attenuate high-intensity, potentially damaging light such as focused laser beams. In fact, for the laser radiation at 532 nm C_{60} is among the best of all materials in optical-limiting properties,⁹⁴ and its derivatives may be considered as potent broadband optical limiters due to the broad coverage of the characteristic ground- and excited-state absorptions over a wide wavelength range.⁹⁵ However, technical difficulties in the material processing, mainly due to poor solubility of fullerene derivatives in common organic solvents and insolubilities in polar solvents, led to work to conjugate C_{60} with polymers for better processability characteristics. Thus, in 1995 were reported the first examples in which random solid fullerene-containing polystyrenes (PS) showed NLO properties about 5 times greater than that of a C_{60} solution.⁹⁶ Also, random poly(methyl methacrylate)⁹⁷ and linear PS⁹⁸ containing fullerene were found to be optical limiters. Nevertheless, the best results have been achieved with crosslinked polyurethanes **66** and **67** (Scheme 4.7), which showed a third-order NLO response with 1–2 orders of enhancement in



Scheme 4.7

comparison with other C_{60} materials, probably due to the successful incorporation and good dispersion of large amounts of C_{60} (19.1 wt% for polymer **66**) into a highly crosslinked polymer.⁹⁹ Such materials would find application in optical signal processing in communication systems.

4.4.2 Photodynamic Therapy and DNA Cleaving

Photodynamic therapy (PDT) has attracted attention as a less-invasive method for treating cancer. In PDT, the photosensitiser is administered to the patient and the tumour is irradiated with the appropriate wavelength of light. Illumination is absorbed by the photosensitiser, and an electron is excited to the first excited singlet state that can undergo the intersystem crossing to the long-lived triplet state. This latter can, in turn, interact with ground-state molecular oxygen to form cytotoxic reactive oxygen species (ROS) and consequently to cell death and tissue destruction.¹⁰⁰ Although fullerene is a well-known radical scavenger, when excited in the ultraviolet region (340–400 nm) it generates ROS acting as an effective photosensitiser.¹⁰¹ This behaviour is useful also in the visible-light cleavage of DNA, an important subject for medical treatments. Once again, photosensitised DNA cleavage takes place *via* generation of ROS, such as singlet oxygen (1O_2) and a superoxide anion radical (O_2^-), or by means of direct electron transfer between DNA and a photoexcited sensitiser. Although fullerene represents a good candidate for both therapies, in order to be successfully employed it needs to be transformed in a water-soluble derivative, and its incorporation in hydrophilic polymers was revealed to be an excellent choice. As already stated supramolecular polymer **49** proved DNA-cleavage ability under light irradiation,⁵⁹ but also the main-chain polymer **67**, formed through nucleophilic polyaddition reaction between fullerene and the β -cyclodextrin-bis(*p*-aminophenyl) ether, has been successfully employed as a highly efficient DNA-cleaving agent under visible-light conditions (Figure 4.15).¹⁰²

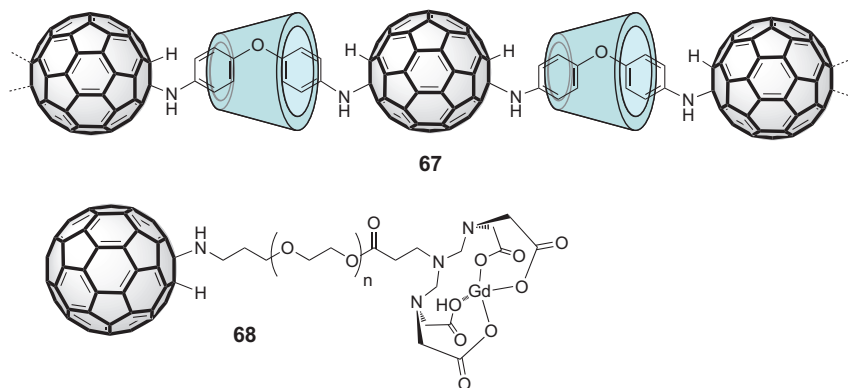


Figure 4.15 Structures of DNA cleaving and PDT fullerene polymers.

On the other hand, Tabata *et al.* in 1997 reported the first polyfullerene being used to carry out PDT of actual tumours.¹⁰³ When injected intravenously into mice carrying a subcutaneous tumour on the back, a C₆₀-containing polyethylene glycol presented higher accumulation and more prolonged retention in the tumour tissue than in normal tissue. Histological examination revealed that conjugate injection plus light irradiation strongly induced tumour necrosis without any damage to the overlying normal skin. More recently, Liu and coworkers synthesised a polyethylene glycol linked to fullerene and the other end to the diethylenetriaminepentaacetic acid chelating Gd³⁺ (**68**, Figure 4.15).¹⁰⁴ Similar generation of superoxide upon illumination was observed with or without Gd³⁺ chelation. Intravenous injection of **68** into tumour-bearing mice followed by irradiation showed significant antitumour PDT effect that depended on the timing of light exposure that correlated with tumour accumulation as detected by the enhanced intensity of MRI signal. Finally, in recent years star-shaped C₆₀-poly(vinyl alcohol)¹⁰⁵ and both linear¹⁰⁶ and star-shaped¹⁰⁷ poly(vinylpyrrolidone) have proven to be effective as photosensitisers to produce singlet oxygen and, subsequently, they are good candidates for PDT.

4.4.3 Photovoltaics

Among all the possible applications for fullerene polymers, organic photovoltaic devices very likely seems to be the most realistic. It is interesting to note that, although at the beginning of the new millennium several scientists put their trust on the success of polymer incorporating fullerene as the right approach in order to improve solar devices, the disappointing results destroyed all their largely synthetic efforts. In fact, the ambipolar polymers, containing both fullerene and a conjugated donor backbone, did not pay back in terms of efficiency the time consumed in their preparation, especially if compared with the results obtained simply mixing C₆₀ derivatives and conjugated polymers. Nevertheless, the very recent years are witnessing a kind of rebirth of this approach, probably due to improved technologies and methodologies, that are allowing scientists to achieve efficiencies comparable with those obtained in bulk-heterojunction cells.

In 2001 Inganäs and Janssen reported the synthesis of donor–acceptor polymers **69**¹⁰⁸ and **70**,¹⁰⁹ respectively (Figure 4.16). These were the first examples of C₆₀-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 incident monochromatic photon-to-current efficiency (IPCE) (6% at 480 nm for **69**, 14% at 340 nm for **70**) probably due to their low content of acceptor (**69**, 38.5%; **70**, 7–14%) compared to the usual content of bulk-heterojunction devices that can reach up to 80 wt% of fullerene derivatives.

In 2002 Nierengarten described the highly soluble polymer **71**.¹¹⁰ This macromolecule was blended together with MDMO-PPV and spin coated in order to prepare organic solar cells. However, even though some photovoltaic activity has been found, the overall performance was very low.

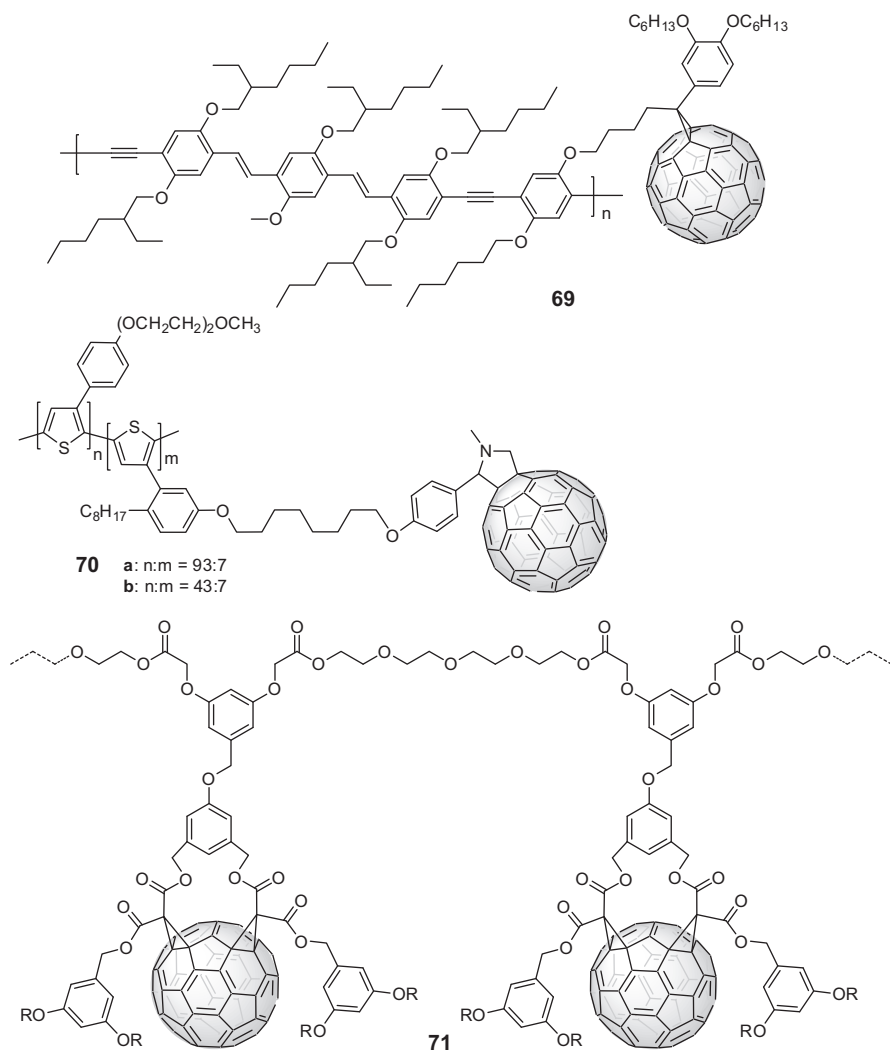


Figure 4.16 Polymers used in the fabrication of organic solar cells.

Drees, Sariciftci, and coworkers in 2005 succeeded in improving polyfullerene-containing organic solar-cell performances. They tried a new approach in which first the glycidol ester of 6,6-phenyl C₆₁butyric acid was prepolymerised in the presence of a Lewis acid as the initiator. Then, after spin coating the prepolymer in blend with P3HT, ring-opening polymerisation was completed by heating the photovoltaic device that showed 2% conversion energy efficiency, probably due to morphological stabilisation of the bulk heterojunction (**72**, Figure 4.17).¹¹¹ Even better performance was displayed by the amphiphilic diblock-copolymer **73** when added to a blend of PCBM:P3HT

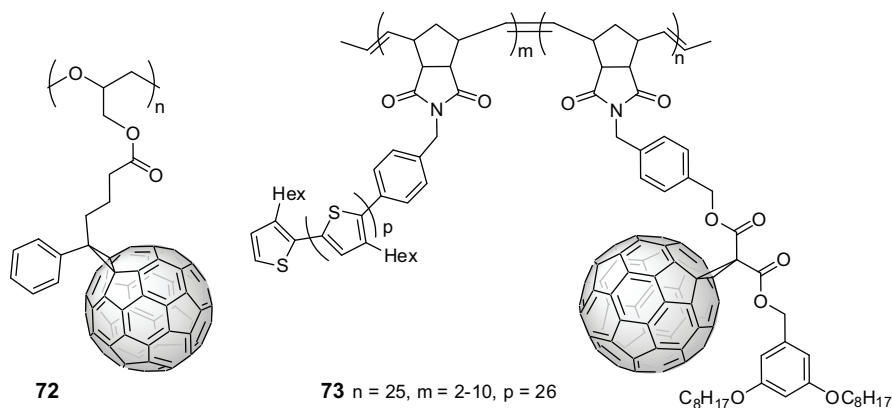


Figure 4.17 Structures of polymers employed in improved solar cells.

in 17 wt%.¹¹² The photovoltaic device prepared had an efficiency of 2.8%, together with enhanced stability of the devices against destructive thermal phase segregation. This improvement has been accounted for by the higher control in the blend morphology of the active layer due to the presence of fragments of P3HT in the polymer backbone that act as a compatibiliser between PCBM and P3HT.

It is interesting to note that, at the beginning of polymer-based photovoltaics, chemists devoted their attention almost exclusively to double-cable (DC) polymers in order to overcome the segregation phenomenon. Although recently some interesting examples of DC-based solar cell with interesting efficiency (1.59%)¹¹³ have been reported,¹¹⁴ nowadays this approach has been set aside, whilst the attention is strongly devoted to block-copolymers in solar cells,¹¹⁵ thanks to their natural tendency to self-assemble into periodic ordered nanostructures. Moreover, they can be employed in diverse manners to control the final material morphology. In this regard, several synthetic strategies have been designed, and a number of C₆₀-containing block-copolymers have been prepared and their morphological organisation has been reported.¹¹⁶

In 2010 Holdcroft and coworkers reported the synthesis in solid phase of block-copolymer **74** by annealing the azido-containing precursor polymer and PCBM (Figure 4.18).¹¹⁷ Photovoltaic devices prepared from these stabilised layers exhibited 1.85% power conversion efficiencies (PCE) which dropped to 0.93% after 3 h at 150 °C, whereas control P3HT/PCBM devices, initially displaying 2.5% PCE dropped to 0.5% over the same period. Analogously, Wudl, Heeger and coworkers described the synthesis, characterisation and application in photovoltaic devices of the novel block-copolymer **75**.¹¹⁸ After GRIM polymerisation, the P3HT fragment has been in turn copolymerised in the presence of styrene and a suitably functionalised acrylate monomer able to subsequently incorporate fullerene. The so-obtained rod-coil block-copolymer **75**, showed an interesting nanofibrillar structure and it has been used at various concentrations as surfactant/compatibiliser for the active

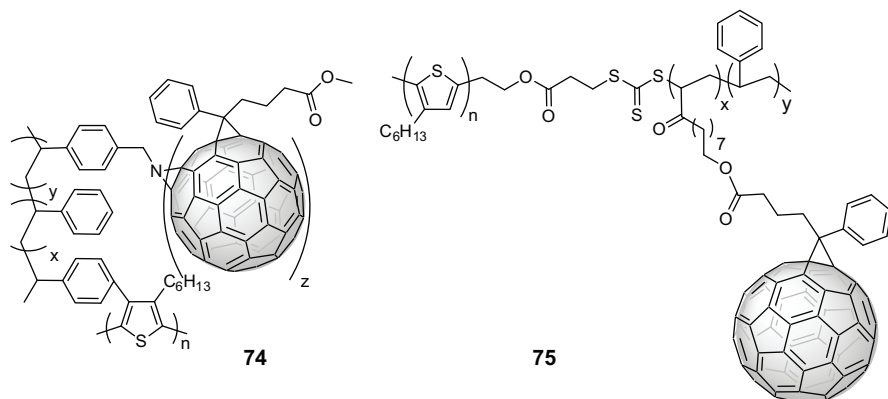


Figure 4.18 Block-copolymer used in photovoltaic cells.

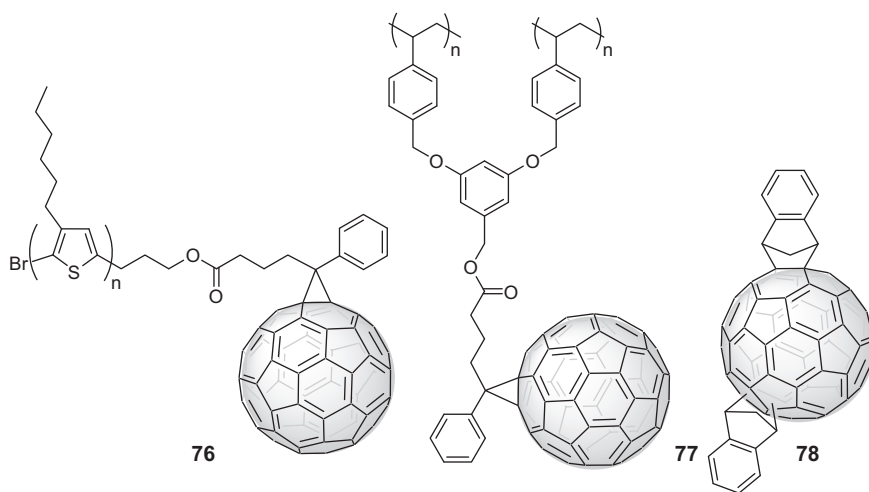


Figure 4.19 End-capped and crosslinked polymer used in solar cells.

layer of bulk-heterojunction solar cells in blends with PCBM. This approach resulted in a 35% increase of the photocurrent efficiency, rising from 2.6 to 3.5% when the copolymer was used in 5 wt%. The outstanding enhancement has been accounted for by the authors by the improvement in the bicontinuous interpenetrating network due to the compatibilising action of the copolymer, as also evidenced by AFM studies.

The same strategy has been exploited in 2010 by Jo, who employed the PCBM-end-capped polythiophene **76** in 2.5 wt%, as compatibiliser between PCBM and P3HT, suppressing large-scale phase separation of P3HT/PCBM composite (Figure 4.19).¹¹⁹ The resulting P3HT:PCBM:**76** bulk-heterojunction

solar cells exhibited excellent long-term thermal stability of device performance with a starting PCE of 2.8% that fell to 2.5% after 200 h at 100 °C, which corresponds to thousands of hours at 25 °C according to the Arrhenius model. On the other hand, a novel approach has been just described by Cheng and Hsu, which surely will presage a revolution in the field.¹²⁰ They generated *in situ* a robust crosslinked C₆₀ polymer (**77**), which allows sequential deposition of the active layer, avoiding interfacial erosion. The inverted solar cell ITO/ZnO/**77**/P3HT:PCBM/PEDOT:PSS/Ag showed an outstanding device characteristic with a PCE of 4.4% together with an improved cell lifetime with no need for encapsulation. The strength of the new approach is not the isolated good result but its wide and general application. In fact, some month later, the same author reported the results obtained employing another promising acceptor in an inverted bulk-heterojunction cell. They used fullerene bis-adduct **78** in a device with architecture ITO/ZnO/**77**/P3HT:**78**/PEDOT:PSS/Ag achieving the impressive value of 6.22% efficiency, which retains 87% of the magnitude of its original PCE value after being exposed to ambient conditions for 21 days.¹²¹ Very likely, incorporation of this crosslinked C₆₀ interlayer could become a standard procedure in the fabrication of highly efficient and stable multilayer inverted solar cells.

4.5 Outlook and Perspective

During the last two decades we have witnessed the development of a variety of new materials constituted by fullerenes and different polymers combining the singular properties of former with the many advantages for processing of the latter. As a result, new polymer materials exhibiting unusual structural, electrochemical, and photophysical properties have been obtained. The preparation of these fullerene-containing macromolecules has represented a big synthetic effort in which well-known synthetic protocols in modern organic chemistry have allowed a wide variety of chemical structures to be achieved, limited only by the imagination of chemists.

In this interdisciplinary field in which C₆₀-based polymers should afford unprecedented materials where the presence of fullerenes as photo- and electroactive components of the polymer structure, but also as a hydrophobic moiety in a hydrophilic polymer, should give rise to new properties of interest for the development of real technological applications. Actually, in some cases very promising materials have already been prepared, representing the starting point to be developed during the next few years. Polymers are certainly among the most important achievements that chemistry has given to society in terms of practical applications and, surely, the presence of fullerenes will open new avenues for remarkable materials. In this regard, 25 years after the discovery of fullerenes, the scientific community is looking for real applications of the new carbon allotropes. Once more, the ease of processability and availability of polymers could be the key for application of fullerenes for practical purposes

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