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REVIEW ARTICLE

POLYMERIC MODIFICATION AND FUNCTIONALIZATION OF [60]FULLERENE

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Abstract—This article reviews the developments in the polymerization and functionalization of C_{60}. C_{60} and its n-doped derivatives exhibit a variety of outstanding electronic, conducting, and magnetic properties. The combination of the advantages of this molecule with the properties of other materials such as polymers is very challenging and will probably become of great importance in the future. Results show that the C_{60} molecule, a special functional group, may be introduced into the main chain of an organic polymer to form a "pearl necklace" polymer, in which the [60]fullerene unit is part of the polymer chain, or into the side chain of a polymer as a pendant group to form a "charm bracelet" polymer. In addition, it may be mixed with other polymers to form C_{60}-doped polymers, and it also forms organometallic macromolecules and lattice-type polymers. In general, fullerene-containing polymeric materials may be prepared in four ways: (1) the reaction of C_{60} or a C_{60} derivative with a preformed polymer or a transition metal complex such as $Pd_2(dba)_3.CHCl_3$; (2) polymerization of a monomer containing [60]fullerene functional groups; (3) free radical copolymerization of C_{60} with a monomer; and (4) doping of C_{60} or C_{60} derivatives into polymer matrices. Unfortunately, the structures of some of the fullerene-containing polymers obtained are uncertain and a matter of speculation, and further detailed investigations using a variety of characterization techniques are required. The contents of this review are split into nine sections, as follows: introduction; organometallic polymers; charm bracelet polymers; pearl necklace polymers; dendritic macromolecules and star-like polymers; lattice-type polymers; covalent attachment of C_{60} on to polymer supports; C_{60}-doped polymers; and outlook and concluding remarks. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

In recent years, considerable interest [1–8] has been shown in the structure, properties and chemical reactivity of C_{60} owing to its potential applications in the fields of physics, chemistry and materials science. The spherical all-carbon I_h molecule [60]fullerene (C_{60}) has 12 pentagons, all of which are fully surrounded by hexagons (a total of 20) in a "corannulene-type" fashion [8] (Fig. 1). Considerable bond alternation and localization is found in X-ray crystal structures. All double bonds are located exocyclic to the pentagons, giving a radialene character [6] to the pentagons and a cyclohexa-1,3,5-triene character to the hexagons. The length of the short bonds (6-6 bonds) is ~1.38 Å, and that of the long bonds (6-5 bonds) is ~1.45 Å. Electrochemical methods [9–14] have demonstrated that C_{60} readily accepts electrons to form fulleride anions and is very difficult to oxidize but is readily reduced in multiple one-electron reduction steps, which suggests that fullerenes prefer to react with electron-rich reagents (nucleophiles) [8]. Theoretical calculations of the electronic structure of C_{60} have predicted an energetically low-lying, three-fold-degenerate lowest unoccupied molecular orbital (LUMO), which should readily accept up to six electrons in electrochemical reductions or which, in chemical conversions, should be occupied by the electrons transferred by the lone pair of an attacking nucleophile [8, 15].

Due to the richness of unusual structures and outstanding electric, conducting, magnetic and photophysical properties, including UV-visible absorption, photoluminescence and photoconductivity, of C_{60} and its derivatives, intense interest and activity are focused on covalent fullerene chemistry [16–20]. The chemical reactivity of C_{60} is that of a strained, electron-deficient polyalkene with rather localized double bonds [21]. The possible organic reactions of C_{60} are [22–24]: (1) the addition of 1,3-dipoles and dienes; (2) the addition of nucleophiles; and (3) the addition of radicals. One-step additions to C_{60}, namely the addition of OsO_4, transition-metal complexes or 1,3-dipoles, take place exclusively at the 6-6 bonds [23]. All these additions are exothermic and are presumably driven by the relief of strain in the C_{60} cage that largely results from the pyramidalization of its sp^2 C atoms [21, 25]. In the adducts, the functionalized fullerene C atoms change their hybridization from a trigonal sp^2 to a less strained tetrahedral sp^3 state. However, owing to the identical physical environment of each carbon atom on C_{60}, for chemical modification of C_{60} it is not easy to control the attaching sites on the C_{60} cage and the number of

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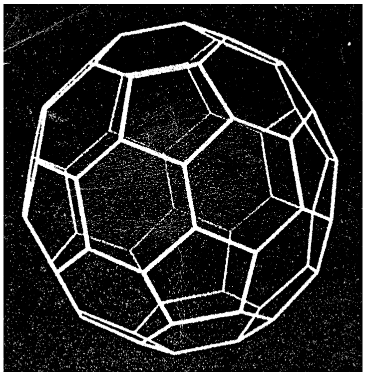


Fig. 1. View of I_h-C_{60} showing the isolation of a pentagon in a corannulene-type substructure [8].

the modified functional group, which leads to a huge number of different addition products which are impossible to isolate. Though there are already many papers concerning the chemical modification of C_{60}, most of the products reported are mixtures. Several methods are now available for the formation of C_{60} monoadducts [26–29]. Regioselective formation of multiple adducts has allowed the study of changes in chemical and physical properties that occur when the conjugated fullerene chromophore is reduced during an increase in functionalization [8].

The systematic development of covalent fullerene chemistry provides an unprecedented diversity of tailor-made three-dimensional building blocks for technologically interesting materials. Obviously, the combination of the outstanding characteristics of [60]fullerene with the desired properties of other materials such as the polymers poly(*N*-vinylcarbazole), polystyrene, poly(3-alkylthiophene) etc., is very challenging and will probably become of great importance in the future. Results show that the C_{60} molecule acting as a special functional group can be introduced into the main chain of an organic polymer to form a “pearl necklace” polymer, or into the side chain of a polymer as a pendant group to form a “charm bracelet” polymer. In addition, it may be mixed with other polymers to form a C_{60}-doped polymer, and it also forms organometallic macromolecules, and lattice-type polymers. This review concerns only those several branches of fullerene-containing macromolecular chemistry in which chemists and physicists are interested.

ORGANOMETALLIC POLYMERS OF BUCKMINSTERFULLERENE

An interesting feature of C_{60} is the high reactivity of its surface towards metallic species [30–33]. Nagashima and co-workers [34] reported an application of this particular reactivity of C_{60} with transition metal species in the synthesis of the first fullerene-based organometallic polymer, $C_{60}Pd_n$ ($n = 1$–3). The reaction of C_{60} with a palladium complex, $Pd_2(dba)_3.CHCl_3$ (dba = dibenzylideneacetone), results in facile replacement of the dba ligand by C_{60} to form $C_{60}Pd_n$, [see equation (1)], which is neutral, amorphous and stable to air.

$$C_{60} + n/2Pd_2(dba)_3.CHCl_3 \rightarrow C_{60}Pd_n + 3n/2\ \mathrm{dba} + CHCl_3 \quad (1)$$

The proposed mechanism for the formation of $C_{60}Pd_n$ is illustrated in Fig. 2. The palladium to C_{60} ratio (n) can be varied by thermal disproportionation. It is of interest that $C_{60}Pd_n$ ($n > 3$) was formed from a 4:1 mixture of $Pd_2(dba)_3.CHCl_3$ to C_{60}. In this case, an excess of palladium atoms would be deposited on the surface of $C_{60}Pd_3$. The heterogeneous hydrogenation of diphenylacetylene occurred with a catalytic amount of $C_{60}Pd_{3.5}$ in cyclohexane, whereas catalytic activity was not observed with $C_{60}Pd_n$ ($n < 3$). This result indicates that surface palladium species exist on $C_{60}Pd_{3.5}$ but not on $C_{60}Pd_n$ ($n < 3$).

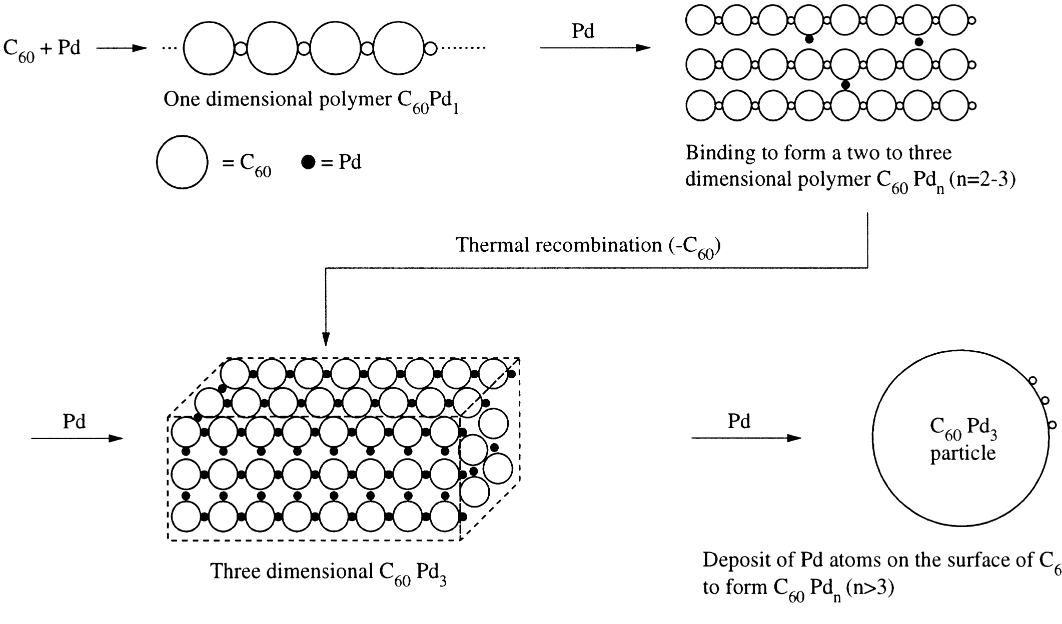
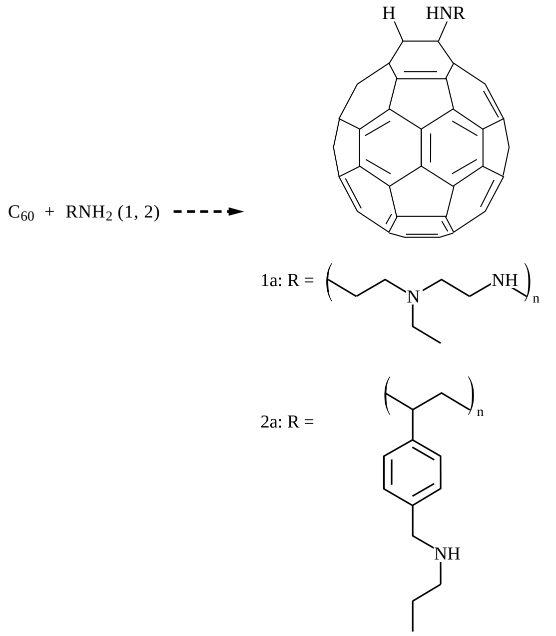


Fig. 2. Proposed mechanism for the formation of $C_{60}Pd_n$.



Scheme 1. Covalent binding of C_{60} to an amino polymer.

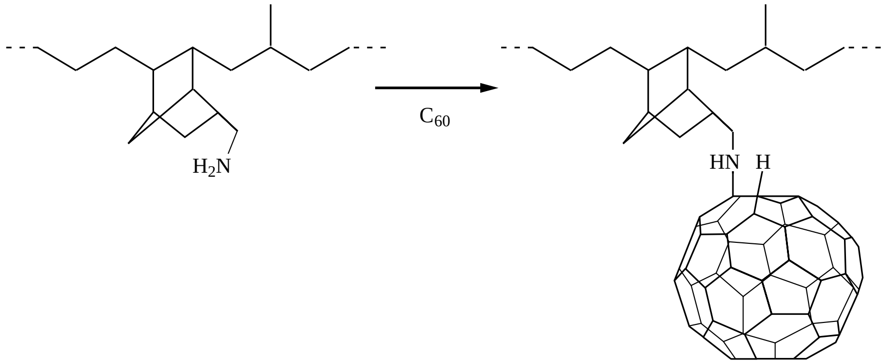
"CHARM BRACELET" POLYMERS

The C_{60} molecule may be introduced into the side chain of a polymer as a pendant group to form "charm bracelet" polymers in two ways: (1) the reaction of C_{60} or a C_{60} derivative with a preformed polymer; and (2) polymerization of a monomer containing [60]fullerene functional groups. These polymers have several intrinsic advantages over "pearl necklace" polyfullerenes which are mainly due to the defined, stereochemical arrangement of the C_{60}. The syntheses of charm bracelet polymers and pearl necklace polymers are being actively pursued.

Shi *et al*. [35] described the syntheses and characterization of two charm bracelet-type polymers containing C_{60} molecules dangling from the polymer backbone. The remarkable retention of the electronic structure of the C_{60} moieties as witnessed by UV-vis spectroscopy and cyclic voltammetry is a very encouraging result, which augurs well for the observation of unusual fullerene-type properties in products fabricated from these polymers. Geckeler and Hirsch [36] prepared C_{60}-on-chain polymers (Scheme 1) by titrating toluene solutions of C_{60} with the aminopolymers: **1**, poly(ethylene imine); **2**, poly[4-[[(2-aminoethyl)imino]methyl]styrene]; and **3**, poly(propylene imine). The coupling to the polymer chain proceeded according to the well-known amine addition to fullerene double bonds [37, 38]. Polymer **2a** can be dissolved in toluene and carbon disulfide, thus being the first soluble fullerene-containing polymer.

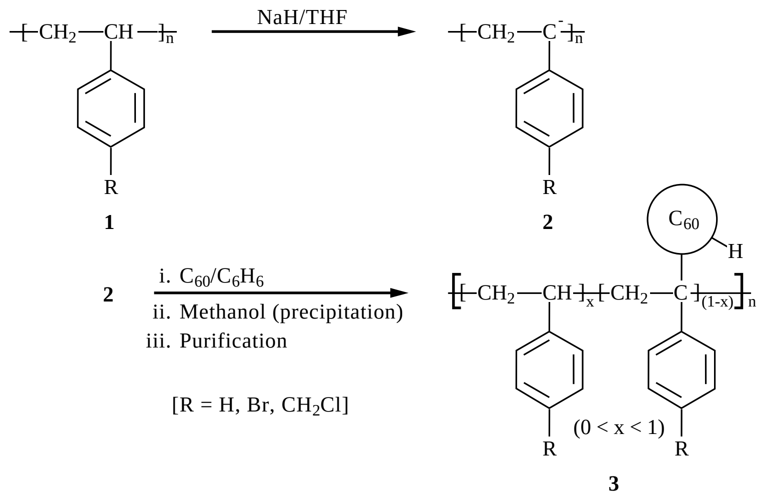
As shown in Scheme 2, fullerenes were found to add to amine-containing flexible hydrocarbon polymers such as ethylene propylene terpolymer(EPDM-amine) to obtain novel C_{60}-functionalized polymers [39]. These materials are soluble in common solvents.

A new route for the preparation of soluble fullerenated polymers via the reaction of fullerenes, particularly C_{60}, with the carbanion intermediates of such polymers as polystyrene, poly(*p*-bromostyrene) and poly(vinylbenzylchloride) etc, has been demonstrated [40–43]. Both the stereo-electronic effect and the steric hindrance of C_{60} have an important influence on the structure and physical properties of these polymers. A typical synthetic method is shown in Scheme 3. Addition of the bulky C_{60} molecule to polystyrene by a novel organometallic reaction modified the optical properties of the parent polystyrene considerably. The lattice periodicity of pure PS film is subject to some perturbation or distortion in varying degrees due to the covalent attachment of the bulky C_{60} moiety to the polymer backbone. C_{60}–PS copolymers possess a new energy band structure with indirect forbidden bands when compared with the parent PS. Dai *et al*. [44] have also demonstrated that fullerene-functionalized polymers with multiple pendant "buckyballs" dispersed along their polymer backbones can be obtained through the lithiation of polydienes followed by addition of C_{60} to the lithiated polymer chains. The highly soluble and fusible materials thus prepared may open up novel applications for the buckyballs.



Scheme 2

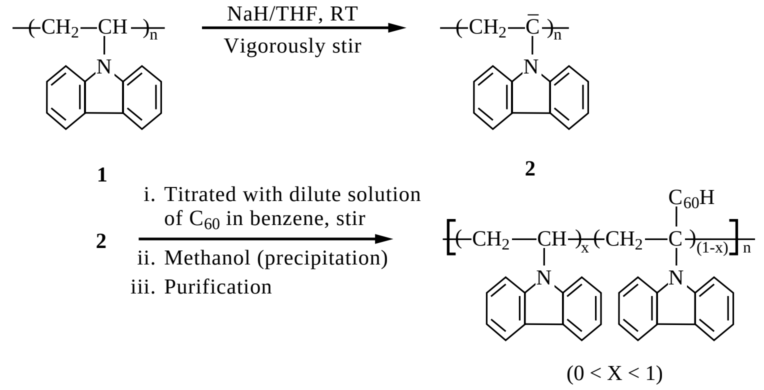
Photoconductivity [45, 46] is one of the commercially significant photoresponses of polymeric systems. It is fundamental to photodetection and electrostatic imaging, as well as a number of related processes. Photoconductivity and its component processes, charge generation and charge transport, can be controlled by chemical modification of



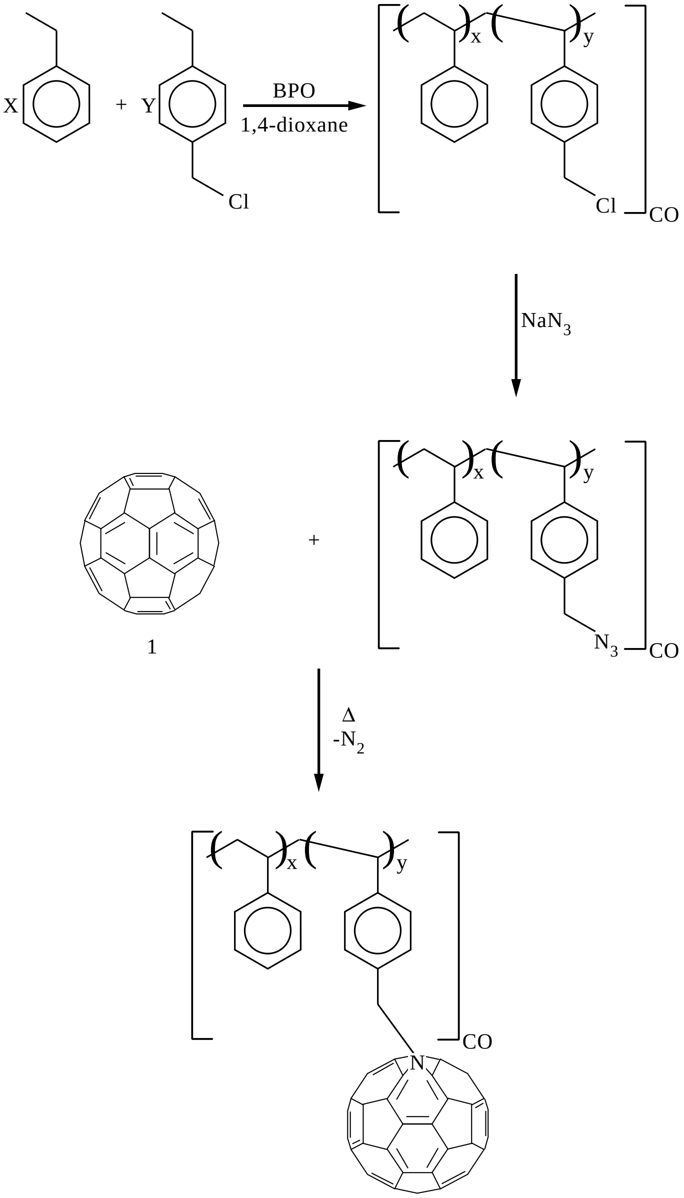
Scheme 3

polymers [47]. The considerable interest in the structural characterization and photophysical properties, including UV-visible absorption, photoluminescence and photoconductivity, of fullerene-based polymeric photoconductors has increased rapidly in recent years. However, to date all researchers have focused their attention on photoconductive investigations of simple blends of fullerenes and polymers. Although the doping of hole-transporting, donor polymers with electron acceptors results in extended spectral sensitivity as well as enhanced photogenerated efficiency, there are, however, problems associated with this approach. These problems stem from the tendency for the dopant molecules to aggregate in the solid state, leading to difficulty in achieving homogeneous dispersions and ultimately phase separation at high loadings. Chemical modification of the polymer matrix can circumvent these problems.

Chen *et al.* [48–53] first reported the synthesis of C_{60} chemically modified polymeric photoconductors such as C_{60}-modified poly(*N*-vinylcarbazole) (PVK) and its bromine- and iodine-modified derivatives, and described the results of an investigation into their electrochemical behaviors and the effect of C_{60} chemical modification on the structure of the organic polymers. The soluble fullerenated poly(*N*-vinylcarbazole) was prepared under a purified nitrogen atmosphere as shown in Scheme 4. The confirmation of the structure of this material was carried out by a viariety of techniques such as UV-vis, FTIR, ESR, XRD, ^{13}C NMR, DSC, TGA, SEM, TOFMS, transient absorption (TA) and cyclic voltammetry. Addition of the C_{60} moiety, a powerful electron acceptor (EA = 2.6–2.8 eV), to poly(*N*-vinylcarbazole) by chemical reaction results in a marked enhancement in photoconductivity relative to pure PVK and C_{60}/PVK mixtures (C_{60}-doped PVK) [49]. The photo-induced discharge rates for pure PVK, C_{60} chemically modified PVK (C_{60}–PVK copolymer) and C_{60}-doped PVK under the same experimental conditions are found to be in the following order: C_{60}–PVK copolymer > C_{60}-doped PVK > pure PVK. A "charge-transfer" interaction between the positively charged carbazole, resulting from charge transfer towards C_{60}, and near-neighboring carbazole moieties of the resultant copolymer may be credited with bringing about the enhanced photoconductivity relative to PVK itself via increased photogeneration of charge carriers. The photoconductive performance in the copolymer is closely related to the fullerene level in the polymer. A qualitative comparison of the



Scheme 4

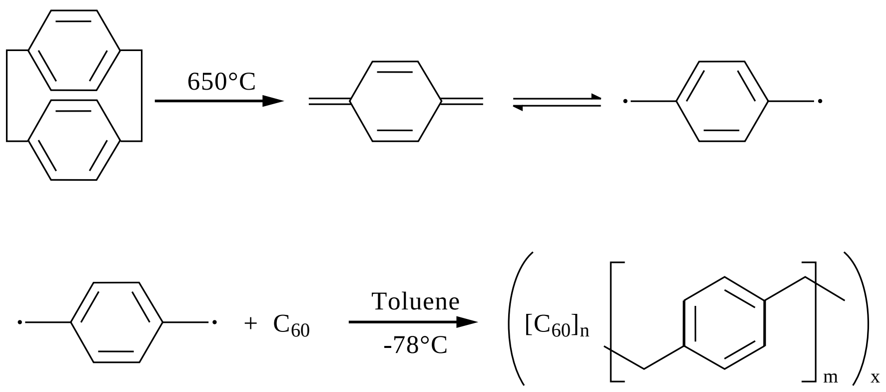


Scheme 5

submicromorphological structures of PVK, C_{60}, C_{60}–PVK, and C_{60}-doped PVK has been given.

In addition, Chen *et al.* also reported the first electrochemical intercalation of lithium into photoconductive fullerenated poly(*N*-vinylcarbazole). A mechanism for the electrochemical intercalation reaction is suggested for the discharge of the first Li-fullerenated poly(*N*-vinylcarbazole) battery on the basis of experimental data obtained from cyclic voltammetry. FTIR, XRD, and ESR. The above battery has a higher open-circuit voltage (ca. 3.2 V) than that without the fullerene, and its discharge may be ascribed to the electrochemical intercalation process of lithium into fullerenated poly(*N*-vinylcarbazole) [51]. Very recently, Benincori *et al.* [54] prepared the first conjugated electroconducting "charm bracelet" polymer: polythiophene with covalently bound fullerene moieties. One of the potential areas of interest in associating a p-type conjugated polythiophene and an n-type fullerene lies in the possibility of charge transfer between these two moieties.

In 1994, Hawker [55] reported a simple and versatile method for the synthesis of "charm bracelet" type C_{60}–polystyrene copolymers. He found that simple linear polymers containing azide functional groups, such as azidomethyl-substituted polystyrenes, can be used and would be expected to react with C_{60} to give soluble processable polymers. To investigate the versatility of this method, the synthesis of a mainly monosubstituted polystyrene copolymer from azido-substituted polystyrene is shown in Scheme 5. In addition, pendant "charm bracelet" type C_{60}–PS polymers are prepared by



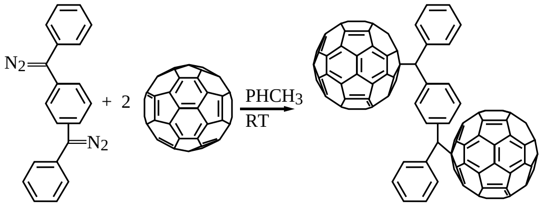
Scheme 6

fullerenating polystyrenes in Friedel–Crafts type reactions [56]. However, puzzlingly, only in the "fresh" case are these materials soluble in such organic solvents as chloroform, etc., whereas Olah *et al.* [57] obtained only a highly crosslinked fullerenated polystyrene using a similar Friedel–Crafts type reaction. Therefore, the synthesis and structural characterization of the soluble fullerenated polymers seem to require further detailed investigation.

"PEARL NECKLACE" POLYMERS

The C_{60} molecule may be introduced into the main chain of organic polymers to form "pearl necklace" polymers, in which the [60]fullerene unit is a part of the polymer chain. However, most of these products will be crosslinked, insoluble and intractable, and one needs to approach their preparation by either a precursor polymer route or the incorporation of solubilizing groups. Loy and Assink [58] have reported the synthesis of a C_{60}–*p*-xylylene copolymer (Scheme 6). This polymer is a highly crosslinked insoluble material. The synthesis of insoluble two-pearl sections of the pearl necklace polymers *m*-phenylene- and *p*-phenylenebis(phenylfulleroids) has also been described by Suzuki and co-workers [59] (Scheme 7).

The fullerene-terminated polymers are intriguing from a chemical point of view, e.g. for the preparation of well-defined stars based on C_{60}. Weis *et al.* [60] prepared the first soluble well-defined fullerene-end-capped polystyrenes by reaction of amino-terminated polystyrene with C_{60} and subsequent fractionation (Scheme 8). The polymers formed clear and homogeneous films, i.e. no micro- or nanophase separation was observed. Micro- or nanophase separation for physical blends of C_{60} with polystyrene is common.



Scheme 7

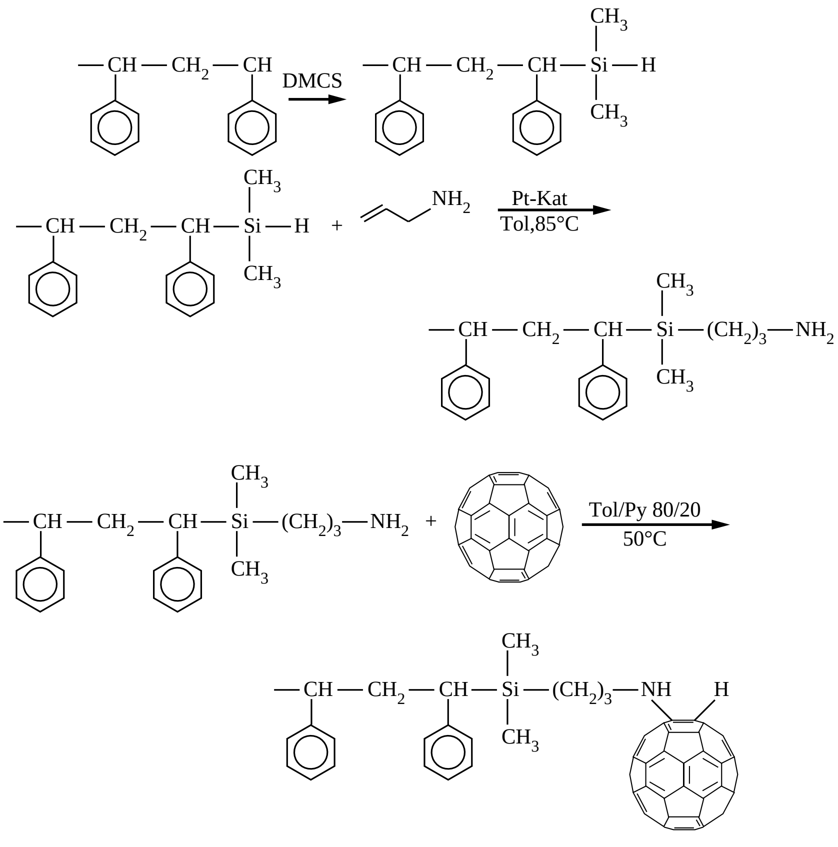
It is worth noting that stitching the C_{60} molecules together might create a linear chain polymer, a "pearl necklace" of buckyballs [61] (Fig. 3). In addition to being chemically elegant and intrinsically beautiful, such a material might be expected to exhibit interesting electronic and nonlinear optical properties.

DENDRITIC MACROMOLECULES AND STAR-LIKE POLYMERS

Dendritic macromolecules are themselves a novel area of increasing interest [62]. A potential advantage of the application of polymer chemistry to the functionalization of fullerenes is the encapsulation of fullerene clusters having conducting capabilities by a polymeric insulating layer, which also alters the physical properties and provides novel materials for investigation of the properties of individual isolated carbon clusters. Hawker *et al.* [63] described the preparation of dendrimer-modified C_{60} by the controlled one-step cyclo-addition reaction of a dendritic azide with C_{60} (Scheme 9). The dendrimer chosen was the terminally deuterated fourth-generation azide, D_{112}-[G-4]-N_3 ($M_r = 3429$ amu), which was prepared by reaction of the corresponding bromide with sodium azide in dimethyl sulfoxide. The physical properties of the dendritic fullerene obtained show influences from both the parent dendrimer and C_{60}.

Wooley *et al.* [64] have demonstrated the functionalization of the surface of buckminsterfullerene with a controlled number of dendritic macromolecules (Scheme 10). The dendritic macromolecules dramatically improved the solubility of the fullerenes and should provide a more compact insulating layer around the clusters than would linear polymers, while maintaining the globular shape of the structures.

Chen *et al.* [65] reported on the preparation and structural characterization of a novel star-like $C_{60}(CH_3)_x(PAN)_x$ copolymer by the reaction of living *n*-butyl-terminated polyacrylonitrile (PAN) with C_{60} in a heterogeneous medium, followed by a capping reaction with methyl iodide (see Scheme 11). Multiple PAN arms are attached to the C_{60} core. The chemical



Scheme 8

and physical properties of this polymer depend largely on the concentrations of the fullerene covalently bound to the polymer matrix or on the chain length of the PAN units attached to a C_{60} center. The *n*-butyl-terminated polyacrylonitrile (PAN) and novel $C_{60}(CH_3)_x(PAN)_x$ copolymers have been pyrolyzed [66] under vacuum at between 25 and 475°C. The *in situ* infrared absorption measurements demonstrated that the nitrile groups of the polymers disappear gradually as heating progresses, and conjugated C=N chains appear. As pyrolysis proceeds, evidence for aromatic ring formation is found. Below 200°C, a few of the nitrile groups begin to form conjugated chains. In consideration of the existence of the strong steric hindrance effect and dipole and electric effects in the copolymer, a reasonable pyrolysis scheme is suggested. *In situ* paramagnetism has been investigated using a variable-temperature ESR technique. The unique temperature dependence of the ESR spectra is intriguing. These results indicate the evolution of radical sites during pyrolysis and the delocalization of carriers, as well as the formation of conjugated double bonds by pyrolytic modification. Finally, the morphological structure and electric properties of the above samples and their pyrolytic products are also described. Similar star-like $C_{60}(PMS)_{1\text{–}3}(CH_3)_{1\text{–}3}$ copolymer have also been prepared by Yu and co-workers [67].

Urethane-connected polyether star polymers utilizing fullerenol as a molecular core were synthesized [68] as a soluble material containing six chemically bonded polymer arms per C_{60} on average, with a narrow distribution of the number of arms per molecule and a polydispersity index of 1.45 (Scheme 12).

In 1995, Chiang *et al.* [69] reported the remarkable advantages of incorporation of polyhydroxylated fullerenes in the synthesis of poly(urethane-ether) networks, giving high-performance elastomers with greatly enhanced tensile strength, elongation, and

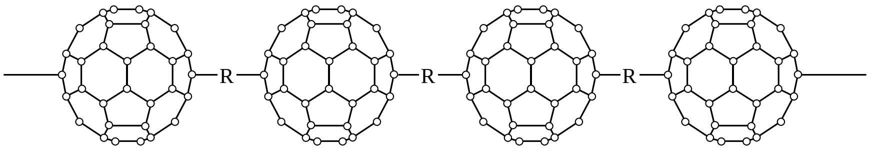
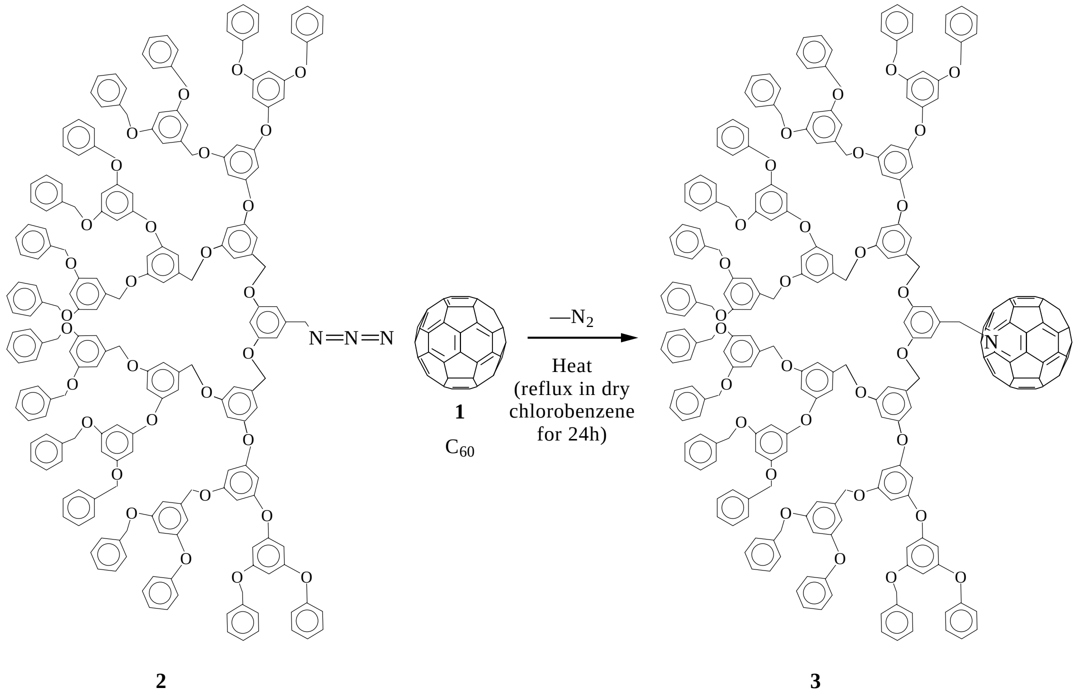


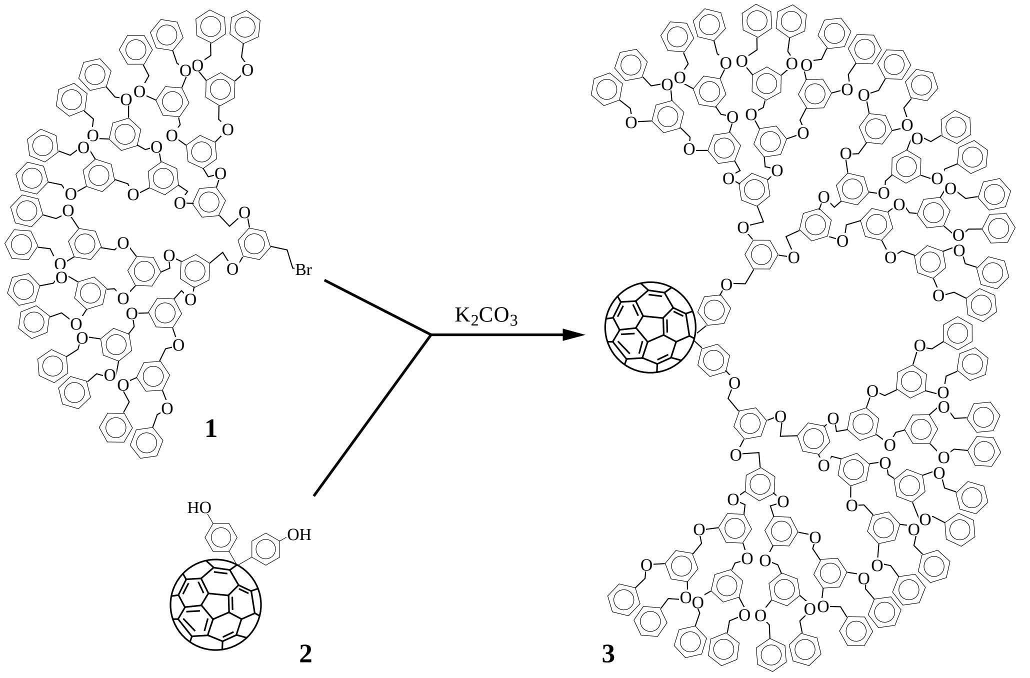
Fig. 3. Hypothetical fullerene polymers. Solution reactions of C_{60} and other molecule might produce something like the upper structure, which shows an adduct R bridging adjacent fullerenes in a cyclopropane bonding configuration (R bridges a hexagon, with hexagon fusion on each molecule). All carbon chain obtained by [2 + 2] cycloaddition [61].



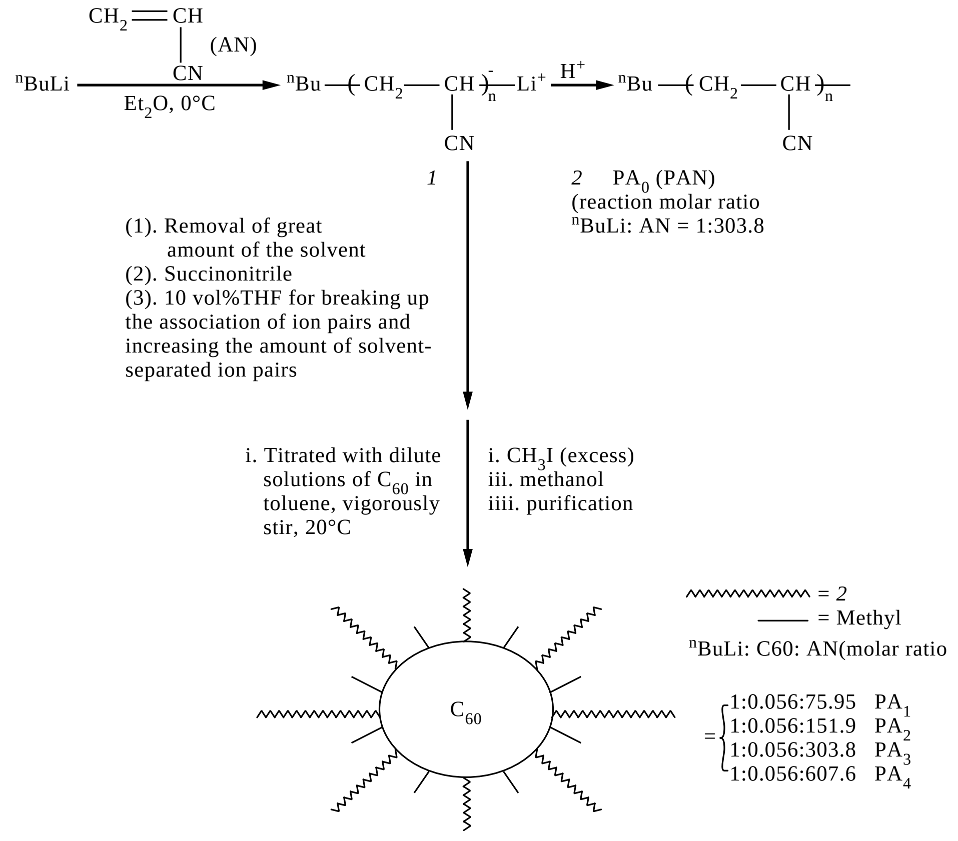
Scheme 9

thermal mechanical stability, in comparison with their linear analogs or conventional polyurethane elastomers crosslinked by trihydroxylated reagents (Scheme 13).

The reaction of living polystyrene (PS) carbanion with C_{60} gives novel star-like materials with the formula $C_{60}(PS)_x$ [70, 71]. These materials were characterized by gel permeation chromatography (GPC), ^{13}C NMR, transmission electron microscopy (TEM) and small-angle neutron scattering (SANS). They are highly soluble and melt processable and as such they may be spin-coated, solvent-cast or melt-extruded to give films and fibers having high concentrations of the fullerene covalently bound to the polymer matrix. Cloutet *et al*. [72] reported the functionalization of the six branch termini of the hexa



Scheme 10



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$C_{60}(CH_3)_x(PAN)_x$

Scheme 11

arm star-shaped polystyrene polymers with azido, amino and C_{60} groups. This is the first example of a star polymer containing a precise number of C_{60} units.

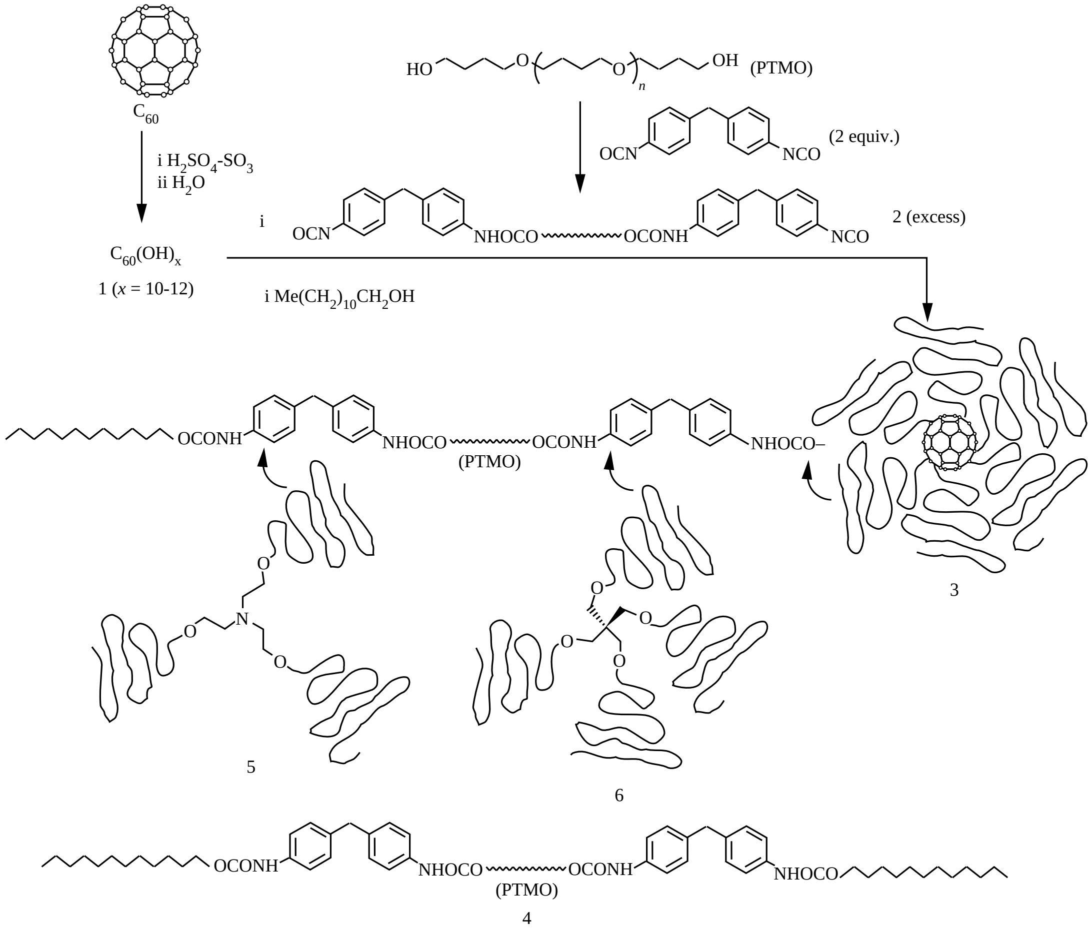
Most recently the reactivity of C_{60} towards free radicals has been exploited to obtain C_{60}-containing polystyrene using standard free radical polymerization conditions [73–76]. For example, Cao and Webber [74] reported a very simple method for direct incorporation of C_{60} or C_{70} into polystyrene by direct free radical copolymerization under routine conditions. While a great deal remains to be done to characterize fullerenes as comonomers in free radical polymerization, this method is so direct and simple that it may be of interest to a wide range of 1av researchers working in the area of fullerene chemistry. Bunker and co-workers [75] have also prepared star-like C_{60}–styrene random copolymers with different C_{60} contents using bulk and solution polymerization methods. These copolymers have significantly different spectroscopic properties from both polystyrene and C_{60}. A proposed copolymer structure is shown in Fig. 4. The role of C_{60} in the free radical polymerization of styrene is likely to be that of retarding the free radical polymerization of styrene and it results in polymers containing stable free radicals [73]. However, the polymers obtained by such free radical polymerization are mainly mixtures because of multiple additions of radicals to C_{60}.

LATTICE-TYPE POLYMERS

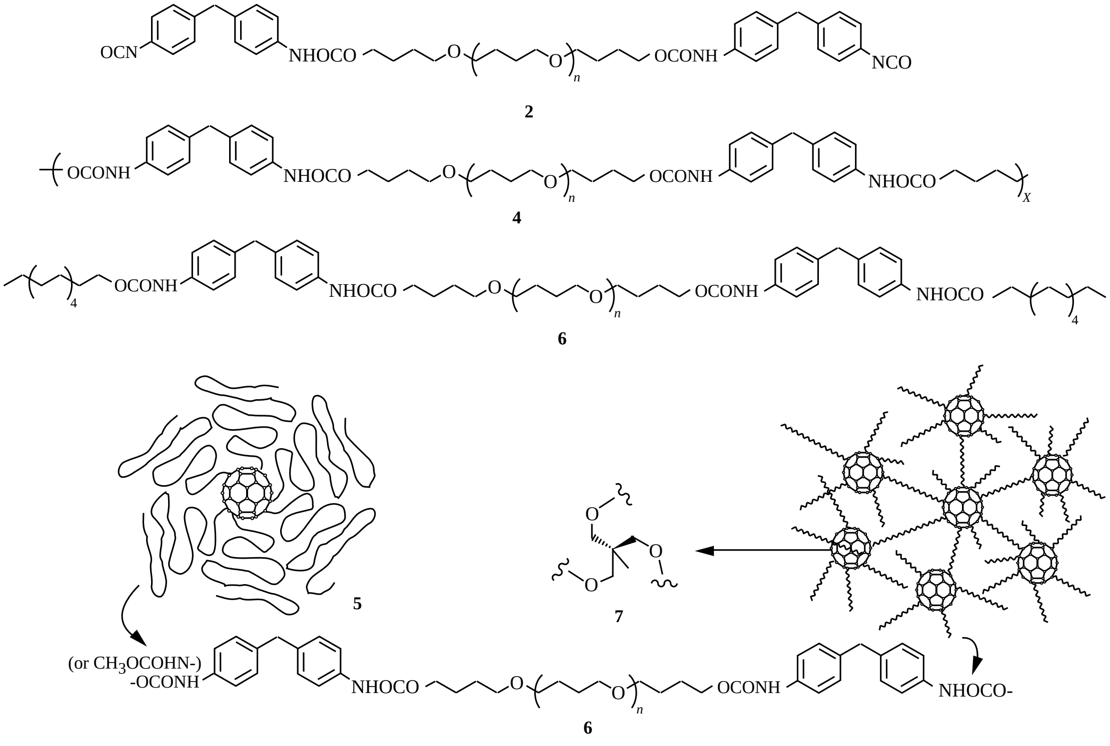
In 1993, Taylor and Walton [77] proposed a lattice-type polymer which is a two- or three-dimensional variant of the "pearl necklace" polymers. Nigam *et al.* [78] reported a simple synthesis of an adduct of [60]fullerene and 2-methylaziridine (approx. composition 1:10, Scheme 14), and the preparation of lattice-type polymers from it via aziridine ring-opening polymerization (the aziridine rings are very susceptible towards nucleophilic addition, and it is possible to crosslink phenolic compounds such as novolacs or bisphenols). These products are three-dimensional polymers containing [60]fullerene with low coefficients of friction and good wear properties, which bode well for their potential use as solid lubricants.

COVALENT ATTACHMENT OF C_{60} ON TO POLYMER SUPPORTS

Bergbreiter and Gray [79] reported their work which takes advantage of C_{60} reactivity by grafting electrophilic C_{60} moieties on to a pregenerated lithiated polyethylene surface. Polyethylene films functionalized with diphenylmethyl groups are deprotonated to form a nucleophilic lithiated surface which is in turn used to covalently bind C_{60} to polyethylene. Both the steric effects of a diphenyl-



Scheme 12



Scheme 13

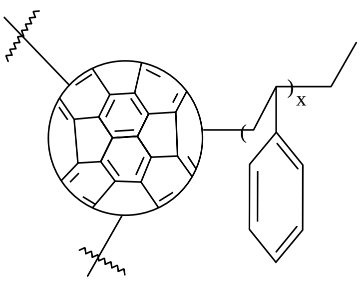
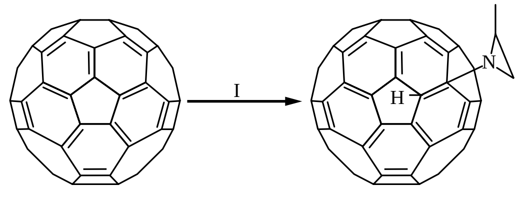


Fig. 4. A proposed structure of the star-like C_{60}–styrene random copolymer.



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Scheme 14. Reagents and conditions: 2-methylaziridine (30 equiv.), benzene, room temperature, for several days.

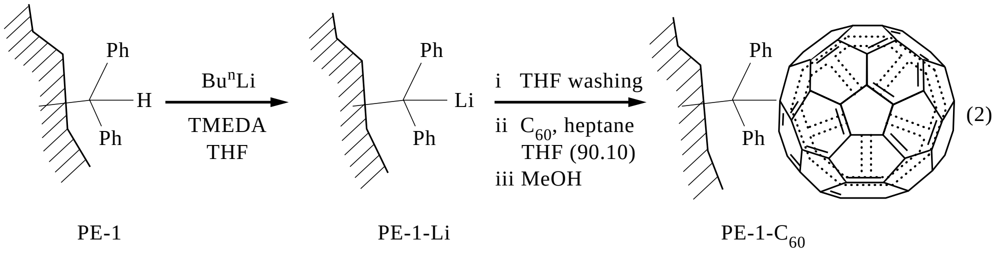
methyl group and the entropic constraints of a surface should preclude polysubstitution. The reaction process is as follows:

$$CH_3CH_2CH_2CH_2Li \xrightarrow[\text{TMEDA.heptane}]{CH_{60}=CH_2.207\ \text{kPa}}$$

$$CH_3CH_2(CH_2CH_2)_nCH_2CH_2Li \xrightarrow[\text{ii MeOH}]{\text{i } H_2C=CPh_2} (1)$$

$$\underset{1}{CH_3CH_2(CH_2CH_2)_{n+1}\,CH_2CHPh_2} \xrightarrow[\text{ii film casting}]{\text{i PE-H.110°C.PhMe}} (1)$$

$$\underset{\text{PE-1}}{\text{PE-H}/CH_3CH_2(CH_2CH_2)_{n+1}\,CH_2CHPh_2}$$



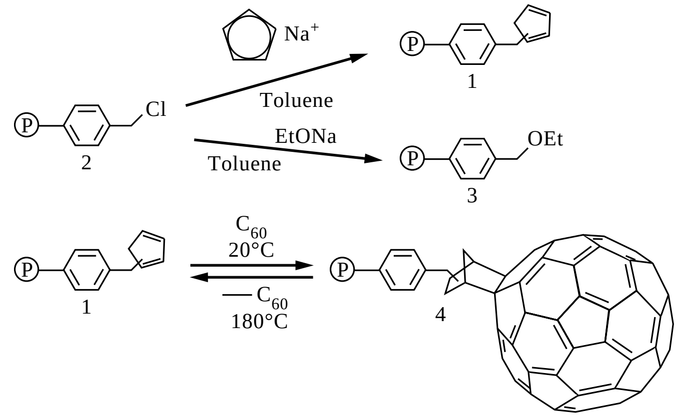
Scheme 15

Fullerenes readily undergo Diels–Alder cycloaddition with a variety of reactive dienes, including anthracene and cyclopentadiene [80]. These adducts are generally thermally unstable, undergoing cycloreversion to their component molecules upon heating [81, 82]. To determine the applicability of Diels–Alder cycloadditions to the formation of polymer-bound fullerenes, Guhr and co-workers [83] investigated the synthesis of cyclopentadiene-functionalized polymers (Scheme 16). This addition has been shown to be readily reversible, allowing recovery of C_{60} upon heating of the resin.

C_{60}-DOPED POLYMERS

Fullerenes are known to be good electron acceptors (EA = 2.6–2.8 eV). They have thus been considered to be hosts for dopants which are, in most cases, donors. Hence various donor dopants were doped into fullerenes and their derivatives. Wang [84] reported the preparation of photoconducting films of polyvinylcarbazole (PVK) doped with fullerenes (a mixture of C_{60} and C_{70} in the ratio of approx. 85:15). It is said that the performance of this material is comparable with some of the best photoconductors available commercially, such as thiapyrylium dye aggregates [85].

The wavelength dependence of photoconductivity is essentially determined by the absorption spectrum of the fullerenes, with the active range extending from about 280 to 680 nm. Figure 5 gives a qualitative comparison of the photoinduced discharge curves for PVK and fullerene-doped PVK. In 1993, Wang and co-workers also reported that fullerenes can be doped into polysilane to greatly enhance its charge-generation efficiency [86]. Polysilanes are usually not recognized as good electron donors, yet this study indicates the existence of efficient excited-state electron transfer between fullerenes and polysilanes. Xu *et al.* [87] also reported the photoconductivity of fullerene-doped zinc phthalocyanine. However, a partial incompatibility of fullerenes and polymer matrices lead to difficulties in achieving homogeneous dispersions and ultimately phase separation at high



Scheme 16

loadings. For this reason, the photophysical performance of C_{60}-doped polymers would be unstable, and meanwhile the active range of the absorption spectrum of these materials cannot meet practical needs. Chemical modification of the polymer matrix can circumvent these problems [47].

Evidence for the photoinduced electron transfer from the excited state of poly[2-methoxy,5-(2′-ethylhexyloxy)-*p*-phenylene vinylene] (MEH-PPV) on to C_{60} has been reported [88, 89]. Photoinduced absorption (PIA) studies demonstrate a different excitation spectrum for the composite compared to that for the separate components, and the photoinduced electron resonance signal exhibits the spin-labeled signatures of both the conducting polymer cation and the C_{60} anion. It is interesting that the carrier collection efficiency (η_c) and energy conversion (η_e) of polymer photovoltaic cells were improved by blending the semiconducting polymer with C_{60} or its functionalized derivatives [90]. The schematic diagram of the photoinduced charge transfer process in MEH-PPV–C_{60} donor/acceptor blends is shown in Fig. 6. Lee *et al.* [91] have investigated the effect of photoinduced electron transfer on the photoconductivity (PC) of conducting polymer–C_{60} films by comparing the photoconductivity (carrier generation and carrier transport) of the conducting polymer sensitized with C_{60} with that of the conducting polymer (MEH-PPV or P3OT [poly(3-octylthiophene)]) alone (see Figs 7 and 8). Both the magnitude and the lifetime of the transient PC increase substantially on increasing the concentration of C_{60}. As a result, this sensitization of conducting polymers by C_{60} is effective because the electron transfer rate is ultrafast ($<10^{12}$ sec^{-1}).

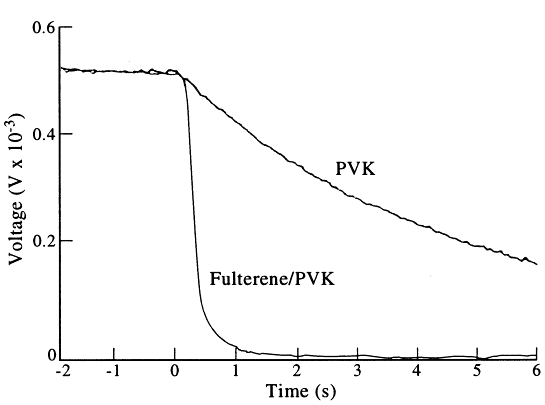


Fig. 5. Qualitative comparison of the photoinduced discharge curves for pure PVK and fullerene-doped PVK under the same experimental conditions. A tungsten lamp (50 mW cm^{-2}) is used as the light source.

Morita *et al.* [92] prepared a poly(3-alkylthiophene)/C_{60} junction device. The photovoltaic effect in this device was observed. The current–voltage characteristics were found to depend on the wavelength of the illuminating light. Wei *et al.* [93] presented their preliminary results on doping emeraldine bases (EB) prepared from polyanilines (i.e. polyaniline and polytoluidine) with fullerenes, including C_{60} (purity > 99%) and a mixture of C_{60} and C_{70} (75:25 molar ratio), in *N*-methylpyrrolidin-2-one (NMP)–toluene (50:50 by volume) solution at ambient temperature. The conductivities of the EB of polyaniline as free-standing, solution-cast films were found to increase significantly to ca. 10^{-4} S cm^{-1} at a fullerene content of ca. 1 mol%. It should be noted that further increases in fullerene content may not necessarily improve the conductivity to the values obtained from the conventional doping process. This could be attributed to the relatively large sizes of the fullerene molecules, which, as dopants, might result in distortion of the conjugation and coplanarity of the polymer backbones and in an increase in the interchain distance. Thus, both intra- and interchain charge transfer processes would be hindered, leading to a lower conductivity.

OUTLOOK AND CONCLUDING REMARKS

As a new form of carbon, C_{60} has generated considerable recent interest in the fields of physics, chemistry, life science [5, 94], materials science, etc. Polymeric fullerene derivatives are highly intriguing in view of the peculiar electro-optical, magnetic and chemical properties of materials containing C_{60} homogeneously dispersed in polymer matrices [95]. Covalent attachment of C_{60} to specific polymers may allow combination of the outstanding characteristics of fullerene with those of the polymeric matrix. Polymer-bound C_{60} should be easily processable into

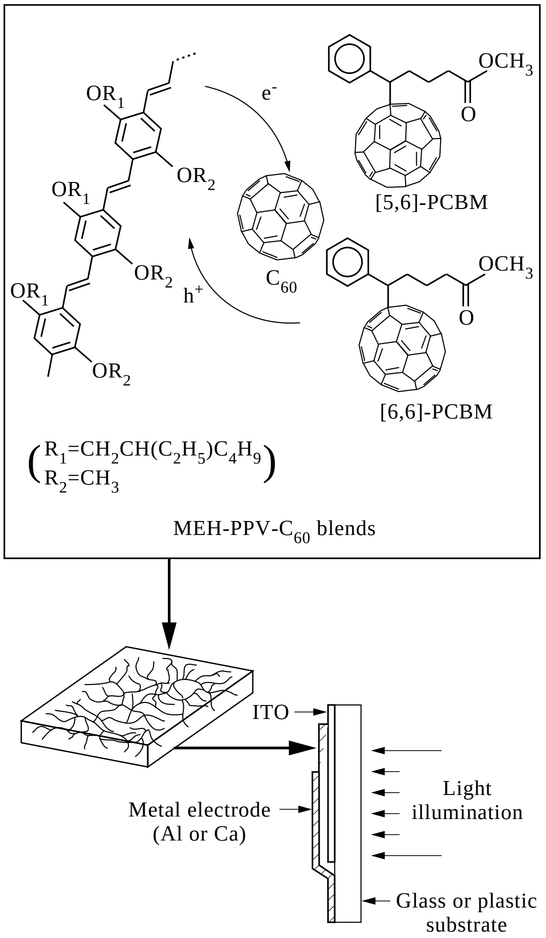


Fig. 6. Schematic diagram of the photoinduced charge transfer process in MEH-PPV–C_{60} D-A blends. The structures of the two soluble C_{60} derivatives used (denoted as [6,6]PCBM and [5,6]PCBM) are included. When cast as a film, the D and A species phase-separate into a bicontinuous network (bulk heterojunction material), as shown schematically. The structure of the photovoltaic cell fabricated with this bulk heterojunction material is sketched at the bottom [90].

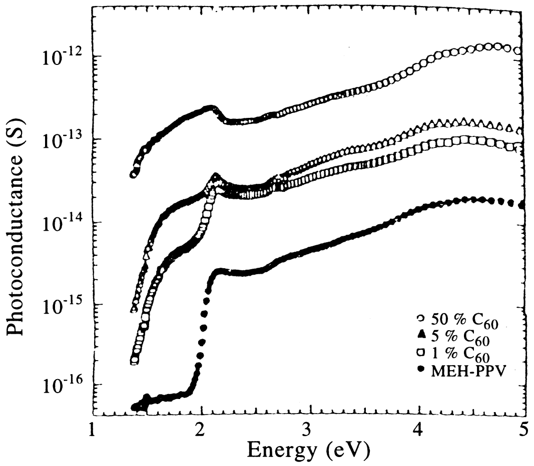


Fig. 7. Spectral response of the steady-state PC of MEH-PPV and MEH-PPV–C_{60} films with several concentrations of C_{60} at room temperature. The data were normalized to a constant incident photon flux of $\sim 7.5 \times 10^4$ photons cm^{-2} sec^{-1} (mechanically chopped at 35 Hz).

thin films by spin-coating or casting. Furthermore, polymer–fullerenes should also represent interesting model systems to study individual, isolated carbon clusters with respect to charge transport [96] and magnetic properties [97].

Unfortunately the ability to fabricate devices based on C_{60} has been limited due to its poor processability and multi-addition of the organic groups. Monofunctionalized C_{60} has nine different 6-6 bonds that can react in a second addition [25]. Therefore, controlling the regiochemistry of the second addition in order to direct the attack to one desired position poses a considerable challenge [8]. Similar problems arise in the polymeric modification of fullerenes. Some crosslinking has been observed from the reaction of more than one polymer chain with a given fullerene molecule, resulting in crosslinked, intractable and insoluble materials. Though there are already many papers concerning the polymer modification of C_{60}, only a few recent papers have reported the preparation of soluble fullerenated polymers. The use of prefunctionalized fulleroids and monofunctional polymers leads to soluble processable polymers, but either increases the complexity of the synthesis or limits the choice of polymers that can be attached to the C_{60} nucleus [55]. For this reason, the key to the development of polymer-modified fullerene is to form selectively soluble fullerenated polymers with interesting specific properties in high yield under very mild conditions. On the other hand, we also found that the structures of some reported fullerene-containing polymeric materials are unclear or only a matter of speculation. Further detailed characterization is thus required in the future. It is reasonable to predict that the polymerization and polymer modification of fullerenes will become important and will be put to use in the fields of materials and life sciences. The

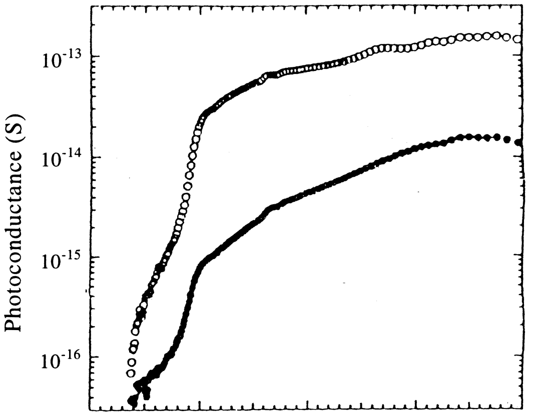


Fig. 8. Spectral response of the steady-state PC of a pristine P3OT film (●) and a 5 wt% P3OT–C_{60} film (○) at room temperature. The data were taken under the same experimental conditions as in Fig. 7.

preparation and application of the water-soluble fullerenated inhibitor for the human immunodeficiency virus (HIV), and the fullerene–nucleotide conjugate as a G-selective DNA-cleaving agent (Nu, nucleotide), as well as novel fullerene-supported transition-metal catalysts for olefin polymerization, are among major ongoing areas of effort.

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