Palm Tree- and Dumbbell-Like Polymer Architectures Based on C_{60}

Y. Ederlé and C. Mathis*

Institut Charles Sadron (CNRS-ULP), 6, rue Boussingault, 67083 Strasbourg Cedex, France

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ABSTRACT: By reacting 6 PSLi per C_{60} molecule, fairly pure star-shaped polymers with six branches and six carbanions located on the fullerene core are obtained. Only one of these six carbanions is able to initiate the anionic polymerization of styrene or isoprene leading to well-defined palm tree-like architectures $(PS_a)_6C_{60}PS_b$ or $(PS)_6C_{60}PI$. At its end, the out-growing chain bears a carbanion that has been allowed to react with the coupling agents dibromo-*p*-xylene and dibromohexane to produce the dumbbell-like structures, $(PS_a)_6C_{60}PS_b$-pX-$PS_bC_{60}(PS_a)_6$ and $(PS)_6C_{60}$PI-Hex-$PIC_{60}(PS)_6$. If C_{60} itself is allowed to react with the "living" palm tree, a third fullerene molecule is introduced in the center of the macromolecular architecture.

Introduction

The influence of the architectures of polymers on their solution properties is well established and is of great importance for practical applications.[1] Block copolymers have found attention and applications because of their unique solution and solid-state properties.[2] Star-shaped polymers and block copolymers have been widely studied,[3] but only a little work has been devoted to more elaborately branched architectures. To our knowledge, only a few articles report the synthesis of super H-shaped or dumbbell-like polymers[4−9] and examine their solution and solid-state properties.[10,11] The design of new well-defined polymer structures is still an important challenge. Recent progress in the knowledge of the mechanisms involved in the reaction of "living" anionic polymers with C_{60} allowed us to synthesize well-defined "living" grafted fullerene.[12] As an example, fairly pure six-branched PS stars with a C_{60} core bearing six carbanions have been reported. The ability of the carbanions located on the fullerene core of a "living" star to initiate anionic polymerization of monomers with various reactivities, as a function of the number of negative charges present on the C_{60} (i.e., number of branches), has been reported.[13] In this article, we show that these new results can lead to the synthesis of new model polymer structures containing C_{60}. The advantage of using C_{60} in the building of these structures is not only the higher functionality of the fullerene molecule than the silane derivatives generally used but also the possibility of introducing specific properties resulting from the presence of this conjugated molecule.

Experimental Section

The experiments were conducted in glass apparatus sealed under high vacuum using the break-seal technique[14] to fulfill the high-purity conditions required.

Purification of Solvents, Monomers, C_{60}, and Initiator Preparation. Toluene free of protonic impurities was distilled through the vacuum line directly into the apparatus from a red solution of 3-methyl-1,1-diphenylpentyllithium. Styrene and isoprene (Aldrich), first distilled over sodium, were distilled under high vacuum directly in ampules equipped with break-seals from a *n*-butyllithium solution (prepolymerization). To remove impurities present in the commercial fullerene, the C_{60} (>99% from TechnoCarbo) was stirred several hours in pure tetrahydrofuran (THF) and recovered by centrifugation. This procedure was repeated until the THF stayed colorless. The C_{60} was then dried under high vacuum ($<10^{-5}$ Torr) at 100−150 °C, kept under argon in a glovebox, and never exposed to air. *sec*-Butyllithium (*sec*-BuLi) was prepared by reacting 2-chlorobutane with lithium metal in cyclohexane and stored in sealed ampules equipped with break-seals. The concentration of the initiator was determined by titration with acetanilide. The concentration of "living" polymers was further confirmed by molar mass determination.

Palm Tree and Dumbbell Synthesis (Scheme 1). The anionic polystyrenes (PSLi) and polyisoprenes (PILi) were prepared in toluene with *sec*-BuLi as the initiator, and each "living" polymer solution was divided in several ampules. One was deactivated with acidified methanol and the polymer characterized. An ampule of a known volume of a given concentration of "living" polymer was sealed on a new apparatus, a weighted amount of C_{60} introduced, and toluene distilled into, through the vacuum line. After sealing off and breaking the break-seal of the ampule, the amount of "living" PS needed to form a pure hexaadduct was added dropwise to the stirred C_{60} solution. After 2 h of reaction, the solution is divided in two by sealing a part of the apparatus. The carbanions contained in the first part were deactivated by breaking the break-seal of an ampule of acidified methanol, and the star was recovered by precipitation and characterized. Styrene or isoprene was added slowly to the other part of "living" grafted fullerenes and the reaction allowed to run for 2 h before addition of acidified methanol. For the synthesis of dumbbell, the experimental procedure is identical with that described above except that a coupling agent such as dibromohexane (DBrHex), dibromoparaxylene (DBrpX), or C_{60} itself is added to the living palm tree. All the products were characterized by size-exclusion chromatography coupled with light-scattering (SEC-LS). A refractive index (RI) and a UV−vis detector were used. This latter was set at 320 nm at which the polymers used in this work are not detected and only C_{60} and its derivatives absorb. Because SEC is unable to give the absolute molar mass of such branched macromolecules,[15] a light-scattering (LS) detector was added to obtain access to this value. All samples being soluble in THF, this solvent was used as eluent; SEC, equipped with various set of columns, was previously calibrated using linear PS standards.

Results and Discussion

1. Palm Tree-Like Structures (Scheme 2). a. Polystyrene.

We recently demonstrated that a simple addition of PSLi and PILi to double bonds on the fullerene is observed in toluene, and a maximum of six chains can be grafted onto C_{60} leading to the formation of well-defined star-shaped macromolecules with a C_{60} core bearing up to six arms and an equal number of

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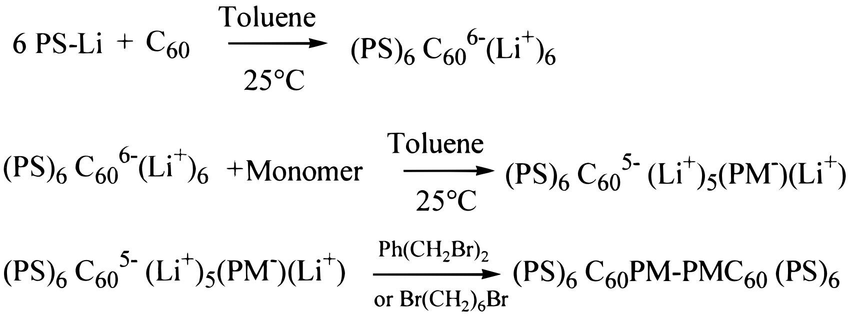
Scheme 1. Synthesis of Palm Tree- and Dumbbell-Like Structures

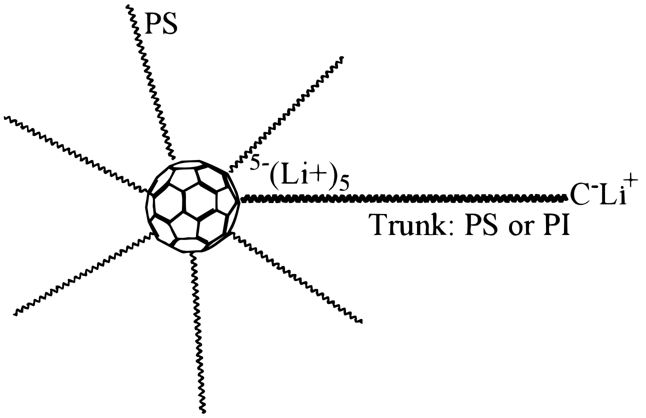


$$6\ \mathrm{PS\text{-}Li} + \mathrm{C_{60}} \xrightarrow[25^\circ\mathrm{C}]{\text{Toluene}} (\mathrm{PS})_6\,\mathrm{C_{60}}^{6-}(\mathrm{Li}^+)_6$$

$$(\mathrm{PS})_6\,\mathrm{C_{60}}^{6-}(\mathrm{Li}^+)_6 + \text{Monomer} \xrightarrow[25^\circ\mathrm{C}]{\text{Toluene}} (\mathrm{PS})_6\,\mathrm{C_{60}}^{5-}\,(\mathrm{Li}^+)_5(\mathrm{PM}^-)(\mathrm{Li}^+)$$

$$(\mathrm{PS})_6\,\mathrm{C_{60}}^{5-}\,(\mathrm{Li}^+)_5(\mathrm{PM}^-)(\mathrm{Li}^+) \xrightarrow[\text{or } \mathrm{Br(CH_2)_6Br}]{\mathrm{Ph(CH_2Br)_2}} (\mathrm{PS})_6\,\mathrm{C_{60}PM\text{-}PMC_{60}}\,(\mathrm{PS})_6$$

Scheme 2. Schematic Representation of the Synthesized Palm Tree Architectures



negative charges.[12] Fairly pure hexaadducts with molar masses ranging from a few thousand to more than 2 million could be prepared and characterized, and their dimensions could be established in a good solvent.[16] These stars are characterized by a low dispersity in functionality. As prepared, these hexaadducts bear six carbanions. To gain information about the reactivity of the carbanions located on the fullerene we used them to initiate the anionic polymerization of monomers of various reactivities. Only one of the six carbanions of a "living" six-armed star is able to initiate the polymerization of styrene,[13] so that a single PS chain is growing out from the fullerene core leading to the formation of palm tree-like structures. That is illustrated in Figure 1, where the SEC traces (RI and UV at 320 nm) of the polymer resulting from the polymerization of styrene initiated by a "living" hexaadduct are shown. The traces corresponding to the "parent" PS and to the star are also given. The RI trace indicates that the polydispersity of the palm tree stays rather good ($I_{\mathrm{apparent}} = 1.2-1.3$; see Table 1) for such a complex architecture. The UV trace at 320 nm, where the PS is not detected and only the fullerene absorbs, reveals that C_{60} is present in this higher molar mass product. However, a peak corresponding to unreacted stars is always observed. The presence of this latter peak is not unexpected. Indeed, as reported in a previous paper,[13] the presence of even a small excess of linear PSLi leads to a nearly total consumption of the added styrene by polymerization initiated by the linear anionic species. To avoid that, the stoichiometry PSLi/C_{60} has to be kept slightly lower than 6 in the synthesis of the "living" stars, so that the presence of some pentaadducts cannot be avoided. It must be stressed at this point that less than 1/6 of the total amount of carbanions is actually involved in the final polymerization step of the synthesis, where the monomer is added to the "living" star. Thus, a concentration of carbanions only about 8% lower than the theoretical one generates 50% of pentaadducts. In addition, the slightest trace of impurities in the added monomer will react preferentially with the 17% more reactive carbanions leading to unreactive hexaadducts. The presence of up to 50% of unreacted stars in our products indicates that the total discrepancy between theoretical and actual concentration of carbanions stays lower than 8%. Such a deviation seems acceptable if one takes into account the drastic requirements for this kind of work. The unreacted stars can be separated from the palm tree- or dumbbell-like polymers by preparative SEC. The slight increase of the polydispersity of the outgrowing chain seems to point toward a slow initiation. Because $(PS)_6C_{60}{}^{6-}(Li^+)_6$ is produced by addition of PSLi to double bonds on C_{60}, it is legitimate to assume that the reactivity of the carbanions introduced on the fullerene stays somewhat lower than that of the PSLi.

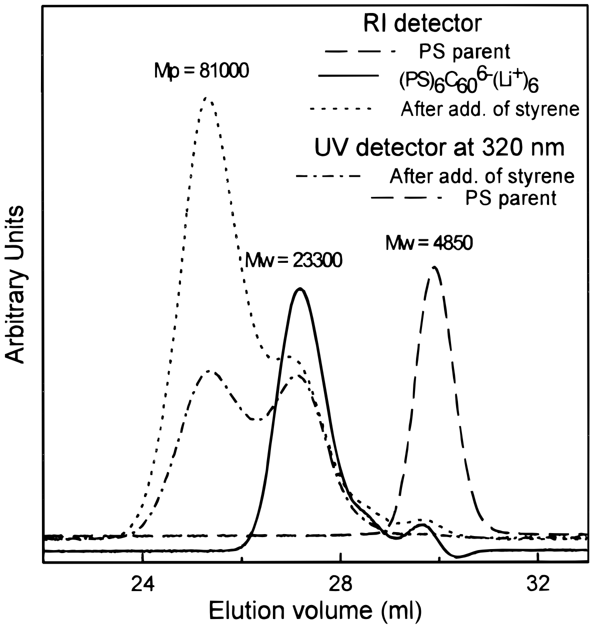


Figure 1. SEC evidence for the production of a palm tree-like structure $(PS_a)_6C_{60}PS_b$ via the anionic polymerization of styrene initiated by a "living" $(PS_a)_6C_{60}{}^{6-}(Li^+)_6$ in toluene.

The synthetic route developed here allows the simultaneous control of the lengths of the star arms and the out-growing chain. Because every step of this procedure involves anionic polymerization, the polydispersity of all the components of the architecture stays low. That allowed us to prepare a set of palm trees where the length of the branches and of the trunk were varied independently (Table 1). SEC coupled with LS allowed the determination of the absolute molar masses of the stars and palm trees. From these data, the length of

Table 1. PS Palm Tree-Like Structures Based on C_{60}

	PS_a "parent"			star $(PS_a)_6C_{60}$				palm tree		trunk
sample	Mn^a	Mw^a	I	Mn^a	Mw^a	I^b	$Mw_{LS}{}^c$	$Mw_{LS}{}^c$	$I_{ap}{}^d$	$Mw_{LS}{}^c$
A	2800	2900	1.03	9000	9600	1.07	16800	76100	1.3	59300
B	2840	2960	1.04	9200	10000	1.08	17400	141000	1.3	123000
C	4700	4850	1.03	19500	22400	1.14	30000	170000	1.25	140000
D	5300	5500	1.04	21100	23300	1.09	33000	114000	1.3	81000
E	6200	6450	1.04	28300	30500	1.07	37000	105000	1.25	68000

[a] SEC values. [b] Apparent polydispersity. [c] LS values. [d] Apparent polydispersity index for the palm tree as estimated from SEC.

Table 2. Palm Tree $(PS_a)_6C_{60}PI$ and Dumbbell $(PS)_6C_{60}PI\text{-Hex-}PIC_{60}(PS)_6$-Like Structures

	PS_a "parent"			star $(PS_a)_6C_{60}$				palm tree $(PS_a)_6C_{60}PI$		dumbbell $[(PS_a)_6C_{60}PI]_2$	
expt	Mn^a	Mw^a	I	Mn^a	Mw^a	I^b	$Mw_{LS}{}^c$	Mp^d	$I_{ap}{}^e$	Mp^d	$I_{ap}{}^e$
F	6200	6450	1.04	28300	30500	1.07	37000	80400	1.08	133000	1.08
G	6200	6450	1.04	28300	30500	1.07	37000	99000	1.1	148000	1.07

[a] SEC values. [b] Apparent polydispersity. [c] LS values. [d] Mpeak (PS calibration). [e] Apparent polydispersity index for the palm tree as estimated from SEC.

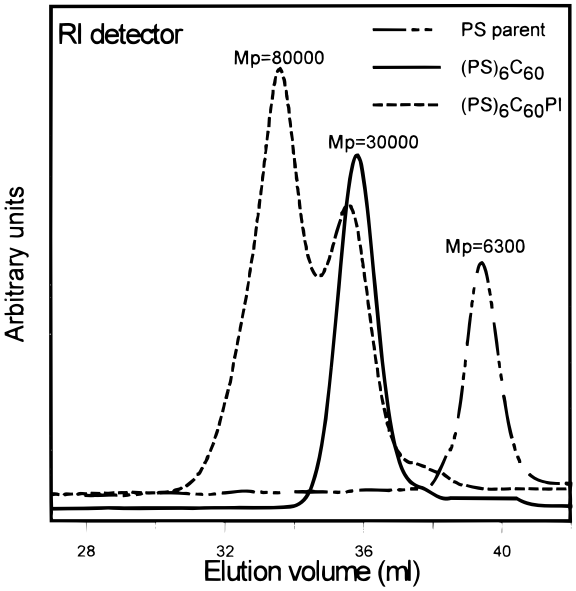


Figure 2. SEC characterization of a palm tree $(PS)_6C_{60}PI$ obtained on polymerization of isoprene initiated by a "living" $(PS)_6C_{60}{}^{6-}(Li^+)_6$ in toluene.

the trunk can be estimated according to the following formula: $Mw_{LStrunk} = Mw_{LSpalm\ tree} - Mw_{LSstar}$. The corresponding molar masses are reported in Table 1.

b. Copolymers Polystyrene−Polyisoprene. This synthetic route, based on the reaction between "living" polymers and a fullerene, can be extended in principle to other anionically polymerizable monomers. Among the various block copolymers conceivable, the ones incorporating incompatible sequences such as PS and polydienes, are of special interest.[17] In particular, the organization in selective solvents or in the solid state of such copolymers may depend on their structure,[10,11] so that the synthesis of novel architectures is an interesting challenge. The production of well-defined "living" six-branched PI stars is possible, and they are able to initiate the polymerization of styrene leading to palm trees of the type $(PI)_6C_{60}PS$. The production of palm trees $(PS)_6C_{60}PI$ depends on the ability of the carbanions present on a "living" hexaadduct to open the less activated double bond of a diene.[18] To verify this last point, we added isoprene to $(PS)_6C_{60}{}^{6-}(Li^+)_6$. The product obtained is shown in Figure 2 along with the star used to initiate it. The RI trace shows that a compound with a higher molar mass is formed at the expense of the hexaadduct, indicating that these "living" stars are able to initiate the anionic polymerization of isoprene. As in the initiation of styrene, the peak corresponding to the "living" star has not totally disappeared. The UV−vis trace at 320 nm confirms the presence of C_{60} in the compound of high molar mass. The observation of a single peak of narrow polydispersity suggests that, as discussed for styrene, only one PI chain is growing out from the fullerene core. That is confirmed because no physical gel or notable increase of viscosity is observed in the reaction medium. Because PI−Li is associated by 4 in toluene,[19] a physical network should be formed if two or more chains were growing from the same core. Taking advantage of this result, we prepared two copolymers $(PS)_6C_{60}PI$ with a palm tree-like architecture. In these products, the PS star stayed the same and only the length of the PI trunk was varied. Because some unreacted $(PS)_6C_{60}$ was always present in the samples, it was not possible to determine precisely the composition of the palm tree $(PS)_6C_{60}PI$ and so the increment of its refractive index. Because the determination of the absolute molar mass of this latter is not possible by LS, we report only the apparent molar masses obtained by SEC using a PS calibration in Table 2.

2. Dumbbell-Like Structures, (Scheme 3). In the initiation of styrene or isoprene by the "living" hexaadduct, the single chain growing out from the fullerene bears on its end a styryl or isoprenyl carbanion, which is much more reactive than the 5 carbanions still located on the C_{60} core. Indeed, these latter can not open the double bond of styrene or isoprene.[13] We have taken advantage of this difference in reactivity to synthesize dumbbell-like structures, where two six-branched stars are connected through a single chain of the same or different chemical nature, by reacting "living" palm trees with a coupling agent.

a. Polystyrene. Dumbbell-like structures have been synthesized by coupling "living" palm trees prepared as described above with dibromo-*p*-xylene. This reactive molecule has been chosen and added dropwise to favor the coupling reaction. The SEC traces of a typical product are given in Figure 3. Compared with the starting palm tree, the whole RI trace is shifted to higher molar masses without broadening, which indicates that all the molecules are coupled. Even if the DBrpX in principle may also react with a carbanion present on the C_{60} core, the styryl carbanion on the out-

Scheme 3. Schematic Representation of the Synthesized Dumbbell Architectures

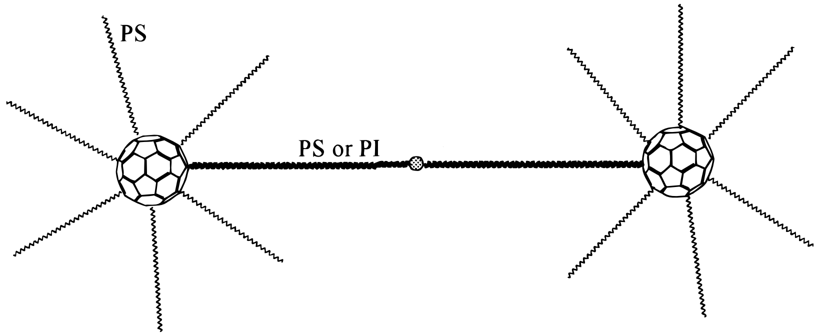


Table 3. PS Dumbbell-Like Structures Based on C_{60}

palm tree "parent"	coupling agent	star $(PS_a)_6C_{60}$ Mw_{LS}[a]	palm tree $(PS_a)_6C_{60}PS_b$ Mw_{LS}[a]	trunk PS_b Mw_{LS}[a]	dumbbell $(PS_a)_6C_{60}PS_b$-pX-$PS_bC_{60}(PS_a)_6$ Mw_{LS}[a]	I_{ap}[b]
A	DBrpX	16800	76100	59300	126200	1.3
B	C_{60}	17400	141000	123000	295000	1.4
D	DBrpX	33000	114000	81000	200000	1.3
E	DBrpX	37000	105000	68000	192000	1.3
E	C_{60}	37000	105000	68000	167000	1.4

[a] LS values. [b] Apparent polydispersity index for the palm tree as estimated from SEC.

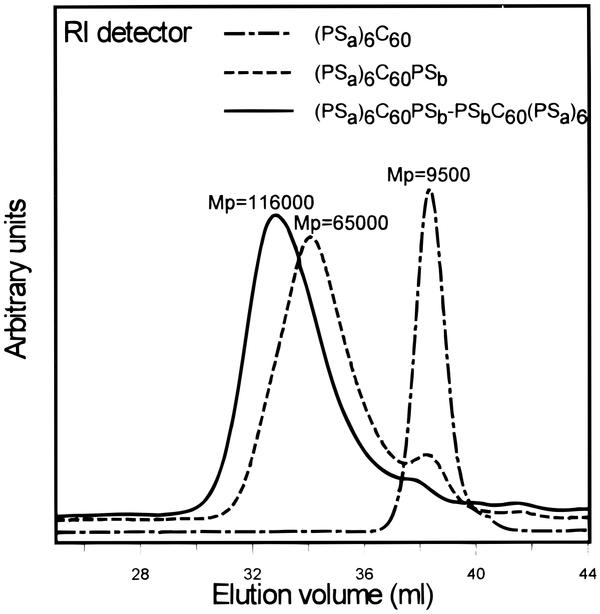


Figure 3. SEC analysis of the dumbbell-like PS obtained by coupling "living" palm trees $(PS_a)_6C_{60}{}^{5-}(Li^+)_5PS_b{}^-Li^+$ with dibromo-*p*-xylene.

growing chain is so much more reactive that only this latter reacts. The UV trace at 320 nm shows that the fullerene is present in this higher molar mass compound. Because of the branched structure of these products, the expected doubling of the molar mass cannot be measured by a simple SEC analysis. But, with LS it could be verified that the molar mass of the coupled product is close to twice that of the palm tree, which indicates that the expected dumbbell is formed. The experimental molar masses of three dumbbells $(PS_a)_6C_{60}PS_b$-pX-$PS_bC_{60}(PS_a)_6$, along with those of the corresponding palm trees $(PS_a)_6C_{60}PS_b$, are reported in Table 3.

The styryl carbanion borne by the out-growing chain of a "living" palm tree was allowed to react with C_{60} in a stoichiometry of six carbanions per fullerene, to try to prepare "multistars" by coupling six palm trees onto a single molecule. SEC analysis of the resulting compound indicates that no detectable polymer with a molar mass higher than twice that of the palm tree is formed, and that a large amount of this latter is still present. The same result is obtained even if the reaction medium is heated at 60 °C. In another type of experiment, the total amount of 0.5 C_{60} per "living" palm tree was added in successive small quantities to this latter so that the carbanions were always in great excess. The addition was slow so that each fullerene had time to add a maximum of chains. The SEC analysis of the product formed is reported in Figure 4. No noticeable amount of higher adducts as 2 was observed, but nearly all the palm tree had been coupled. The somewhat broader RI trace points to some dispersity in functionality for the coupled products. These observations are surprising, because hexaadducts are formed easily if linear chains bearing the same carbanions are reacted in a 6:1 stoichiometry with C_{60}, and that even if the molar mass

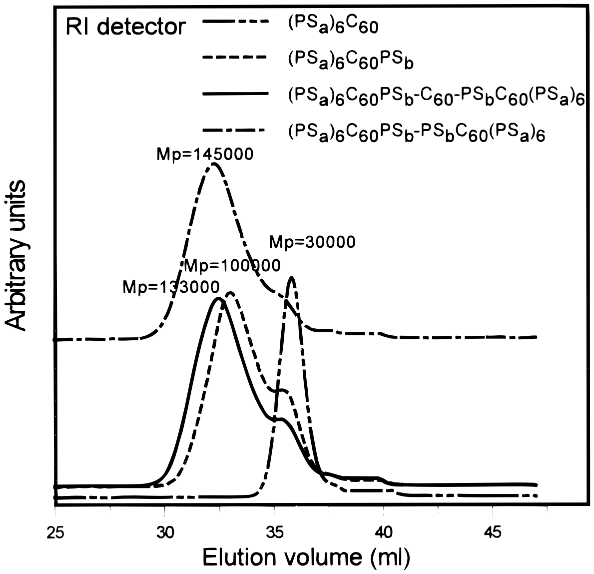


Figure 4. SEC traces obtained on reacting a "living" palm tree $(PS_a)_6C_{60}{}^{5-}(Li^+)_5PS_b{}^-Li^+$ with dibromo-*p*-xylene or C_{60}.

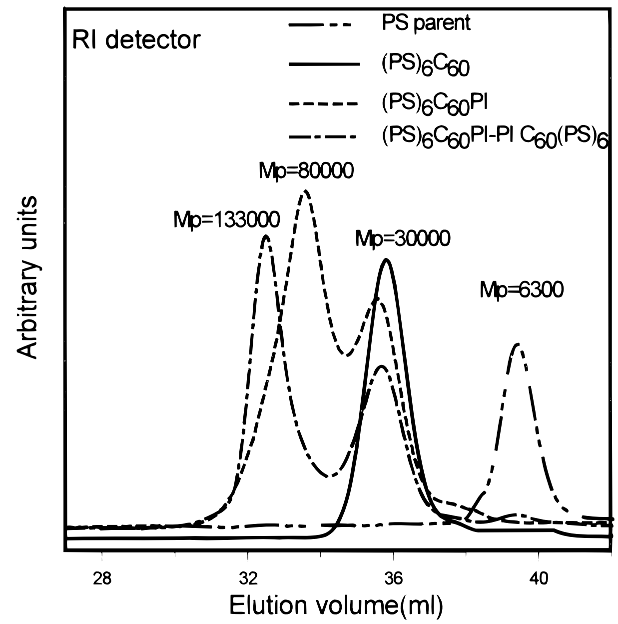


Figure 5. SEC analysis of the dumbbell-like PS−PI block copolymer obtained by coupling "living" palm trees $(PS)_6$-$C_{60}{}^{5-}(Li^+)_5PI^-Li^+$ with dibromohexane.

of the PSLi is as large as 360 000.[16] The chemical reaction involved is the same, so the difference probably comes from the severe steric hindrance induced by the presence of the six-branched star on one end of the palm tree. To confirm this point, coupling experiments with C_{60} and palm trees having very long trunks and small star heads are in progress.

b. Copolymers Polystyrene−Polyisoprene. The same procedure was applied to couple palm trees made of a PS star and a PI trunk. Because the isoprenyl carbanion is somewhat more reactive than styryl, dibromohexane was used as coupling agent. We chose this less active molecule to minimize the probability of reaction with the carbanions still present on the C_{60} core. A typical example of coupling product is given in Figure 5 and compared with the "parent" palm tree. No unreacted palm tree can be detected, and the very narrow shape of the dumbbell peak attests that a single species is formed. The coupling reaction is quantitative in this case, leading to a pure dumbbell molecule. As discussed for the "parent" palm tree, the d*n*/d*c* of the dumbbell could not be measured and so the absolute molar masses could not be determined. But, because the composition PS/PI stayed unchanged on going from the palm tree to the dumbbell, we could verify that the ratio $Mw_{LSdumbbell}/Mw_{LSpalm\ tree}$ is close to 2 using an arbitrary value for d*n*/d*c*. The SEC molar masses using a PS calibration are reported in Table 2.

Conclusion

The reaction of "living" polystyrene or polyisoprene with C_{60} offers an easy synthetic route to fairly pure stars where six branches are connected to a single fullerene core. As prepared, these stars bear six carbanions on the core, but only one of them is reactive enough to initiate the anionic polymerization of styrene or isoprene. Taking advantage of these results, we have prepared well-defined palm tree- and dumbbell-like polymers and block copolymers. The incorporated C_{60} molecules constitute the essential building blocks of these architectures.

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