Carbanions on Grafted C_{60} as Initiators for Anionic Polymerization

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ABSTRACT: Two methods to introduce negative charges on a C_{60} and the further use of these carbanions as initiators for anionic polymerization of styrene and methyl methacrylate were investigated. From the potassium salts of C_{60}, obtained by reduction with potassium naphthalenide, only the hexaanion is able to polymerize MMA, and that by electron transfer so that no fullerene is attached to the PMMA. In a second method, polystyryllithium was added to C_{60} to form "living" star molecules with a C_{60} core bearing a well-controlled number of branches (i.e., carbanions). Six carbanions have to be located on the C_{60} to initiate anionic polymerization of styrene by addition onto the monomer, while five are enough to initiate the more reactive MMA. Stars with seven PS branches and heterostars with six PS and two PMMA have been produced.

Introduction

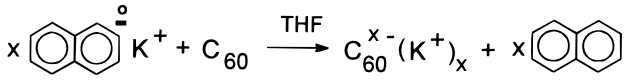
The introduction of negative charges onto C_{60} and the further use of these reactive sites to add various molecules constitute an interesting approach for the production of grafted fullerenes. Two different methods may be used to create negative charges on C_{60}: electron transfer or addition of a carbanion on a double bond. Fullerides can be prepared by several methods such as electrochemistry,[1−3] photochemistry,[4] or reduction with an alkali metal[5] or an organoalkali metal salt.[6] A carbanion is located on the C_{60} each time a charged nucleophile, like a "living" carbanionic polymer, for example, opens a double bond on the fullerene.[7,8] In a previous publication,[9] we have studied in some detail the grafting of anionic polymers onto C_{60} and defined the conditions to obtain "star-shaped" polymers with a C_{60} core and a controlled number of arms (i.e., carbanions). The goal of the work presented here was to prepare well-defined alkali metal salts of C_{60} and carbanionic grafted fullerenes, and then to check if the negative charges introduced onto the C_{60} are able to initiate anionic polymerization of vinyl monomers. In addition to a better knowledge of the reactivity of carbanions located on a fullerene, we may expect new opportunities for the synthesis of polymer structures. Indeed, as far as the initiation proceeds through addition on the monomer, it would offer a way to synthesize star-shaped macromolecules with a fullerene core and well-defined branches fit with anionic sites at their outer end, thus easily functionalized for further reactions. In the case where the carbanions on the fullerene result from the addition of a "living" anionic polymer, the second generation of branches growing from the C_{60} core can be of a different chemical structure, leading to the synthesis of "heterostars".

Experimental Section

All experiments were conducted in glass apparatus sealed under high vacuum using the break-seal technique[10] in order to fulfill the high-purity conditions required.

Purification of Solvents, Monomers, C_{60}, and Initiators. Tetrahydrofuran (THF) and toluene free of protonic impurities were distilled through the vacuum line directly into the apparatus from a purple solution of the sodium salt of benzophenone dianion and a red solution of (3-methyl-1,1-diphenylpentyl)lithium, respectively. Styrene (Aldrich), first distilled over sodium, was distilled under high vacuum directly in ampules equipped with break-seals from an *n*-butyllithium solution (prepolymerization). Methyl methacrylate (MMA) was distilled under vacuum first over sodium wire and then over calcium hydride directly in ampules. The C_{60} (>99% from TechnoCarbo) was stirred several hours in pure THF and recovered by centrifugation. To remove impurities present in the commercial fullerene, this procedure was repeated until the THF stays 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 (*s*-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.[11] Potassium naphthalenide (NK) was prepared in THF by reacting naphthalene (Aldrich) on a potassium mirror. All these initiators were stored in sealed 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,[10] an optical cell being sealed on the apparatus. The concentration of "living" polymers was further confirmed by molecular weight determination.

Scheme 1



Synthesis of Alkali Metal Salts of C_{60}. These salts were prepared by electron transfer from potassium naphthalenide to C_{60} (Scheme 1). Known amounts of NK in solution in THF were progressively added to a weighted amount of C_{60} in suspension in THF, and the reaction was monitored by UV−vis−near-IR spectroscopy. Once all the fullerene is converted to the radical anion (one NK per C_{60}), a homogeneous solution, displaying the characteristic absorption peak at 1075 nm, is obtained. To prepare the trianion, more NK was added until pure soluble $C_{60}^{3-}(K^+)_3$ was formed (three NK per C_{60}), as demonstrated by its near-IR spectra. The excess of NK was then removed by sealing of the corresponding ampule, the reduced fullerene solution was cooled to −70 °C, and styrene or MMA was slowly added at this temperature. After about 1 h of reaction, the "living" species were deactivated with acidified methanol and the solution was centrifuged in order to remove ungrafted fullerenes (C_{60} and protonated C_{60} are not soluble in THF). The soluble part is precipitated in methanol.

To produce the insoluble hexaanion of C_{60}, six NK were added per fullerene. No unreacted NK can be found by UV spectroscopy in the solution, demonstrating that all NK have

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Table 1. Comparative Redox Potentials

Electroreduction of C_{60} $E_{1/2}$ (V vs SCE), Li^+/THF		redox potential of "living" polymers	redox potential of radical-anions (V vs SCE)
C_{60}^-	−0.5 [1]		
C_{60}^{2-}	−1.2 [1]	PMMA$^-$	
C_{60}^{3-}	−1.8 [2]		
C_{60}^{4-}	−2.3[2]		
C_{60}^{5-}	−2.6[1]	polystyryl$^-$	naphtalene−K$^-$, −2.5
C_{60}^{6-}	−2.8[3]		

transferred one electron to the fullerene. Further addition of NK results in the detection of the characteristic absorption peaks of NK, which increases with the added amount. This observation shows that a maximum of six electrons can be transferred to C_{60} by NK. The hexaanion being insoluble in THF, the excess of NK can be easily removed by internal distillation of the solvent, yielding pure $C_{60}^{6-}(K^+)_6$. The monomer was then added to the suspension of $C_{60}^{6-}(K^+)_6$ as described for the trianion.

"In−Out" Synthesis of Grafted C_{60}. The anionic polystyrenes (PS) were prepared in toluene using *s*-BuLi as initiator and each "living" polymer solution was divided in several ampules. One was used to determine the concentration of carbanions and then 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 the apparatus was sealed off, the break-seal of the ampule was broken and a determined amount of "living" PS was added dropwise to the stirred C_{60} solution in order to obtain the required functionality. After 2 h of reaction, the solution is divided in two by sealing of 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. Styrene was slowly added to the other part of the "living" grafted fullerenes and the reaction allowed to run for 2 h before addition of acidified methanol. All the products were characterized by SEC−LS to find out the number of branches of the star molecules formed.

In the case of reaction with MMA, once the "living" grafted fullerene formed, the reaction media was cooled to −70 °C and about 10% of pure THF introduced before addition of the monomer.

Size Exclusion Chromatography (SEC). The various samples were analyzed by size exclusion chromatography (SEC) using a refractive index (RI) 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. As SEC is not able to give the absolute molecular weight of star-shaped macromolecules,[12] a light scattering (LS) detector was added to get access to this value. All samples being soluble in THF, this solvent was used as eluent and SEC, equipped with various set of columns, was previously calibrated using linear PS standards.

Results and Discussion

1. Initiation of the Anionic Polymerization of Vinyl Monomers by Alkali Metal Salts of C_{60}. Fullerides were prepared in THF via electron transfer from the potassium radical-anion naphthalenide (NK) to the C_{60} molecule (Scheme 1). The control of the molar ratio NK to C_{60} leads to various reduction states ranging from the monoanion to the hexaanion. As the ability for an organoalkaline compound to initiate the anionic polymerization of a vinyl monomer is related to its redox potential,[10] we decided to test fullerides of various

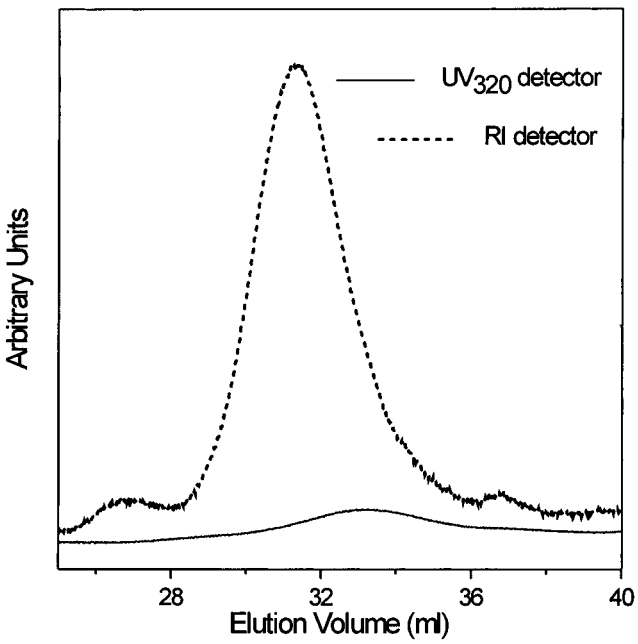
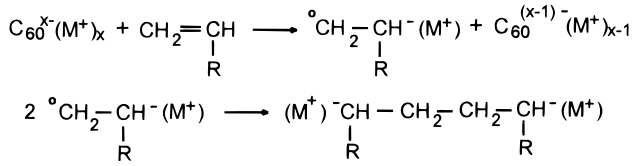


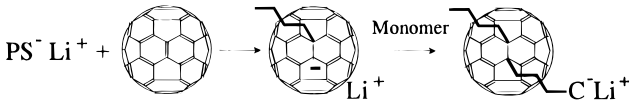
Figure 1. SEC analysis of PMMA (M_n = 51 700, M_w = 130 900, I = 2.53) obtained in THF using $C_{60}^{6-}(K^+)_6$ as initiator.

reduction states with two monomers of various reactivities: styrene and MMA. In a first set of experiments, respectively styrene and MMA were added to a THF solution of the trianion $C_{60}^{3-}(K^+)_3$. In both cases, the characteristic UV−vis−near-IR spectra of the trianion stayed unchanged after addition of the monomer and no polymer was obtained; just protonated C_{60}s, insoluble in THF, are recovered. That indicates that, as could be anticipated from the respective redox potentials (Table 1), the C_{60} trianion cannot initiate the anionic polymerization of styrene. More surprising is the fact that $C_{60}^{3-}(K^+)_3$ is also unable to initiate the polymerization of the more polar MMA, although the redox potential attributed in the literature to the trianion appears to be negative enough (Table 1). In a second set of experiments, the two monomers were reacted with $C_{60}^{6-}(K^+)_6$. The hexaadduct being hardly soluble in THF, the reaction media is heterogeneous. Styrene was slowly added to the hexaanion at −70 °C and the reaction allowed to proceed for 1 h before deactivation with acidified methanol. Only insoluble products corresponding to protonated C_{60} are recovered. No polymer is obtained, indicating that the hexaanion is unable to initiate the anionic polymerization of styrene. Under the same conditions MMA was added to the hexaanion. An increase of the temperature is detected, indicating that polymerization occurs. No insoluble compounds are found, and the polymer obtained was characterized by SEC (Figure 1). The RI trace shows a single peak with a broad polymolecularity (M_n = 51 700, M_w = 130 900, I = 2.53). The flat signal of the UV detector set at 320 nm, where the PMMA has no absorption and only C_{60} or its derivatives are detected, indicates that no C_{60} has been attached to the polymer. The respective heights of the two traces given in Figure 1 are the ones directly given by the experiment. For comparison, the SEC analysis of a hexaaduct PS_6C_{60} of similar molecular weight (M_n = 130 200, M_w = 141 500) using the same setting gives rise to a UV_{320} trace of about the same amplitude as the RI trace.[9] So we can conclude that the initiation of the polymerization occurs through electron transfer from the reduced C_{60}

Scheme 2



Scheme 3



to MMA, leading to a difunctional "living" PMMA (Scheme 2). This is the classical initiation mechanism observed with radical anions or dianions of aromatic or conjugated compounds.[10] The initiation with $C_{60}^{6-}(K^+)_6$ being a heterogeneous reaction, this step is low compared to the very fast propagation of the anionic polymerization of MMA even at −70 °C; that contributes to the broad polymolecularity observed. In addition, the C_{60} hexaanion being highly nucleophilic, some side reactions on the ester group of the monomer cannot be excluded.

Even if alkali metal salts of C_{60} may be used to initiate the anionic polymerization of some vinylic monomers, this reaction is of little interest, as no fullerene is attached to the polymer chain and much better initiators are known.[10] Nevertheless, our results seem to indicate that the redox potentials for the potassium salts of strongly reduced fullerenes are somewhat less negative than published for other counterions.[1−3]

2. Initiation of Anionic Polymerization of Vinyl Monomers Using Charged Grafted Fullerenes. Each addition of a carbanion onto a double bond on C_{60} introduces a negative charge on the fullerene molecule (Scheme 3). We wanted to find out under which conditions the carbanions located on the fullerene molecule become reactive enough to initiate polymerization of vinyl monomers such as styrene or MMA. It is well-known, in anionic polymerization, that the ability of a carbanion to open a double bond of a vinyl monomer increases if the charge is more localized.[13] As the delocalization of a charge on the fullerene should decrease when the number of charges present increases, we can expect that the ability of a carbanion on a grafted fullerene to initiate polymerization will depend on the total number of charges present on the C_{60}, i.e., the number of grafts. So, first of all, a good control and knowledge of the functionality of the grafted fullerenes is necessary. We have previously reported that, in nonpolar solvents, a maximum of six "living" polystyrene chains can be grafted onto C_{60} and fairly pure lower adducts (going from the triadduct to the pentaadduct) can be synthesized by controlling the molar ratio polystyryllithium (PS−Li) to C_{60}.[9] So we have used this so called "arm-first" procedure to synthesize "living" stars bearing various numbers of negative charges and checked their ability to initiate anionic polymerization of vinyl monomers.

2a. Polymerization of Styrene. In a first set of experiments, "living" stars bearing six branches, and so six negative charges, have been synthesized in toluene. The molecular weight of the PS branch (M_w = 4850, M_n = 4700, I = 1.03) was chosen large enough so that the functionality could be confirmed by the weight of the star-shaped macromolecules determined by light scattering (M_{wLS} = 30 000; experimental functionality 6.2).

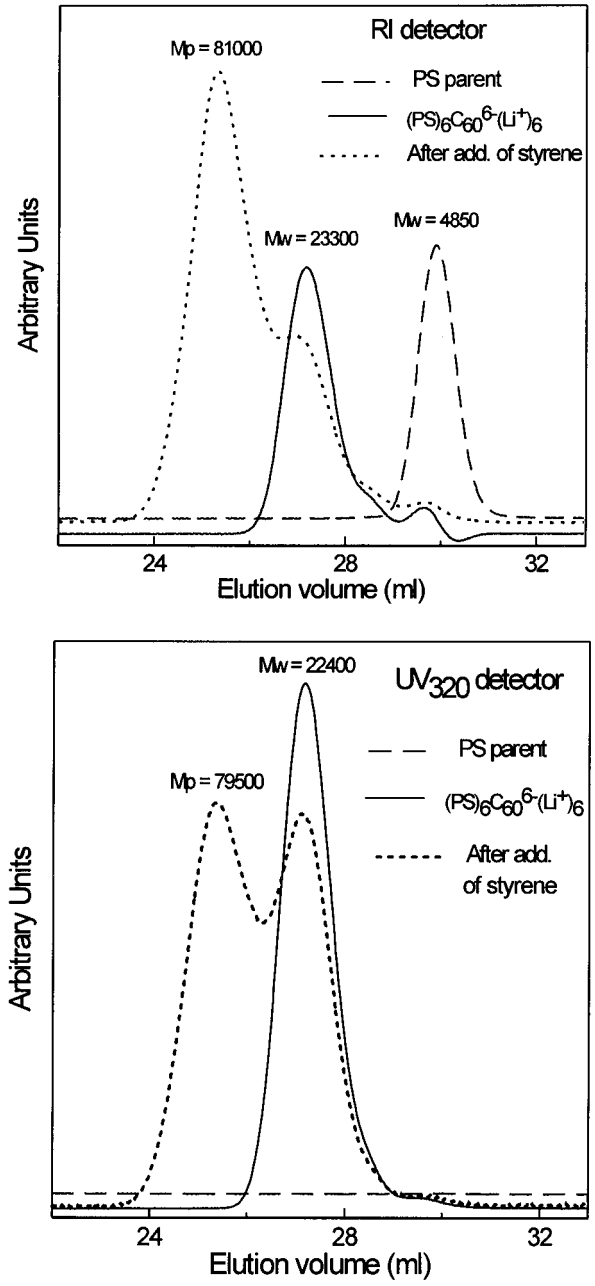


Figure 2. SEC evidence for the initiation of anionic polymerization of styrene by a "living" hexaadduct.

In addition, the shape of the SEC trace corresponding to the star (Figure 2) indicates that the hexaadduct is fairly pure (M_{wSEC} = 23 000, M_{nSEC} = 21 000, $I_{apparent}$ = 1.1) and that very little ungrafted PS−Li is present. Styrene was then slowly added, at room temperature, to the $(PS)_6C_{60}^{6-}(Li^+)_6$ solution, and the increase of temperature observed in the reaction media indicates that polymerization occurs. After 2 h of reaction, the carbanions were deactivated with acidified methanol and the polymer was recovered and analyzed by SEC (Figure 2). The RI trace shows that a compound with a higher molecular weight is formed at the expense of the hexaadduct, indicating that these "living" stars are able to initiate the anionic polymerization of styrene. The fact that the peak corresponding to the "living" star has not totally disappeared could point to some initiation problems which will be discussed below. The UV−vis trace at 320 nm confirms the presence of C_{60} in the compound of high molecular weight. Some information about the number of initiated chains may be found in

the fact that no physical gel or important increase of viscosity is observed in the reaction media. As PS−Li is associated by two in toluene,[14] a physical network should be formed if more than two chains were growing from the same core. That suggests that only one or two chains are initiated. Although the determination of the number of branches growing from the core is very difficult just by analyzing the SEC diagram, the monomodal distribution of the higher molecular weight peak seems to indicate that only one chain is growing from the "living" core of the $(PS)_6C_{60}^{6-}(Li^+)_6$ star molecules.

To confirm that only one carbanion of a "living" hexaadduct is able to initiate styrene, $(PS)_5C_{60}^{5-}(Li^+)_5$ was synthesized and characterized by LS (experimental functionality 5.1). Styrene was added under the same conditions as before to this "living" star and the resulting polymer characterized by SEC. No change in molecular weight can be detected before and after the introduction of monomer, demonstrating that a "living" pentaadduct is unable to initiate anionic polymerization of styrene. So, six negative charges need to be located on the same C_{60} to make the carbanions reactive enough so that one of them becomes able to add to the double bond of styrene. Once this initiation is done, the reactivity of the five residual carbanions on the C_{60} decreases and becomes close to that observed for a pentaadduct that is unable to initiate styrene. In a preliminary report we assumed that a pentaadduct was able to initiate styrene, but these first results were obtained with "living" stars of low molecular weight so that no control of the functionality by LS was possible and the compound used was in fact mainly a hexaadduct.[7,8]

For a direct determination of the number of chains growing out from the C_{60} core of a "living" star, one needs to be able to determine the molecular weight of these additional chains. That can, in principle, be done if an excess of PSLi parent is present when the monomer is added, assuming that the "living" star and the "living" linear chains have the same initiation rate. In this case, the molecular weight of the second generation of branches corresponds to the increase of weight of PS−Li. For such an experiment, we prepared a hexaadduct using an excess of PS−Li. The molecular weight of the latter was chosen low to allow a better determination of the molecular weight of the second generation. The SEC analysis (Figure 3) confirms that six branches have been grafted onto C_{60} and that ungrafted "living" PS is present. After addition of styrene, the PS−Li peak has disappeared and compounds with high molecular weight are detected. The UV−vis curve at 320 nm shows that no C_{60} is present in these compounds of higher molecular weight. The modifications of the peak corresponding to six branched stars before and after addition of styrene are minor. All that indicates that practically only the linear PS−Li has initiated the anionic polymerization of styrene. This points to a lower overall polymerization rate for the chain starting from a charged star as for the PS−Li in excess. As $(PS)_6C_{60}^{6-}(Li^+)_6$ is produced by addition of PS−Li onto 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 PS−Li. This difference of reactivity can induce a slower initiation by $(PS)_6C_{60}^{6-}(Li^+)_6$ but, as the polymolecularity of the outcoming chains is rather narrow (Figure 2), the initiation has to stay fast compared to propagation. The results can be explained if the accessibility of the monomer to

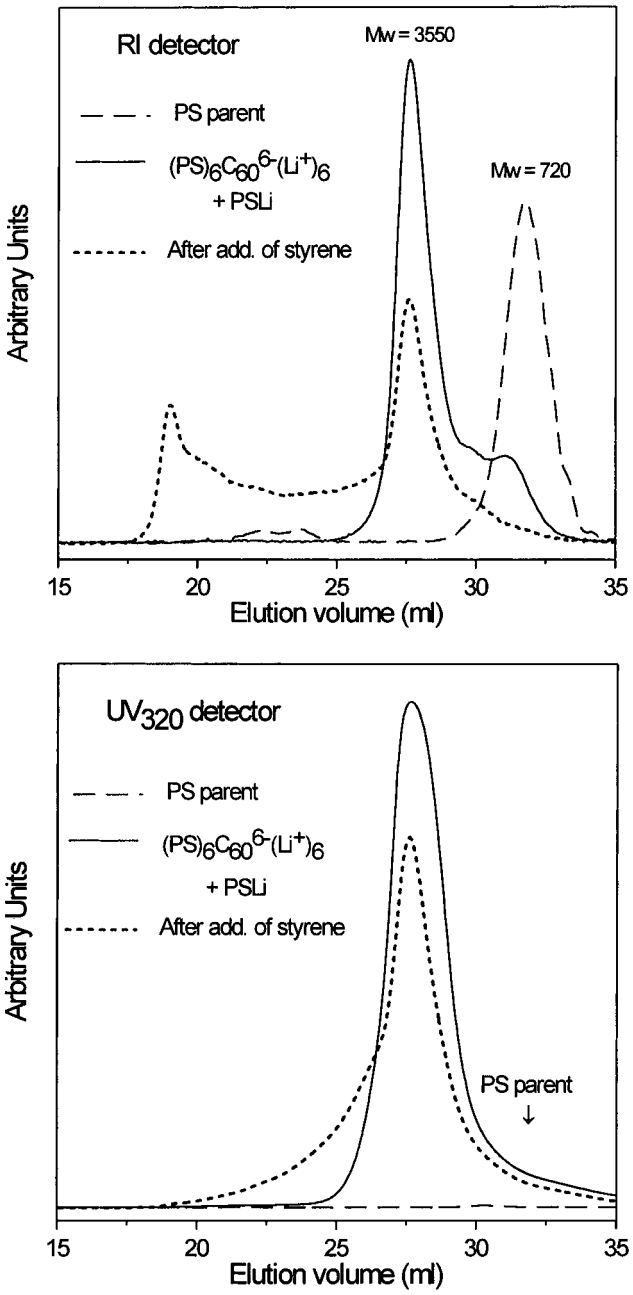


Figure 3. SEC analysis of the products formed if styrene is added to a "living" hexaadduct ($M_w = 3600$, $M_n = 2200$, $I_{apparent} = 1.64$) in the presence of an excess of PS−Li parent ($M_w = 720$, $M_n = 650$, $I = 1.1$).

the active species located on the C_{60} is more difficult, due to the high density of segments in the center of these stars with a very narrow core. In this case, the polymerization rate for the addition of the very first monomers becomes very low. Of course, once the outcoming chain becomes longer, it reaches the polymerization rate of the "normal" PS−Li chains. But at this point, most of the monomer has already reacted with the PS−Li in excess. This effect excludes the possibility of a direct determination of the molecular weight of the second generation of chains and may also explain that some hexaadduct is still present after reaction with styrene. More measurements (kinetics) are needed to confirm this hypothesis.

We extended this study to polar solvents. For that, PEK (first unit of a "living" polystyrene) was reacted with C_{60} in THF. As reported previously, the reaction mechanism of "living" PS with C_{60} is more complicated

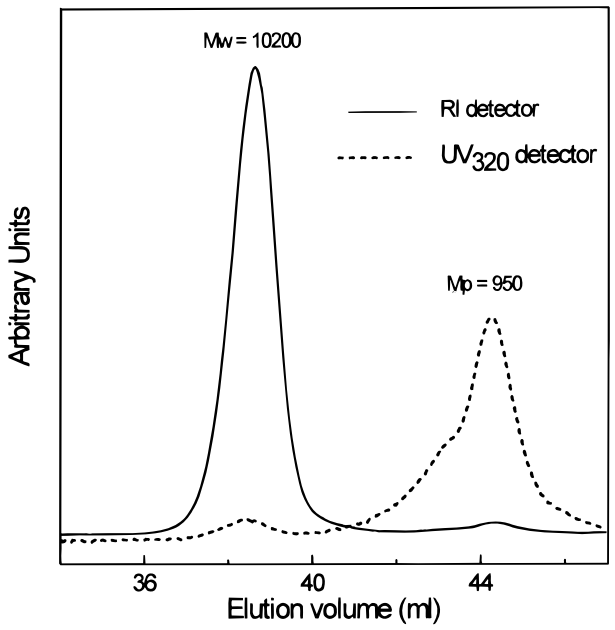


Figure 4. SEC analysis of the polymer produced upon addition of styrene to $PE_4C_{60}^{6-}(K^+)_6$ containing an excess of PEK.

in polar solvents, as in toluene, and consists of two successive reactions.[9,15] First, two electrons are transferred from the carbanions to the C_{60}, leading to the soluble dianion C_{60} ($C_{60}^{2-}(K^+)_2$), and then four carbanions add to the double bonds on C_{60}, leading to a grafted fullerene bearing four chains but six negative charges: $PS_4C_{60}^{6-}(K^+)_6$. In our experiment we have added eight PEK per C_{60} and then reacted the plurifunctional initiator mixed with unreacted PEK with styrene. A fast increase of temperature indicates that polymerization occurs. The resulting polymer was characterized by SEC (Figure 4). The RI trace indicates the formation of a PS of narrow polymolecularity (M_n = 9500, M_w = 10 200, I = 1.07) with no grafted fullerene, as shown by the UV detector at 320 nm. The peak corresponding to $PE_4C_{60}^{6-}(K^+)_6$ is still present after addition of styrene. That shows that, in the presence of PEK, this C_{60} tetraadduct bearing six negative charges is unable to initiate anionic polymerization of styrene by addition on the monomer. Initiation by electron transfer from $PE_4C_{60}^{6-}(K^+)_6$ to the styrene can also be excluded, as it would produce a dicarbanionic PS and no polymer with a molecular weight twice that of the PS initiated by the PEK in excess is observed.

2b. Polymerization of MMA. The same kind of experiments were carried out with the more polar MMA, except that 10% of THF was added to the reaction media to avoid the additional complications of anionic polymerization of MMA in nonpolar solvents and the monomer added at −70 °C. This monomer being easier to polymerize, one can anticipate that more than one chain may grow out from the C_{60} core of a charged hexaadduct.

MMA was added at −70 °C to a "living" hexaadduct containing no PS−Li in excess (experimental functionality 5.6). After a few minutes, the temperature is allowed to warm slowly and the solution turns to a gel. This gel subsists until acidified methanol is added. It is well-known that "living" PMMA are not stable even at very low temperatures and that the carbanions convert to oxoanions.[16] These latter have a high tendency to associate. So, the formation of the observed "physical" network implies that at least two PMMA

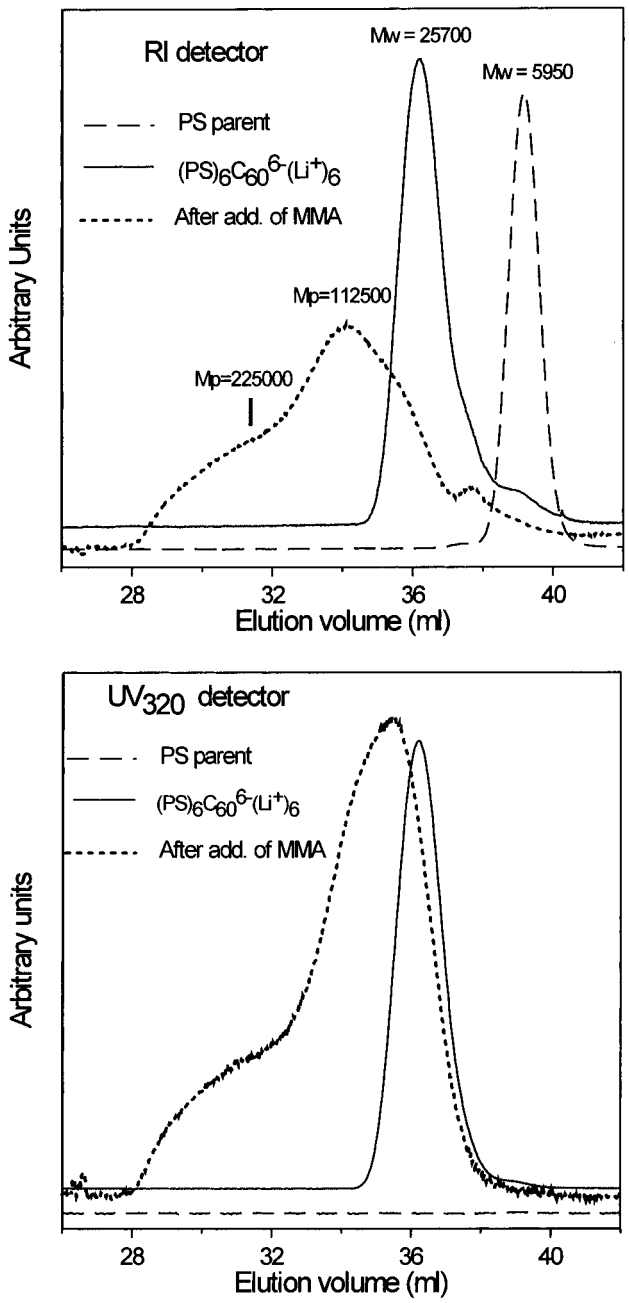


Figure 5. SEC evidence for the initiation of anionic polymerization of MMA by a "living" hexaadduct. (M_w = 25 700, M_n = 22 000, $I_{apparent}$ = 1.17, M_{wLS} = 33 000) (PS−Li parent: M_w = 5950, M_n = 5700, I = 1.04).

chains have grown out from the C_{60} core. SEC analysis of the products (Figure 5) shows a strong decrease of the "living" stars peak and the presence of a dimodal peak at lower elution volumes, indicating the formation of probably two compounds of higher molecular weight. The respective proportions of these compounds may be understood if one takes into account the presence of some pentaadduct, as the experimental functionality of the "living" stars used is only 5.6. The UV−vis trace at 320 nm confirms the presence of C_{60} in these compounds. So, anionic polymerization of MMA is initiated by these "living" stars bearing six PS branches and at least two additional arms of PMMA have been formed, leading to the formation of "heterostars". The broad distribution of the molecular weight after introduction of MMA may reflect some initiation problems, but the low stability of "living" PMMA may also

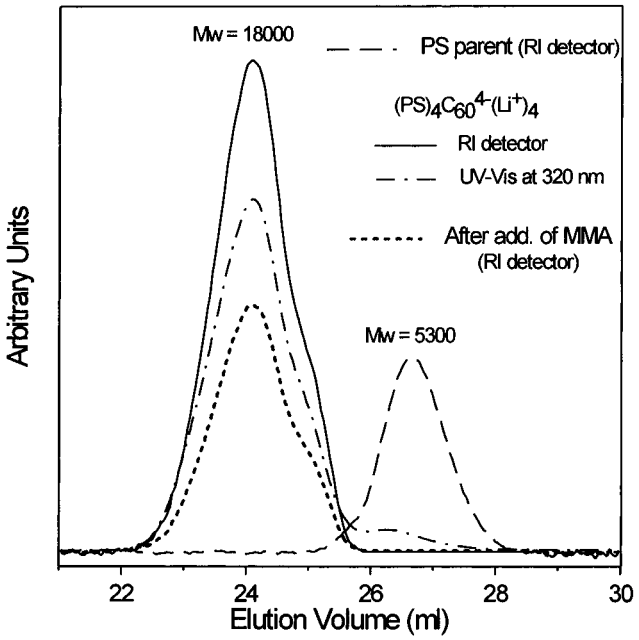


Figure 6. SEC evidence that a "living" tetraadduct is unable to initiate the polymerization of MMA. (M_w = 18 000, M_n = 15500, $I_{apparent}$ = 1.16, M_{wLS} = 20 000) (PS−Li parent : M_w = 5300, M_n = 5050, I = 1.05).

contribute. In addition, as only 10% of THF was added to the toluene, some of the complications observed in the anionic polymerization of MMA in nonpolar solvents may persist.

For a better determination of the number of branches of the second generation, $(PS)_4C_{60}^{4-}(Li^+)_4$ has been synthesized (experimental functionality 3.8) and reacted with MMA under the same conditions. SEC analysis of the resulting polymers (Figure 6) shows that a "living" tetraadduct is not able to initiate anionic polymerization of MMA. So we can conclude that a "living" hexaadduct is able to initiate the polymerization of two and only two chains of PMMA.

Conclusion

Reduced C_{60}s act like radical ions or dianions of aromatic or conjugated compounds, as far as the initiation of vinyl monomers is concerned. The initiation proceeds through electron transfer onto the monomer, so that no fullerene is attached to the polymer formed. The degree of reduction of the C_{60} has to be higher than 3 in order to initiate MMA, and styrene cannot even be polymerized with the hexaanion. "Living" star molecules with a C_{60} core and a well-defined number of arms (i.e., carbanions) can be obtained by addition of PS−Li onto the fullerene in toluene. The carbanions present on these charged grafted C_{60}s are able to initiate anionic polymerization of a vinyl monomer. The initiation occurring through addition to the monomer, the C_{60} star is covalently bonded to the out-growing chain. Six carbanions have to be located on the fullerene in order to initiate anionic polymerization of styrene, while five are enough to initiate the more reactive MMA. That illustrates the increase of reactivity of a carbanion located on a C_{60} with the increase of the number of charges present on the fullerene.

References and Notes

(1) Dubois, D.; Moninot, G.; Kutner, W.; Jones, M. T.; Kadish, K. M. *J. Phys. Chem.* **1992**, *96*, 7137.
(2) Chabre, Y.; Djurado, D.; Armand, M.; Romanow, W. R.; Coustel, N.; McGauley, J. P., Jr.; Fischer, J. E.; Smith, A. B., III. *J. Am. Chem. Soc.* **1992**, *114*, 764.
(3) Xie, Q.; Perez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992,** *114*, 3978.
(4) Arbogast, J. W.; Foote, C. S.; Kao, M. *J. Am. Chem. Soc.* **1992,** *114*, 2277.
(5) Bausch, J. W.; Prakash, G. K.; Olah, G. H. *J. Am. Chem. Soc.* **1991,** *113*, 3205.
(6) Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 293.
(7) Ederlé, Y.; Reibel, D.; Mathis, C. In *Physics and Chemistry of Fullerenes and Derivates*; Kuzmany, H., Fink, J., Mehring, M., Roth, S., Eds.; World Scientific: Singapore, 1995; p 155.
(8) Ederlé, Y.; Mathis, C. *Fullerene Sci. Technol.* **1996**, *4*, 1177.
(9) Ederlé, Y.; Mathis, C. *Macromolecules* **1997**, *30*, 2546.
(10) Szwarc, M. *Carbanions, Living Polymers and Electron Transfer Processes*; Wiley-Interscience: New York, 1968.
(11) Beinert, G.; Zilliox, J. G.; Herz, J. *Makromol. Chem.* **1988**, *189*, 2521.
(12) Jackson, C.; Brath, H. G. *Trends Polym. Sci.* **1994**, *2*, 203.
(13) Rempp, P.; Merrill, E. W. *Polymer Synthesis*; Hüting & Wapf: Basel, 1986; p 216.
(14) Worsfold, D. J.; Bywater, S. *Can. J. Chem.* **1960**, *38*, 1891.
(15) Ederlé, Y.; Mathis, C. In *Fullerenes and Fullerene Nanostructures*; Kuzmany, H., Fink, J., Mehring, M., Roth, S., Eds.; World Scientific Singapore, 1996; p 520.
(16) Szwarc, M. Living Polymers and Mechanisms of Anionic Polymerization. *Adv. Polym. Sci.* **1983**, *49*, 133.

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