Grafting of Anionic Polymers onto C_{60} in Polar and Nonpolar Solvents

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ABSTRACT: The mechanism of addition of various "living" anionic polymers on C_{60} has been investigated in apolar and polar solvents, and well-defined star-shaped macromolecules with a C_{60} core have been prepared. In toluene, only addition of the carbanions onto double bonds on the fullerene is observed. The maximum number of grafted chains depends on the reactivity of the carbanion borne by the chain; this value is six for the very reactive "living" polystyrene and polyisoprene but only three using the more stable diphenylalkyl carbanion. The number of grafts can be, to some extent (3−6), controlled by stoichiometry. In THF, the reaction mechanism is more complicated: 2 electrons are first transferred from the carbanions to the fullerene producing the C_{60} dianion and then addition takes place. The number of grafted chains depends not only on the reactivity of the carbanion but also on its "bulkiness": four chains are grafted with the carbanion styryl, three with 2-vinylpyridyl, and none using diphenylethyl.

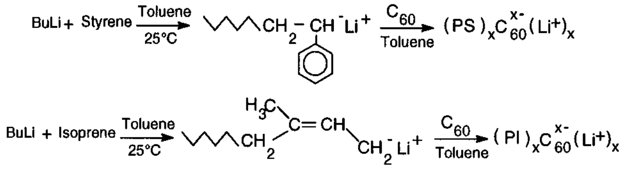
Introduction

Several methods to graft polymer chains onto C_{60}, to incorporate this molecule into the main chain of a macromolecule, or to attach fullerenes onto a polymer backbone have been reported. They include cycloaddition,[1,2] addition of radicals,[3−6] azides,[7] amines,[8,9] charged nucleophiles,[10−14] etc. This last reaction, first reported for the reaction of *t*-BuLi with C_{60},[15,16] is of special interest as it concerns the addition of carbanions onto C_{60}. Indeed, to incorporate fullerene molecules into well-defined polymer structures like necklace chains, stars, cycles, networks, etc., it is necessary not only to perfectly control the number of chains added to the fullerene but also to be able to adjust the molar mass of the grafted polymer and keep its polymolecularity very low. Only if this last requirement is fulfilled does the experimental determination of the functionality of the fullerene in the structure become possible. Of all methods of polymerization, the anionic polymerization leads to the products with the lowest polymolecularity,[17] and furthermore, the "living" chain is able, as prepared, to add to the double bonds on the C_{60}. The first report on the addition of such "living" polystyrene−Li onto C_{60} in toluene has been made by Samulski et al.[10] But it seemed to us that, in order to prepare model polymer structures including fullerenes, a better knowledge of the mechanism of the reaction of carbanions with fullerenes was necessary, in particular to gain good control of the number of grafted chains. Furthermore, it is necessary to extend the work to α,ω difunctional chains to get access to more elaborate structures than just star-shaped macromolecules. Such difunctional chains are generally prepared only in polar solvents like THF.[17] So it was of special interest to study the reaction of various "living" polymers with C_{60} in both polar and nonpolar solvents.

Experimental Section

All this work was done under the high purity conditions required for anionic polymerization. The experiments were conducted in closed reactors under pure argon or in a glass apparatus sealed under high vacuum using the break-seal technique.[17]

Scheme 1



Purification of Solvents, Monomers, C_{60}, and Initiators. Tetrahydrofuran (THF) and toluene free of protonic impurities were distilled through a vacuum line directly into the apparatus from a purple solution of the sodium salt of the benzophenone dianion and a red solution of (3-methyl-1,1-diphenylpentyl)lithium respectively. Styrene and isoprene (Aldrich) were distilled twice over sodium wire under a controlled atmosphere and then distilled under high vacuum from a solution of *n*-butyllithium (prepolymerization) directly in sealed ampules equipped with break-seals. 2-Vinylpyridine (2VP) was distilled under vacuum first over sodium wire and then over calcium hydride directly into ampules. 1,1-Diphenylethylene (DPE) was distilled under vacuum over sodium wire directly into ampules. The C_{60} (gold grade from Hoechst) was stirred for several hours in pure THF and recovered by centrifugation. To remove impurities present in the commercial fullerene, this procedure was repeated until the THF remained practically colorless. The C_{60} was then dried under high vacuum ($<10^{-5}$ Torr) at 100−150 °C, kept under argon in a glovebox, and then never exposed to air. During the heat treatment, the incorporated THF comes out in a very narrow domain of temperature and its instantaneous vaporization provokes probably some kind of "explosion" of the crystals. That could explain that, the so treated fullerene dissolves instantaneously in toluene. *sec*-Butyllithium (*sec*-BuLi) was prepared by reacting 2-chlorobutane with lithium metal in cyclohexane. Potassium 1-phenylethylide (PEK) was prepared in THF by cleavage of the bis(1-phenylethyl) oxide with potassium metal.[18] Potassium naphthalenide (NK) was prepared in THF by reacting naphthalene (Aldrich) on a potassium mirror. All these initiators were stored under vacuum in ampules equipped with break-seals. The concentration of initiators as well as that of "living" polymers was determined by titration using acetanilide and/or by spectroscopic methods using the extinction coefficients published in the literature.[17] The concentration of "living" polymers was confirmed by molar mass determination.

Synthesis and Reaction of the "Living" Polystyrene and Polyisoprene with C_{60}. Synthesis of "living" polystyrene (PS) and polyisoprene (PI) (Scheme 1) in toluene were carried out under high vacuum in a sealed apparatus using *sec*-BuLi as initiator. After introduction of the solvent by distillation through the vacuum line, the apparatus was sealed

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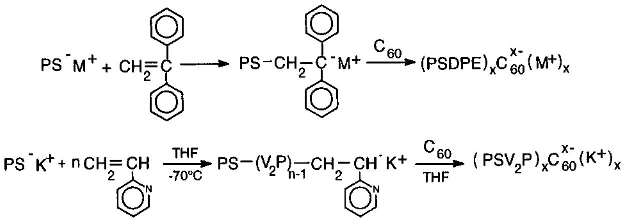
Scheme 2



off and the initiator added by breaking the break-seal of the ampule previously sealed on the apparatus. In the same manner styrene (isoprene) was added under efficient stirring to achieve homogeneous distribution of the monomer. The color turns red-orange (yellow) which is characteristic of styryl (isoprenyl) carbanions in toluene. After complete consumption of the monomer, the "living" polymer solution was divided into several ampules for further use. One was deactivated by methanol and characterized. Then an ampule of a known volume of a given concentration of "living" polymer was sealed onto a new apparatus. A weighted amount of C_{60} was introduced and toluene distilled into it, through the vacuum line. After the reactor was sealed off and the break-seal of the ampule was broken, increasing amounts of "living" PS were added dropwise to the stirred C_{60} solution. The color turns from purple (C_{60} in solution in toluene) to brown-dark. After 2 h of reaction, "living" species were deactivated using acidified methanol. Toluene was removed by distillation under vacuum, and the crude product was dissolved in THF and centrifuged to remove the eventual unreacted C_{60} (C_{60} is insoluble in THF). The polymer was precipitated into an excess of methanol, filtered, and dried under vacuum. To avoid oxidation, the air-sensitive polyisoprene was stored under vacuum.

The syntheses of "living" PS in THF were conducted in the same way, except that the initiators were *sec*-BuLi and potassium 1-phenylethylide and that the monomer was diluted in THF and added at −70 °C.

"Capping" of a "Living" PS with DPE and 2VP. A slight excess of DPE (DPE does not homopolymerize) was added to a "living" polystyrene in toluene (THF) (Scheme 2). The red-orange (red) color of the $PS^{-}Li^{+}$ ($PS^{-}K^{+}$) carbanion turns dark red, a color characteristic for the diphenylethyl carbanion in toluene (THF). The reaction of PS−K with 2VP in THF, done at −70 °C, leads to a block-copolymer (Scheme 2). In order to facilitate the SEC analysis of the products, we kept the size of the 2VP sequence low (degree of polymerization of about 8). All these "capping" reactions were monitored by UV−vis spectroscopy. The "capped" PSs have been then added dropwise to C_{60} dissolved in toluene or in suspension in THF.

Size Exclusion Chromatography (SEC). The various samples were analyzed by size exclusion chromatography (SEC) using a refractive index (RI) detector and a UV−vis detector. This latter was set at 320 nm where the polymers used in this work are not detected and only C_{60} and its derivatives absorb. If not stated otherwise, the SEC molar masses reported are those obtained using the RI detector. However, it is well-known that SEC is not able to give the absolute molar mass of star-shaped macromolecules. This technique is based on a hydrodynamic volume separation: the hydrodynamic volume of a star-shaped macromolecule is smaller than that of the linear homologue of the same molecular weight and varies with the number of branches.[19] Moreover, SEC requires calibration with polymer standards of narrow molecular weight distribution and of the same architecture and nature as the polymer under analysis. This method cannot be used for the characterization of stars because of the lack of star-shaped standards, but it gives access to the molecular weight distribution. Light scattering (LS) is a well-known technique for the characterization of star-shaped macromolecules, but it gives no access to the molecular weight distribution and requires preliminary separation if the sample consists of a mixture of several molecular weight compounds. For accurate characterization, a light scattering detector was added on line to SEC to ally the advantages of these two techniques. All samples are soluble in THF, so THF was used as eluent, and SEC, equipped with various set of columns, was previously calibrated using linear PS standards.

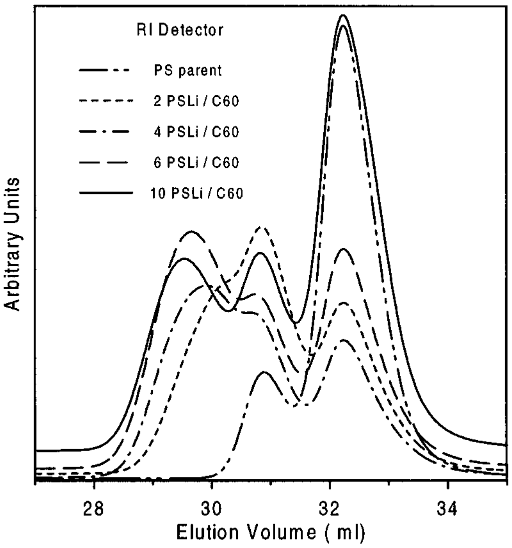


Figure 1. SEC analysis of products obtained upon reacting various ratios of PSLi with C_{60} in toluene.

UV−Vis−Near-IR Spectroscopy. All the UV−vis−near-IR analyses were conducted under high vacuum, in a sealed glass apparatus equipped with a quartz cell. The optical path was adjusted using a quartz spacer. These apparatus were specially designed to allow the recording of the spectra after successive addition of precise volumes of a "living" polymer solution of known concentration to a given amount of C_{60}.

Results and Discussion

1. Reaction of "Living" Polystyrene with C_{60}. 1a. In Nonpolar Solvents. The reaction of "living" PS with C_{60} was first investigated in nonpolar solvents like toluene, a solvent where C_{60} is soluble [20] and "living" PS−Li can easily be prepared, in order to keep a homogeneous reaction media. The work of Samulski[10] clearly shows that a fairly high number of polystyryl−Li chains are able to add to C_{60} in toluene and that there seems to be a limit of the number of grafted chains. In order to get more information about this limit and to find a way to control lower adducts, we first repeated these experiments[21] and studied the resulting compounds by size exclusion chromatography (SEC) coupled with light scattering (LS). Only this last method is able to furnish the absolute molar mass of a star-shaped macromolecule[19,22] and as such provides information on the number of grafts. Increasing amounts of "living" PS−Li (M_w = 24 000, M_n = 22 700, I = 1.06) prepared in toluene were added dropwise to a solution of C_{60} in this same common solvent. As the "living" PS is added to the C_{60} solution, the purple color characteristic of C_{60} in solution in toluene turns to dark-brown, indicating that a reaction occurs. In order to find the highest number of branches one can graft onto C_{60} the molar ratio $PS^{-}Li^{+}$ to C_{60} was varied from 1 to 10. The resulting compounds were analyzed by SEC/LS coupling. Figure 1 shows the SEC diagrams obtained for various molar ratio PS to C_{60} and values of molar masses for the various compounds of higher molar mass are gathered in Table 1 along with the value for the "parent" PS. This latter was voluntary deactivated in air to obtain some coupling and so have an internal standard. As the proportion of "living" PS increases, the molecular weight of the resulting polymer increases. It is interesting to see that the highest molar mass stays practically unchanged if 6 or 10 PS−Li are added per

Table 1. Determination of the Molar Masses of the Compounds of Higher Mass Produced by Reacting $PS^{-}Li^{+}$ with C_{60} in Molar Ratios Varying from 2 to 10[a]

	SEC (RI)			SEC (UV_{320nm})		light scattering	
PS/C_{60}	M_w	M_n	M^*/M_b	M_w	M_n	M_w	M^*/M_b
parent	24 000	22 700				25 000	
2	64 500	57 100	2.7	67 400	60 500	90 000	3.6
3	73 500	66 300	3.1	80 700	73 400	100 000	4.0
4	71 700	59 200	3.0	76 900	66 500	125 000	5.0
6	91 600	86 400	3.8	91 400	85 000	146 000	5.8
10	98 700	91 600	4.1	102 300	94 400	148 000	5.9

[a] M^* and M_b are the molar masses of the star polymer and the PS "parent".

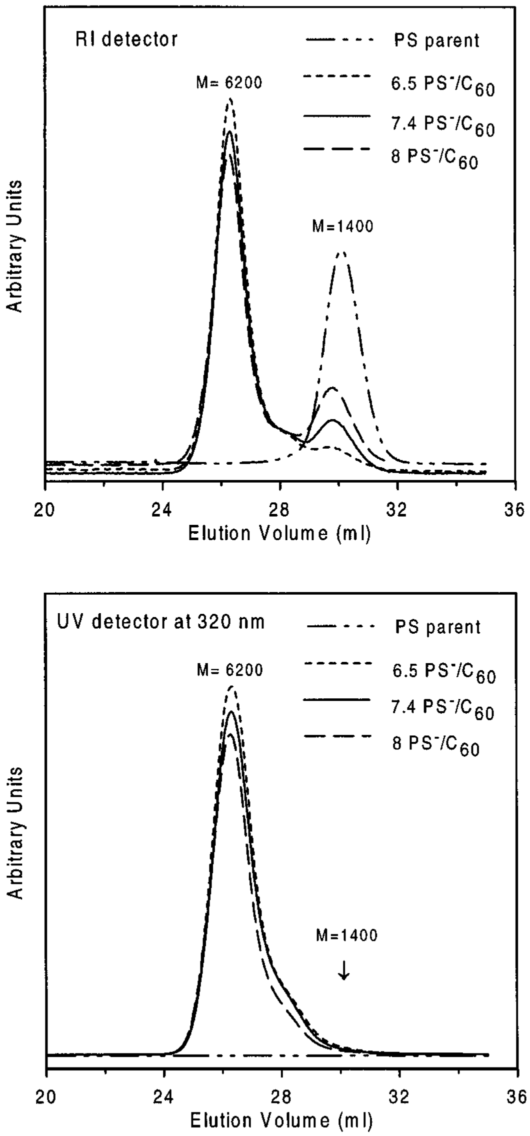


Figure 2. SEC characterization of the addition products obtained by reacting 6.5, 7.4, and 8 PSLi per C_{60}.

Table 2. Experimental Proportions of Stars and Unreacted Chains Obtained by Deconvolution of the RI trace, No Monoadduct Being Present As Demonstrated by the UV_{320} Trace (Figure 2)[a]

	wt % of Star		wt % of ungrafted PS	
$PS-Li/C_{60}$	theor	exptl	theor	exptl
6.5	92.3	90	7.7	10
7.4	81	83	19	17
8	75	78	25	22

[a] Comparison is made with the calculated amounts in the hypothesis that pure hexaadducts are produced. $PS-Li/C_{60}$: number of PS−Li reacted per C_{60}.

fullerene. Furthermore, the determination by LS of this higher mass seems to indicate that there is a limit of six chains grafted onto the C_{60}. But in these experiments, some unreacted polymer was always found and a mixture of adducts of various functionalities obtained. These observations are in agreement with the results earlier reported.[10] In order to definitively establish if these limitations to obtain pure adducts really result from the mechanism of addition of carbanions or from some experimental difficulties, we decided to improve as much as possible the synthesis procedure. For that we conducted our experiments in a sealed glass apparatus using the "break-seal" technique.[17] We also improved the purification of the C_{60}, which was kept under argon in a glovebox and transferred to the reaction vessels without further exposure to air. An example of the kind of addition products it is possible to obtain under these conditions is given in Figure 2. A 6.5, 7.4, and 8.0 excess of PS−Li ($M_w = 1500$, $M_n = 1400$, $I = 1.07$) was respectively reacted with C_{60} in toluene. The compounds were analyzed by SEC using an RI detector and an UV detector set at 320 nm where the PS is not longer detected and only the C_{60} or its derivatives absorb. The UV traces show that C_{60} is only present in the higher molar mass peak. The RI traces in Figure 2 indicate very clearly that there is indeed a limitation as the molar mass does not increase if the amount of PS−Li is increased from 6.5 to 8; only the amount of ungrafted PS increases. Furthermore, the proportion of unreacted chains in the compounds, determined from the deconvolution of the SEC traces (Table 2), is very close to that calculated in the hypothesis that a pure hexaadduct is produced. Also the shape of the SEC peak corresponding to the grafted C_{60} ($M_w = 6500$, $M_n = 5500$, apparent $I = 1.18$) indicates that an adduct with a fairly narrow distribution in functionality is obtained under these conditions. To definitively prove that indeed there is a limit of six chains grafted onto C_{60} using "living" PS in toluene, we prepared PS-Li having a molar mass high enough for an accurate determination by LS of the mass for both the branch and the star-shaped macromolecules formed if six or more "living" chains are reacted with the fullerene. The SEC analysis of the products obtained upon reacting 8 PS−Li ($M_w = 34000$, $M_n = 32500$, $I = 1.04$) per C_{60} is reported in Figure 3. The RI trace shows the presence of two products. The most important peak corresponds to a compound having an apparent molar mass about 4.3 times higher than that of the PS parent, and the shape of the trace indicates that the polymolecularity of this product is fairly narrow (apparent $I = 1.09$). C_{60} is present only in this compound as shown by the UV−vis trace at 320 nm. The lower molar mass product corresponds to ungrafted chains. In Table 3 we report the molar masses determined by SEC and light scattering for the addition products upon reacting "living" PS of various molar masses with C_{60} in the proportion 8/1 or 6/1. The number of branches of the star-shaped macromolecule formed is found by dividing its $M_{w_{LS}}$ by the M_w of the PS parent. The values obtained are very close to 6, indicating that indeed six PS chains are grafted. Fairly pure hexaadducts can be obtained even with long PS chains, indicating that there is no steric effect. At this point it is interesting to note that, as expected, the masses determined by SEC using linear PS as standards are underestimated for the hexaadducts. In fact, the difference between $M_{w_{LS}}$ and $M_{w_{SEC}}$

Table 3. Characterization of Various Hexaadducts[a]

	PSLi/C_{60}	RI detector M_n	RI detector M_w	UV_{320} detector M_n	UV_{320} detector M_w	LS M_w	X	% star	S^*_{RI}	S^*_{UV}	D
PS parent		32 500	34 000								
product	8	130 200	141 500	116 800	133 600	191 000	5.9	73	1470	384	5.0
PS parent		17 600	18 300								
product	8	77 500	84 800	75 500	82 700	104 000	5.9	71	1480	653	4.6
PS parent		5 700	5 900								
product	8	22 000	25 600	21 500	25 000	33 000	5.8	77	3660	6200	5.6
PS parent		1 100	1 200								
product	6	4 050	4 500	4 000	4 900			100	1944	16300	5.5

[a] PSLi/C_{60}: proportion of "living" PS reacted with C_{60}. X: number of branches of the star. % star: weight % of PS contained in the star, determined by deconvolution of the RI trace (no monoadduct being formed as shown by the UV_{320} trace—see Figures 2 and 3 for example) S^*_{RI} and S^*_{UV} are the areas under the RI and $UV_{320\ nm}$ SEC traces, respectively, for the star molecule. $D = (S^*_{UV}/S^*_{RI})M_{w_{LS}}10^{-4}$.

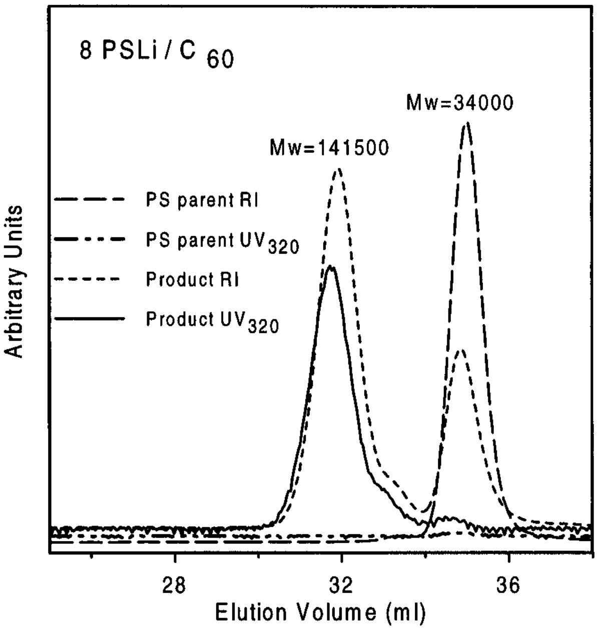


Figure 3. SEC−LS evidence of the formation of hexaadducts ($M_{w_{LS}}$ = 191 000) upon reacting 8 PSLi (M_w = 34 000) with C_{60}.

determined experimentally is close to what can be calculated for a star with six branches using a relation proposed in the literature[22] In Table 3, the proportions of chains grafted onto C_{60} determined from deconvolution of the RI traces are also reported. These values are in good agreement with what is expected if pure hexaadducts are formed. More quantitative information can be deduced from the determination of the areas S^*_{RI} and S^*_{UV320} under the peak corresponding to the star polymer and determined by deconvolution of the RI SEC trace and the UV trace at 320 nm. S^*_{RI} is directly proportional to the concentration of star polymers and S^*_{UV320} to the concentration of C_{60} molecules forming the core of the star. We can assume that the extinction coefficient of a C_{60} hexaadduct is independent of the length of the grafts, and since the optical path is always the same, the C_{60} concentration is directly proportional to S^*_{RI} divided by the $M_{w_{LS}}$ of the star. If all our assumptions are valid and the measurements accurate, the experimental value $D = (S^*_{UV320}/S^*_{RI})M_{w_{LS(star)}}$ should be a constant what ever is the molar mass of the branch. The values reported in Table 3 show that D is indeed constant for molar masses of the branch varying from 1100 to 35000. That indicates that the extinction coefficient of a C_{60} adduct is independent of the length of the graft and that the UV measurement at 320 nm is a quantitative proof of the presence of the fullerene in the star molecules.

The addition of "living" PS onto C_{60} constitutes a very interesting method to produce star-shaped macromolecules where six branches of controlled molar mass and low polymolecularity are covalently bonded to a very small and well-defined core: the C_{60} molecule. The core size of the star molecules synthesized by other methods[23] is never as small as in our case, and even the control of a precise number of grafts is generally difficult.

The limitation to six grafted chains using the addition reaction of a reactive carbanion like PS−Li onto double bonds on C_{60} points to the presence of six double bonds with a special reactivity on this fullerene. Even if the reactivity of the double bonds may change upon addition of chains, it is interesting to note that a computer simulation of the C_{60} molecule shows the presence of six double bonds which are shorter than the others and as such have a higher reactivity. The addition of six carbanions on C_{60} leads to the formation of a hexaadduct bearing six negative charges. So it is also interesting to consider this limitation in regard to the six electrons it is possible to transfer to this fullerene even if a direct comparison between the reactivity of the double bonds and the redox properties is difficult.

We have demonstrated that fairly pure hexaadducts can be produced by reacting PS−Li with the right stoichiometry (6PS/C_{60} or in a slight excess in toluene). However, is it also possible to produce well-defined lower adducts, and how is it possible? As it is generally the case for plurifunctional molecules, one may anticipate that the reactivity of the various double bonds will decrease if the number of grafted chains increases. Thus it may be possible to produce grafted fullerenes with a lower functionality by a simple control of the stoichiometry or by an adequate decrease of the reactivity of the carbanion.

To check the possibilities offered by stoichiometric control, we ran a set of experiments where the ratio PS-Li over C_{60} was well controlled. Some examples of SEC analysis of adducts produced for ratio PS−Li/C_{60} equal to 0.5 and 2 (Figure 5) or 3, 4, and 5 (Figure 4) are shown. The RI traces in Figure 4 demonstrate that no unreacted or deactivated PS−Li is present. The quantitative addition of the "living" polymer onto the fullerene is further confirmed by the similarity between the RI traces and the UV traces at 320 nm where only the compounds that included a C_{60} are detected. It appears that reasonably pure tri-, tetra-, and pentaadducts can be prepared by this simple method as confirmed by the narrow shape of the SEC peaks and the absolute value of the molar masses determined by light scattering. But, we confirmed earlier observations[11,21] that it is difficult to produce pure mono- or diadducts by keeping the

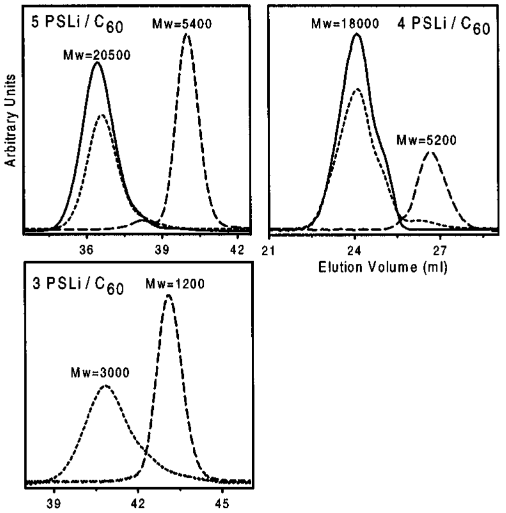


Figure 4. SEC–LS evidence of the formation of lower adducts by stoichiometric control (large dotted line, RI trace for PS parent; solid line, UV trace at 320 nm for the adducts; short dotted line, RI trace for the adducts). Conditions: pentaadduct (5 PSLi/C_{60}; $M_{w_{branch}}$ = 5400; $M_{w_{Star(LS)}}$ = 27 500); tetraadduct (4 PSLi/C_{60}; $M_{w_{branch}}$ = 5200; $M_{w_{Star(LS)}}$ = 20 000); triadduct (3 PSLi/C_{60}; $M_{w_{branch}}$ = 1200; $M_{w_{Star(SEC)}}$ = 3000) (the UV response was too strong in this case).

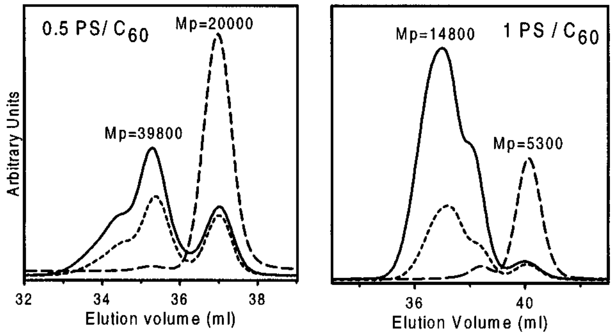


Figure 5. SEC diagrams of products obtained upon reacting 0.5 PS/C_{60} and 1 PSLi/C_{60} (large dotted line, RI trace for the PS parent; solid line; UV trace at 320 nm for the adducts; short dotted line, RI trace for the adducts).

stoichiometry low. The results reported in Figure 5 show that a mixture of mono- and diadducts is obtained if the stoichiometry is lower than 1 and that the triadduct is always the main product if the molar ratio is between 1 and 3. In this range of stoichiometry various amounts of unreacted C_{60} are found depending on the molar fraction of "living" polymer added (72%, 55%, and 19% for PS/C_{60} of respectively 0.5, 1, and 2). The consumption of the fullerene upon addition of increased amounts of PS–Li has been followed by SEC in toluene where C_{60} is easely detected and by UV–vis–near-IR spectroscopy by monitoring the decrease of absorption at 320 nm characteristic of C_{60} (Figure 6). In all cases, unreacted fullerene is found until more than two PS–Lis per C_{60} are added and no peak around 420 nm, often attributed to the formation of monoadducts,[8] is observed. This technique also allowed us to verify that no absorption around 1000 nm characteristic of reduced fullerenes[24] develops in toluene. That confirms that, as expected in nonpolar solvents, no electrons are transferred from the carbanion to the fullerene molecule and pure addition takes place.

All these observations can be explained if one considers that the decrease of reactivity of the double bonds on the fullerene after the first, or even the second addition, is not pronounced enough compared to the very high reactivity of the carbanion PS^- in order to favor the mono- or the diadduct. The decrease of the reactivity of the remaining double bonds being more pronounced after three additions, it becomes possible by a control of the stoichiometry to obtain well-defined adducts of functionality 3, 4, or 5. Another explanation for the difficulty to control the formation of mono adducts has been brought forward by Samulski.[11] It is based on the well-known association by two of the polystyryllithiums in toluene, and the addition of a given amount of polar solvent like THF has been proposed to destroy this aggregation[11] and so favor the formation of monoadducts. However, it is well-known that these aggregates in toluene are in fast equilibrium with unassociated "free" chains and that the latter are in fact the active species in the polymerization of vinyl monomers.[17] It is very likely that the same is true for the addition of PS–Li onto a double bond on C_{60}. Furthermore, the addition of polar solvents where C_{60} is insoluble and electron transfer favored may lead to some complications in the mechanism of reaction.

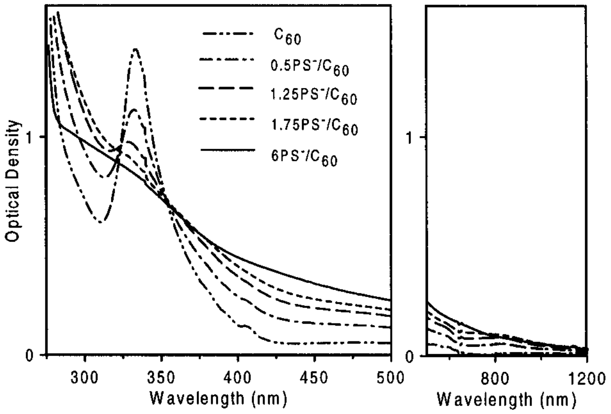


Figure 6. Evolution of UV–vis–near-IR spectrum if increasing amounts of PSLi are added to C_{60} in toluene.

1b. In Polar Solvents. It was important to establish the mechanism of reaction between "living" polymers and fullerenes in polar solvents like THF where the latter are not soluble, in particular since the preparation of the α,ω-dicarbanionic chains needed for the incorporation of C_{60} in architectures like cycles, necklace chains, or networks requires such solvents. For that study, reported in a preliminary form at a conference,[25] we used polystyryl–K because of its better stability at room temperature in THF compared with PS–Li.

The SEC analysis of the compound, obtained when "living" PS^-K^+ prepared in THF (M_w = 24 500, M_n = 23 000, I = 1.07) was added to C_{60} in suspension in THF in a ratio of 7 to 1, is given in Figure 7. The RI trace shows the presence of a mixture of three different compounds in the sample. The SEC mass of the first one is 3.2 times higher than that of the PS parent; this is about the difference expected for a star-shaped polymer bearing four branches.[22] The actual molar mass determined by LS ($M_{w_{LS}}$ = 95 000), is 4 times that of the PS "parent" and the UV–vis trace at 320 nm shows that C_{60} is mostly present in this tetraadduct. The second peak with a molar mass double than that of the PS parent is a mixture of two compounds as deduced from the comparison of the RI and UV traces. If some diadduct PS_2C_{60} is present, the major product contains no C_{60} and must result from coupling of two parent PS chains. The presence of coupled chains (PS–PS) can be explained if one takes into account the fact that, in polar solvents, carbanions are able not only to

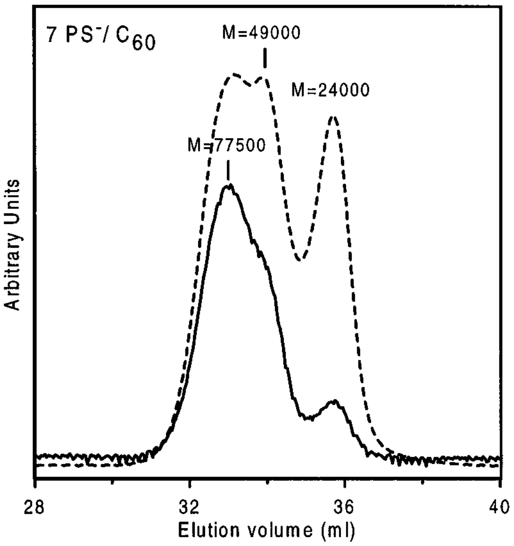


Figure 7. SEC analysis of the products resulting from the reaction of 7 PS−K per C_{60} in THF (solid line, UV trace at 320 nm for the adducts; short dotted line, RI trace for the adducts).

add to double bonds but also to transfer electrons to conjugated molecules.[26,27] If such an electron transfer occurs from the PS^-K^+ to the highly electroaccepting C_{60}, the carbanionic PS converts to a radical, and it is well-known that the main reaction of these very reactive polystyryl radicals is recombination.[28] The third compound corresponds mainly to unreacted PS coming from the excess of "living" PS used. Some monoadduct is also formed as shown by the UV trace at 320 nm, and the presence of some PS chains bearing a terminal proton or a double bond, resulting from the minor disproportionation reaction of PS radicals,[28] is also possible.

In order to establish if really an electron transfer from the PS−K to the fullerenes takes place in THF, we have followed by UV−vis−near-IR spectroscopy successive additions of well-defined amounts of "living" PS^-K^+ ($M_w = 4400$, $M_n = 3900$, $I = 1.13$) to a known quantity of C_{60} in suspension in THF. The spectra are shown in Figure 8. An absorption peak at 1075 nm, assigned to the C_{60} monoanion,[24] was detected already after the first addition (0.1 PS−K/C_{60}). The presence of this near-IR peak indicates that, in contrary to what is observed in nonpolar solvents, an electron transfer from the carbanion to C_{60} takes place in THF. As the amount of added "living" PS increases, the reduced C_{60} goes into solution and the intensity of the corresponding absorption peak increases and reaches a maximum when the ration PS-K/C_{60} becomes close to 1. At this point, addition of more PS^-K^+ induces the formation of a new peak having its maximum at 950 nm and a shoulder at 840 nm. This new peak, assigned to C_{60}^{2-},[24] develops at the expense of that of the monoanion at 1075 nm, giving evidence for the transfer of a second electron to C_{60}^-. The presence of an isosbestic point demonstrates that the conversion of C_{60}^- to C_{60}^{2-} is quantitative. These observations also allowed us to claim that no simultaneous addition of carbanions to double bonds on the fullerene takes place up to this point; the reaction is a pure electron transfer. This statement is strengthened by the absence of any additional hypsochromically shifted absorptions in our spectra. Indeed, if simultaneous addition would take place it should lead to the formation of the anion and the dianion of the monoadduct, which should exhibit an absorption respectively close to 1006 and 858 nm: values reported in the literature for another type of monoadduct.[29] After reaching a maximum for a ratio PS−K/C_{60} close to 2, the C_{60}^{2-} peak is decreasing and no other near-IR peak is observed even if the excess of carbanions becomes very large. The fact that no C_{60}^{3-} peak[24] is obtained shows that no third electron is transferred to the fullerene. Further introduction of PS^-K^+ leads to an addition reaction onto C_{60}^{2-} as no peak at 343 nm, characteristic of the "living" PS, can be observed until the excess PS^-K^+ over fullerene ratio becomes higher than 6. This is in agreement with the production of tetraadduct as seen by SEC analysis. Similar experiments conducted at low temperature using PS−Li lead to similar results, indicating that the counterion seems to have no influence on the reaction mechanism. Special care has to be taken to avoid the presence of products bearing an oxanion (coming from the synthesis of the initiator PEK in THF) or to take them into account as they are also able to transfer up to 2 electrons to C_{60}; but further addition of them to $C_{60}^{2-}(K^+)_2$ is negligible.[30]

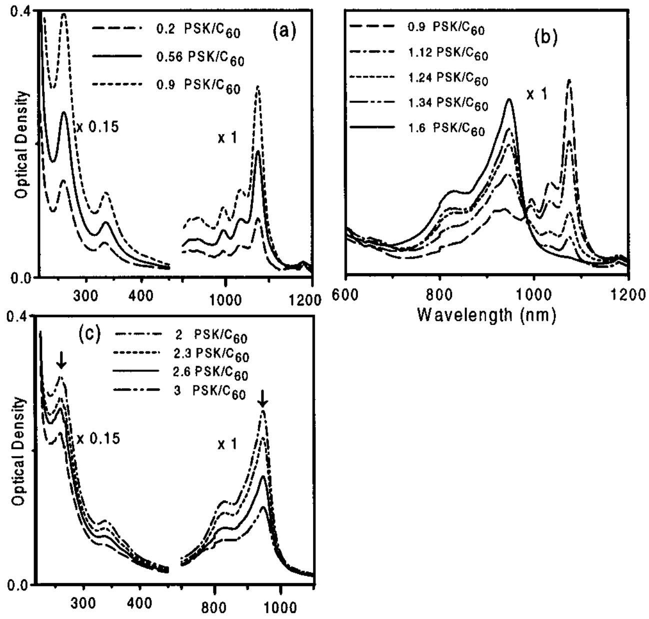
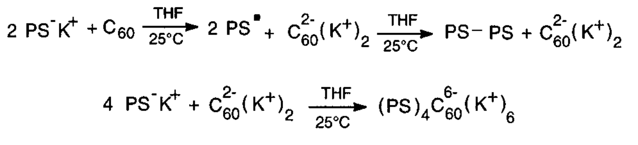


Figure 8. Evolution of the UV−vis−near-IR spectrum if increasing amounts of PS−K are added to C_{60} in THF. Evidence of formation of C_{60} mono- and dianions is observed.

Scheme 3



$$2\,PS^-K^+ + C_{60} \xrightarrow[25°C]{THF} 2\,PS^\bullet + C_{60}^{2-}(K^+)_2 \xrightarrow[25°C]{THF} PS-PS + C_{60}^{2-}(K^+)_2$$

$$4\,PS^-K^+ + C_{60}^{2-}(K^+)_2 \xrightarrow[25°C]{THF} (PS)_4C_{60}^{6-}(K^+)_6$$

The study of the reaction between "living" PS−K and C_{60} reveals that, in a polar solvent like THF, 2 electrons are first transferred to the fullerene and then the addition of four chains occurs according to Scheme 3. That offers the opportunity to prepare well-defined star-shaped macromolecules with a C_{60} core bearing four branches and six negative charges.

To check if the addition of low quantities of a polar solvent to a nonpolar media can already disturb the pure addition mechanism, the reaction between PS−K and C_{60} in toluene containing 10% of THF was studied using UV−vis−near-IR spectroscopy. After the first addition (0.1 PS−K/C_{60}) an absorption is observed at 1075 nm, indicating that electron transfer occurs. As shown by Figure 9, the concentration of the C_{60} monoanion

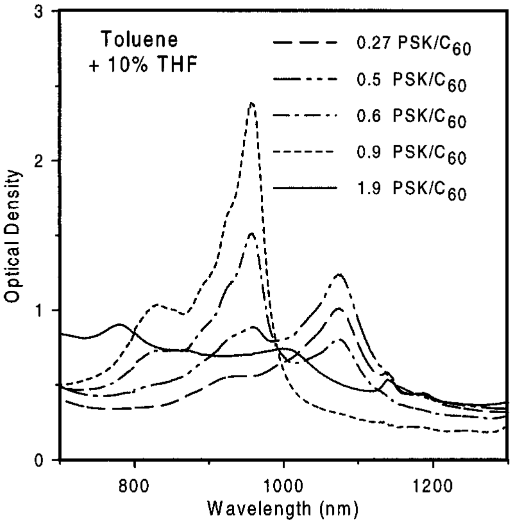


Figure 9. Evolution of the UV−vis−near-IR spectrum if increasing amounts of PS−K are added to C_{60} in toluene containing 10% THF. Evidence of electron transfer is observed.

increases until the number of “living” PS per C_{60} is close to 0.5. At this point an absorption at 950 nm characteristic of the dianion is developing at the expense of the monoanion and it increases until the ratio PS^-/C_{60} reaches about 0.9. Further addition of “living” polymer leads to the disappearance of the dianion but, as in pure THF, no C_{60}^{3-} is observed. The ratios PS^-/C_{60} where the maximum amounts of mono- and dianions are observed are not consistent with a pure electron transfer process; these peaks should disappear for a molar ratio PS^-/C_{60} of 1 and 2, respectively. That indicates that a competition between electron transfer and addition takes place in this mixed solvent. The resolution of the absorption peaks is by far not as good as in Figure 8. The broadening of the bands may result from the presence of reduced monoadducts, but solubility problems of the reduced C_{60} in the mixture of solvent can also play a role. The difference between the absorption maxima of mono and dianion may also reflect solubility problems. The SEC analysis of the final product (after introduction of 8 PS−K per C_{60}) confirms that addition and electron transfer take place simultaneously: a product with a molar mass 6 times higher than the PS parent is observed (about 50% of the grafted chains) and lower adducts (penta- and tetraadducts) are observed. All these compounds contain C_{60}, as demonstrated by the UV trace at 320 nm. These experiments indicate that, by addition of a small amount of polar solvent in a solution of “living” PS in toluene, a competition between addition and electron transfer to C_{60} occurs, leading to a mixture of addition products and reduced fullerenes but not to pure lower adducts.

The reaction between “living” polymers and C_{60} in THF can only be used for the synthesis of “model” polymer structures if one is able to separate electron transfer from the addition reaction onto the fullerene. For example, in the case of α,ω-dicarbanionic chains, the initial transfer of 2 electrons results in the formation of a mixture of mono- and difunctional chains and thus leads to ill-defined final products. We have shown that electron transfer from the carbanions to the fullerene can be avoided by reacting “living” PS−K with C_{60} dianion.[31] This latter can be easily and quantitatively prepared in THF by reacting potassium naphthalenide with C_{60} until the dianion is obtained, with the electron transfer being monitored by UV−vis−near-IR spectroscopy as shown in Figure 10. Once the dianion was obtained, controlled amounts of PS−K (M_n = 7000, M_w = 7800, I = 1.12) in solution in THF were introduced (Figure 11). Upon addition of the “living” polymer, the absorption peak at 950 nm, characteristic of the dianion, decreases and completely disappears when one PS^- per C_{60} is added. No trianion is observed as expected and the absorption peak at 340 nm is decreasing. So we can assume that a pure monoadduct with three negative charges present on the C_{60} molecule−$PS-C_{60}^{3-}(K^+)_3$−is obtained. As the proportion of added PS^- is increasing, a new peak located at 420 nm is detected. After deactivation with acidified methanol, this peak disappears. This absorption at 420 nm can be tentatively attributed to direduced grafted fullerenes bearing more than one chain. When the amount of “living” polymer introduced per C_{60} becomes higher than 4, an absorption peak at 343 nm characteristic of unreacted PS−K is observed. The fact that no absorption at 343 nm is present before this point is in agreement with a limitation to four branches grafted onto C_{60}. The resulting product was then characterized by SEC coupled with LS (Figure 12). As expected, a star-shaped macromolecule with four branches ($M_{w_{LS}}$ = 30 400) is obtained and no product with twice the mass

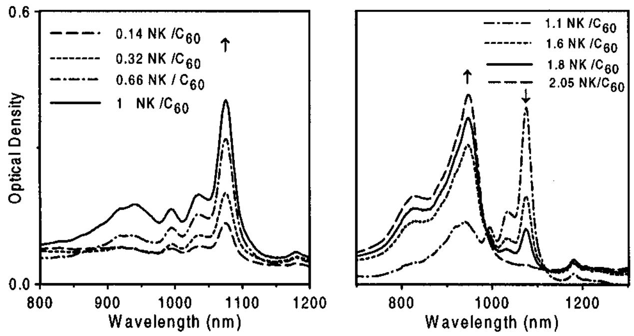


Figure 10. Formation of pure $C_{60}^-K^+$ and $C_{60}^{2-}(K^+)_2$ by reduction of C_{60} with naphthalenide−potassium in THF.

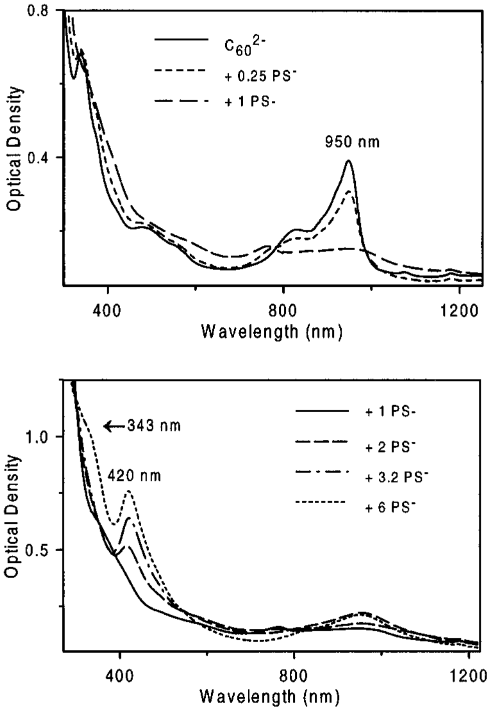


Figure 11. Evolution of the UV−vis−near-IR spectrum upon reaction of PS−K with $C_{60}^{2-}(K^+)_2$ in THF.

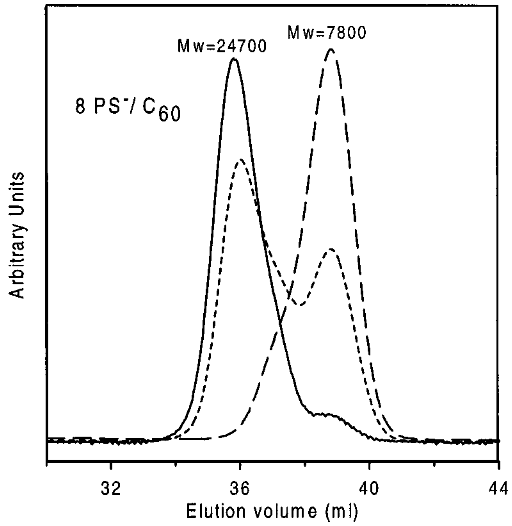


Figure 12. SEC analysis of the products obtained if 8 PS−K are reacted with $C_{60}^{2-}(K^+)_2$ in THF (large dotted line, RI trace for PS parent; solid line, UV trace at 320 nm for the adducts; short dotted line, RI trace for the adducts).

of the PS is detected. It has to be stressed out that this method produces tetraadducts bearing six negative charges so that, after deactivation, six double bonds of the fullerene are opened. The characterization of the monoadducts obtained through this method is underway as well as an extension to α,ω-dicarbanionic chains in order to produce networks with C_{60} knots.

2. Reaction of More Delocalized Carbanions with C_{60}. The production of pure hexa- through triadducts by a simple control of the stoichiometry is possible but difficult as the achievement of an exact ratio PS^-/C_{60} under the high purity conditions required is not easy. Furthermore pure mono- and diadducts can not be obtained as the decrease of reactivity of the double bonds of C_{60} is not pronounced enough until three chains are added. The reactivity of a "living" chain being determined by its last unit bearing the negative charge,[17] another way to control the number of grafted chains would be to decrease the reactivity of this carbanion against the opening of the double bond. In this case the maximum number of chains grafted onto the fullerene would be reduced even if an excess of carbanionic chains is used. The reactivity of the terminal carbanion can be decreased by addition of a vinyl monomer leading to a more delocalized negative charge. The addition of a more electrophilic vinyl monomer to "living" polystyrene leads to a carbanion having a lower nucleophilicity than the "living" PS.[32] Various vinyl monomers with increasing electrophilicity have been used: isoprene, 2-vinylpyridine (V2P), and 1,1-diphenylethylene (DPE). The reactions of the various "living" polymers or "capped" PS with C_{60} were investigated in nonpolar and polar solvents in order to establish the reaction mechanism.

2a. In Nonpolar Solvents. In the first set of experiments we used polyisoprenyl−Li ($M_w = 9100$, $M_n = 8800$, $I = 1.03$, $M_{w_{LS}} = 9400$) as the "living" polymer. To find the maximum number of chains of this highly 1,4-*cis*-polyisoprene which can be grafted onto C_{60}, a 16-fold excess of PI−Li has been added to C_{60} in toluene and the product analyzed by SEC/LS coupling (Figure 13). A mixture of two products is obtained, and the UV−vis detector shows that C_{60} is only present in the compound of higher mass. The latter, with a molar mass determined by SEC ($M_w = 44\,600$, $M_n = 39\,900$, $I = 1.12$) to be 4.6 times higher than the PI parent, corresponds to a star bearing six branches as confirmed by the mass determined by LS ($M_{w_{LS}} = 62\,000$). The slightly higher experimental values for the masses as expected for a hexaadduct comes from the presence of a small fraction of high molar mass products (shoulder in the SEC peak) resulting probably from the beginning of the oxidation of the air-sensitive PI chains during workup and analysis. No lower adducts are observed. The second peak corresponds to unreacted PI and results from the large excess of PI used. The deconvolution of the RI curve indicates that the crude product consists of 37.5% stars and 62.5% unreacted PI; these amounts are expected for the molar ratio PI−Li/C_{60} used in this manipulation if a star with six chains is formed. This result is not surprising as the reactivity of the polyisoprenyl−Li is close to that of the "living" PS.[32] That opens the opportunity to produce well-defined heterostar polymers bearing both PS and PI chains.

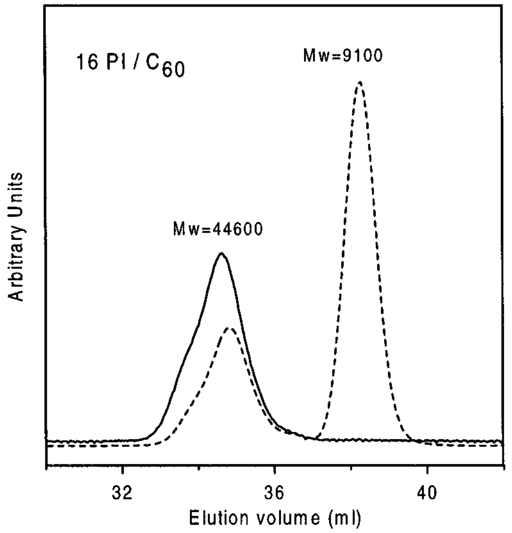


Figure 13. SEC−LS evidence of the formation of a polyisoprene hexaadduct of C_{60} in toluene. ($M_{w_{branch(LS)}} = 9400$; $M_{w_{Star(LS)}} = 62\,000$) (solid line, UV trace at 320 nm for the adducts; short dotted line, RI trace for the adducts).

In a second set of experiences we reacted "living" PS with 1,1-diphenylethylene. Only one of this more electrophilic vinyl monomer adds to the PS−Li, leading to a more stable carbanion, the negative charge being delocalized over two phenyls.[33] Such a "capped" PS or PSDPE−Li ($M_w = 2500$, $M_n = 2400$, $I = 1.04$) has been added to C_{60} in solution in toluene in a molar ratio PSDPE/C_{60} = 7, and the products were characterized by SEC. A compound having a molar mass 3 times higher than that of the PSDPE parent (Figure 14a) is formed and the UV−vis trace at 320 nm confirms the presence of C_{60} in this triadduct. That indicates that indeed a reduction of the reactivity of the carbanion induces a lower limitation of the number of grafted chains: no more than three PS chains bearing the less reactive carbanion diphenylethyl can be grafted onto C_{60}. Small amounts of di- and monoadducts are also detected along with a large fraction of unreacted PSDPE due to the excess of polymer parent used. An interesting effect appeared if PSDPE−Lis of larger molar masses are reacted with C_{60}. As shown in Figure 14a−c, an increase of the length of the chain (2500, 5900, and 25800) results not only in a decrease down to zero of the proportion of the triadduct but also in a decrease of the total amount of grafted chains, which becomes very low as shown by the relative response between the

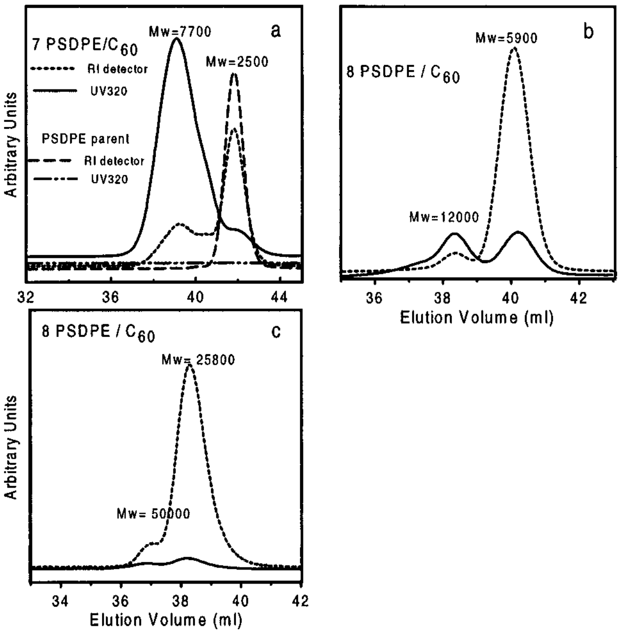


Figure 14. SEC analysis of the products formed upon reacting PSDPEK of increasing molar masses with C_{60} in toluene.

RI and UV detectors for a PSDPE−Li of $M_w = 25\,800$. This effect is not a kinetic effect as the same SEC trace is obtained after 1 or 24 h of reaction. Such a behavior was not observed with PS−Li up to $M = 35\,000$. Addition of DPE on the end of a "living" PS leads to a more stable carbanion and thus allows one to control lower adducts, but the presence of two phenyl groups on the terminal C directly connected to the fullerene introduces an additional steric effect which may be the reason for the difficulty observed in the addition of large chains to C_{60}.

2b. In Polar Solvents. In THF we "capped" "living" PS−K with two vinyl monomers more electrophilic than styrene: 2-vinylpyridine and DPE. The presence of the nitrogen on the pyridine ring allows also the formation of a highly delocalized and thus very stable carbanion but which keeps the same size as the styryl carbanion.[34] The two chosen monomers give rise to carbanions having about the same reactivity[32] but not the same size.

The addition of V2P to "living" PS leads to the formation of a block-copolymer but, in order to facilitate the SEC characterization, we kept the polyvinylpyridine sequence short (about eight monomer units). To establish the reaction mechanism, increasing amounts of PSV2P−K ($M_n = 19\,200$, $M_w = 21\,800$, $I = 1.13$) have been added to a suspension of C_{60} in THF. As in the case of PS−K, 2 electrons are first transferred and then addition takes place. That is shown by the apparition of an absorption at 1075 nm followed by the quantitative conversion of the monoanion to dianion when the molar ratio PS2VP/C_{60} is close to 2 (Figure 15a). The intensity of the peak at 950 nm is observed to decrease when more PS2VP is introduced. No trace of the tri-anion is observed and the PS2VP−Ks continue to react, indicating that addition occurs. This addition is confirmed by the SEC analysis of the products of the reaction of seven PS2VP with C_{60} (Figure 15b). The chromatogram indicates that, with this less reactive carbanion that however keeps the same "size" as a styryl carbanion, three chains are grafted onto the C_{60} molecule.

For comparison, we prepared a "living" PS "capped" with DPE and added small amounts of this PSDPE$^-$K$^+$

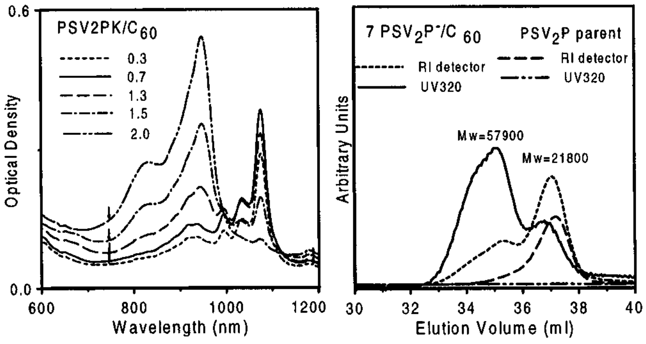


Figure 15. Reaction of PSV$_2$PK with C_{60} in THF: UV−vis−near-IR and SEC characterization.

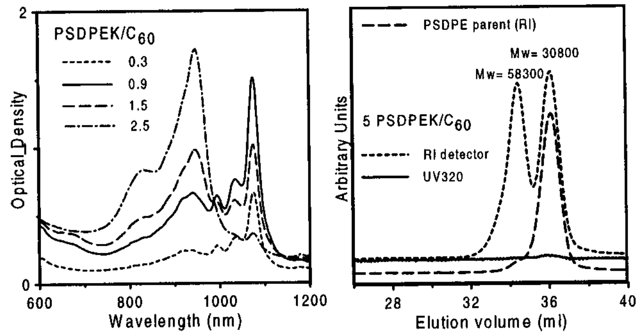


Figure 16. Reaction of PSDPEK with C_{60} in THF: UV−vis−near-IR and SEC characterization.

($M_n = 27\,400$, $M_w = 30\,800$, $I = 1.12$) to C_{60} in suspension in THF up to a final molar ratio PSDPE−K/C_{60} = 5. After each addition the UV−Vis−near-IR spectrum was recorded and reported in Figure 16a. As in the case of PS−K and PS2VP−K in THF, 2 electrons are quantitatively transferred. But, unlike the two other cases, the absorption peak of the dianion does not decrease if more than two PSDPE-K per C_{60} are added, indicating that no PSDPE is grafted onto C_{60}. The SEC analysis of the final product (Figure 16b) confirms that no addition but only electron transfer takes place. Indeed, it consists of only two compounds containing no C_{60} as shown by the UV trace at 320 nm. The first one, with a molar mass double of the "parent" PSDPE, results from the recombination of the PSDPE radicals generated during the electron transfer process, and the second, with the same molar mass as the starting material, to PSDPE in excess as well as to the products coming from an eventual disproportionation of the radicals.

The difference in the reaction mechanism between "living" PS chains "capped" with 2VP and DPE shows that, in addition to the reactivity of the terminal carbanion, the "bulkiness" of the latter plays also a role when it comes to addition onto a double bond on fullerenes.

Conclusions

In this paper we show that, if conducted under the high purity conditions required for work with carbanions, the addition of "living" anionic polymers, first reported by Samulski et al., can be well controlled and used to prepare adducts with good defined functionality. In nonpolar solvents, star-shaped polymers with up to six branches can be prepared using chains bearing reactive carbanions like styryl or isoprenyl and that from oligomers to high molar masses. Adducts of fairly pure functionality can be obtained by stoichiometric control (tri- through hexaadducts) or by adjusting the reactivity of the terminal carbanion on the "living" chain. The number of negative charges present on the C_{60} core of these "living" stars is equal to the number of grafts. In polar solvents where the fullerenes are barely soluble, the transfer of two electrons and only two from the carbanion to the C_{60} is always observed before addition of the "living" chains takes place. The maximum number of chains grafted to the C_{60} cannot exceed four and depends on the reactivity of the carbanion on the polymer as well as on the "bulkiness" of the "living" end. The functionality n of the stars prepared in polar solvents may be controlled between 1 and 4 but the negative charges on the C_{60} core are equal to $n + 2$. By reacting "living" polymers with the C_{60} dianion in THF, it is possible to avoid electron transfer. The possibility to further use of the carbanions present on the fullerene core of these "living" stars to initiate anionic polymerization of vinyl monomers has been demonstrated.[35] Our work confirms that the addition of "living" anionic polymers onto C_{60} offers an unique opportunity to control both the number of chains grafted onto the fullerene and the molar mass and polymolecularity of the grafts.

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