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Polymer 46 (2005) 8519–8527
polymer
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Asymmetric and mikto-arm stars with a C_{60} core by grafting of macro-radicals or anionic polymer chains

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Received 10 November 2004; accepted 7 March 2005
Available online 26 May 2005

Abstract

Asymmetric and mikto-arm stars were synthesized by the stepwise addition of macro-radicals or of anionic polymer chains onto C_{60}. Pure di-adducts $(PS_a)_2C_{60}$ were obtained by atom transfer radical addition of a Br-terminated polystyrene (PS_aBr). Tetra-adducts $(PS_a)_2C_{60}(PS_b)_2$ and $(PS_a)_2C_{60}(PI)_2$ were prepared by grafting, respectively, two additional PS_bBr or PIBr onto $(PS_a)_2C_{60}$. The addition of 'living' polystyryllithium onto C_{60} can be stoichiometrically controlled. For example, the reaction of four PS_aLi with one C_{60} led to the formation of $(PS_a)_4C_{60}^{4-}(Li^+)_4$. The additional grafting of polystyryllithium (PS_bLi) or polyisoprenyllithium (PILi) provided, respectively, $(PS_a)_4C_{60}(PS_b)_2$ and $(PS_a)_4C_{60}(PI)_2$. All the stars were characterized using multiple detectors size exclusion chromatography (SEC).

Keywords: Fullerene; ATRA; Anionic polymerization

1. Introduction

The specific chemical reactivity of the plurifunctional C_{60} (30 conjugated double bonds on a single molecule) opens new opportunities for the synthesis of 'model' polymer architectures such as asymmetric stars and mikto-arm stars. Two routes are of special interest: the grafting of anionic polymers [1–7] and the addition of macro-radicals [8,9] especially those generated from halogen-terminated polymers [10–12] prepared by atom transfer radical polymerization (ATRP). The arms of the stars being prepared by anionic polymerization or ATRP [13–16], their molar masses can be tailored and their polydispersities stay low.

The addition of radicals onto the double bonds (6–6 bonds) of fullerenes was one of the first chemical modifications reported [17] but this reaction is still rather difficult to control. Nevertheless, we have shown that pure di- and tetra-adducts can be obtained by addition of macro-radicals generated from PSBr prepared by ATRP using CuBr/2,2′-bipyridine to promote the breaking of the C–Br bond, according to Scheme 1 [11,12]. The grafting of a maximum of 6 'living' anionic polymers such as polystyrylLi (PSLi) and polyisoprenylLi (PILi) onto C_{60} in non-polar solvents is well established and understood [5]. This upper limit, that originates from the delocalization of the carbanions on the conjugated fullerene molecule, allows preparing well-defined hexa-adducts [18]. The control of the grafting of lower numbers of arms is also possible by adjusting the stoichiometry [5]. Here, we will discuss some of the possibilities provided by these two synthetic routes toward the preparation of asymmetric stars and mikto-arm stars.

2. Experimental

2.1. Materials

1-Phenylethyl bromide, methyl 2-bromopropionate, CuBr and 2,2′-bipyridine (Aldrich) were used as received. Toluene was first distilled under reduced pressure over sodium wire and then directly into the apparatus from a red solution of 3-methyl-1,1-diphenylpentyllithium. Styrene and isoprene (Aldrich) were distilled twice over sodium, and for anionic polymerization these monomers were

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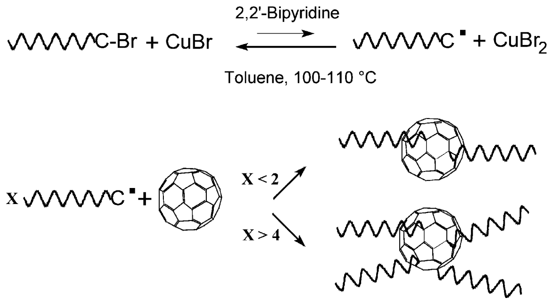
doi:10.1016/j.polymer.2005.03.106



Scheme 1. Preparation of di- and tetra-adducts by atom transfer radical addition ATRA.

further distilled in ampoules equipped with break-seals from a *n*-butyllithium solution (prepolymerization). Fullerene C_{60} (SES Research–purity >99%) was stirred for several hours in THF dried previously over benzophenone^{2-} $(Na^{+})_2$. After sonication of the suspension, the fullerene was recovered by centrifugation, dried at 150–200 °C under high vacuum (10^{-5} Torr) and then stored and handled in a glove box under argon to avoid any exposure to moisture and air. *Sec*-butyllithium (*s*-BuLi) was prepared by reacting 2-chlorobutane with lithium metal in cyclohexane and its concentration determined by titration.

2.1.1. Synthesis of Br-terminated polystyrene (PSBr) and poly(methyl methacrylate) (PMMABr) chains

PSBr chains were prepared by atom transfer radical polymerization (ATRP) [13] in bulk in sealed glass ampoules. The 1-phenylethyl bromide, CuBr and 2,2′-bipyridine were used in the proportions 1:1:2 and the solution degassed three times by freezing in ^{i}PrOH/dry ice before sealing under vacuum. The polymerizations were run at 100–110 °C for several hours and stopped at about 20–40% of conversion. The excess of styrene was removed by distillation. After dissolution of the polymer in THF, the solution was centrifuged to eliminate catalyst residues and the PSBr was recovered by precipitation in methanol. The polymers were further purified by elution with THF through a short silica gel column and finally recovered as white powders after precipitation in MeOH and drying.

PMMABr chains were prepared using the same procedure except that the initiator was methyl 2-bromopropionate [14,15,19,20], the monomer diluted with toluene (50%) and the temperature set at 90 °C.

2.1.2. Synthesis of polystyreneLi (PSLi) and polyisopreneLi (PILi)

The anionic polymerization of styrene and isoprene was conducted in a glass apparatus sealed under high vacuum using the 'break-seal' technique [21]. PSLi and PILi were prepared at room temperature in toluene using *sec*-butyllithium as initiator.

2.1.3. Synthesis of Br-terminated polyisoprene chains

Under vacuum, a toluene solution of a 'living' polyisoprene was added slowly in a concentrated THF solution of dibromoparaxylene. This latter was in 10-fold excess in order to minimize the coupling reaction. Fractionation was used to remove the coupling product from the PI–CH_2–Ph–CH_2Br.

2.1.4. Preparation of di-adducts $(PS)_2C_{60}$, asymmetric and mikto-arm stars by addition of macro-radicals onto C_{60}

In a typical synthesis of $(PS)_2C_{60}$, PSBr chains dissolved in toluene (10% in weight) were reacted with C_{60} ($PSBr/C_{60}=1$) for 2–3 days at 100–110 °C in sealed glass tubes in the presence of CuBr (2/PSBr) and 2,2′-bipyridine (4/PSBr). The same conditions were used to react PMMABr with the fullerene; but only mono-adducts PMMAC_{60} were obtained in this case. The change of color from the typical purple color of C_{60} in solution to brown indicated that addition occurred. The di-adducts were purified from excess of fullerene and catalytic residues as described above for PSBr.

Asymmetric and mikto-arm stars were prepared by reacting purified $(PS)_2C_{60}$ or PMMAC_{60} with, respectively, an excess (≥ 2) of a PS_bBr having a different molar mass or of a PI–CH_2–Ph–CH_2Br. The experimental procedure was identical to the one used for the synthesis of $(PS)_2C_{60}$, except that the reaction time was 4–6 days.

2.1.5. Preparation of polystyrene stars with a fullerene core $(PS)_xC_{60}$ ($x \leq 5$), asymmetric and mikto-arm stars by grafting of PSLi or PILi onto C_{60}

Polystyrene stars with a C_{60} core and up to five arms were prepared in an apparatus sealed under high vacuum, by adding dropwise precise amounts of 'living' PS to a stirred C_{60} solution in toluene of known concentration. As already reported [5], this stoichiometric control allows preparing pure tri- to penta-adducts. In order to characterize the adducts, an aliquot of 'living' species was sealed-off after 2 h of reaction and 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 in excess of methanol, filtered and dried under vacuum.

Asymmetric and mikto-arm stars were prepared by adding an excess ($>6-x$) of a PSLi having a different molar mass or of a PILi to the toluene solution of 'living' $(PS)_xC_{60}^{x-}(Li^{+})_x$ ($x \leq 5$). The experimental procedure was similar to the one used for the synthesis of $(PS)_xC_{60}$. To avoid oxidation and limit the breaking of the PI-fullerene link [7,22,23], the stars containing polyisoprene were stored under vacuum.

2.2. Characterizations

Multiple detectors size exclusion chromatography (SEC) in THF was used to characterize all the polymer chains prepared by ATRP or anionic polymerization as well as the various stars with a C_{60} core. The SEC setup consisted of a Shimadzu LC10AD pump, a ERMA ERC3512 on-line degasser, a WATERS automatic injector and five 300 × 7.5 mm^2 PL Gel columns from Polymer Laboratories (4 × 10 μm^2 Mixed-B and one 500 Å)connected in series. In addition to the refractive index (RI) detector (Shimadzu RID10A), a UV–vis detector (Shimadzu SPD10A) set at 320 nm was used to detect selectively the polymers including C_{60}. At that wavelength, the PS or the PI is no longer detected but the fullerene-containing molecules absorb light. To determine the actual molar mass of star-shaped polymers, an on-line light scattering (LS) detector (MALLS DAWN DSP from Wyatt Technology) was also used. Nevertheless, the strong absorption of light by the fullerene core strongly limits the accuracy of the determination of molar masses by LS for stars with short arms. The d*n*/d*c* for the mikto-arm stars was calculated from the d*n*/d*c* of PS (0.186) and of PI (0.118) taking into account the molar mass of the PS and PI chains and the number of arms of each kind on the fullerene.

3. Results and discussion

As reported earlier, the addition of polystyrene macroradicals prepared by ATRP [11,12] as well as that of polystyrene–Lithium [4–6] onto C_{60} allows controlling the number of grafted arms. In both cases there is a maximum number of grafts that can be added to the fullerene: respectively, 4 [11,12] and 6 [5,18]. If, in a first step, the number of added arms is kept lower than these limits the grafting of additional PS or PI chains becomes possible, leading to the formation of asymmetric or mikto-arm stars. The grafting of additional PS chains to the fullerene core of a mono-adduct PMMAC_{60} allows also preparing mikto-arm stars (see below).

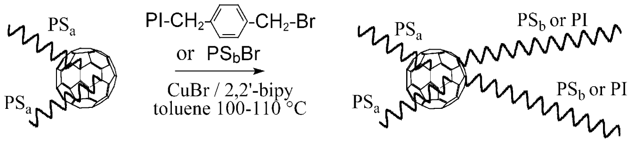
3.1. Asymmetric and mikto-arm stars by atom transfer radical addition (ATRA) onto C_{60}

3.1.1. Asymmetric stars $(PS_a)_2C_{60}(PS_b)_2$

If PSBr are converted to macro-radicals in the presence of C_{60}, using the same catalytic system as ATRP, chains are grafted onto the fullerene [10–12]. We have recently demonstrated that this grafting follows a specific mechanism leading to the addition of even numbers of chains. Tetra-adducts are obtained if the ratio PSBr/C_{60} is higher than four but only di-adducts are formed as long as this ratio stays lower than two (Scheme 1) [12]. In this latter case, the excess of unreacted fullerene is easily removed from the di-adduct due to its insolubility in polar solvents like THF where adducts are soluble. The SEC and LS characterization of some examples of di-adducts $(PS_a)_2C_{60}$, prepared by reacting one C_{60} with one PS_aBr of molar mass ‘a’ in toluene at 100–110 °C in the presence of CuBr/2,2′-bipyridine, are presented in Table 1. Since up to four chains can be grafted onto the fullerene using ATRA, the grafting of two additional chains can be expected if such a di-adduct is further reacted under the same conditions with an excess of a PS_bBr of molar mass ‘b’, leading to the formation of an asymmetric star $(PS_a)_2C_{60}(PS_b)_2$ (Scheme 2). Examples of the formation of such asymmetric stars are depicted in Figs. 1 and 2 and their SEC and LS characterization are given in Table 1. Fig. 1 shows the RI and the UV at 320 nm traces of the starting di-adduct $(PS_a)_2C_{60}$ ($M_{n\ RI}$ = 14,000 g/mol) and of the product obtained after reacting this di-adduct with a four-fold excess of PS_bBr ($M_{n\ RI}$ = 40,000 g/mol) for 4 days in toluene at 100–110 °C in sealed glass tubes in the presence of CuBr (2/PS_bBr) and 2,2′-bipyridine (4/PS_bBr). The comparison between the RI traces (solid lines) of the reaction compound (curve 2) and the di-adduct (curve 1) indicates that all this latter has reacted (less than 3% recovered) to produce a polymer of $M_{n\ RI}$ = 90,000 g/mol. This increase indicates that two additional PS chains of $M_{n\ RI}$ = 40,000 g/mol have been grafted to the di-adduct to produce the asymmetric star $(PS_{10,000})_2C_{60}(PS_{40,000})_2$ as expected. The response of the RI detector being proportional to the amount of polystyrene, it is possible to conclude that the reaction product consists of a mixture of about 45% of the asymmetric star and 55% of unreacted $PS_{40,000}Br$ (peak *b*). That is close to what is expected considering that $PS_{40,000}Br$ was used in a four-fold excess. Comparison between the UV traces at 320 nm (dotted lines)—where only the fullerene-containing polymers are detected—of the reaction compound (curve 2) and the di-adduct (curve 1) confirms that this latter has been completely converted to the compound of highest molar mass and that there is no fullerene present in the polymer responsible for the peak *b* detected by the RI detector. The absence of fullerene in the polymer contained in peak *b* and its molar mass identical to that of the added $PS_{40,000}Br$ proves that it corresponds indeed to the unreacted part of this latter.

The same conclusions can be derived from Fig. 2 showing the SEC analysis of the asymmetric star produced upon reacting a di-adduct $(PS_{19,600})_2C_{60}$ with a four-fold excess of $PS_{40,000}$.

It is known that SEC underestimates the molar masses of branched architectures and that the difference between the actual molar mass of a star and that determined by SEC increases with the number of arms [24]. To get a more accurate determination of the number of additional arms onto the di-adducts, we turned to light scattering to measure the actual molar masses of the various adducts (Table 1).



Scheme 2. Synthesis of an asymmetric star $(PS_a)_2C_{60}(PS_b)_2$ or a mikto-arm star $(PS_a)_2C_{60}(PI)_2$ by ATRA.

Table 1
SEC and LS characterization of the products obtained by reacting Br terminated polystyrene or polyisoprene with a di-adduct $(PS_a)_2C_{60}$ at 110 °C in toluene in the presence of CuBr and 2,2′-bipyridine

Sample	PS_bBr/[a]$(PS_a)_2C_{60}$	% RI[b]	$M_{n\ RI}$	I_{RI}[c]	$M_{n\ UV320}$	I_{UV320}	$M_{w\ LS}$[c]	Added arms (n)
PS_aBr			10,000	1.27			11,000	
$(PS_a)_2C_{60}$			14,000	1.42	18,000	1.24	20,000	
PS_bBr			40,000	1.22			42,000	
PS_bBr	4	55	40,000	1.39			42,000	
$(PS_a)_2C_{60}(PS_b)_n$		45	90,000	1.10	90,000	1.26	120,000	2.3
PS_aBr			19,600	1.29			23,400	
$(PS_a)_2C_{60}$			31,000	1.37	36,000	1.24	46,000	
PS_bBr			40,000	1.22			42,000	
PS_bBr	4	50	42,000	1.38			42,000	
$(PS_a)_2C_{60}(PS_b)_n$		50	110,000	1.10	105,000	1.22	140,000	2.2
PS_aBr			10,000	1.27			11,000	
$(PS_a)_2C_{60}$			14,000	1.42	18,000	1.24	20,000	
PS_bBr			21,000	1.17			25,000	
PS_bBr	6	75	21,000	1.17			25,000	
$(PS_a)_2C_{60}(PS_b)_n$		25	60,000	1.12	61,000	1.36	77,000	2.2
PS_aBr			8000	1.31			10,000	
$(PS_a)_2C_{60}$			16,000	1.30	15,000	1.33	20,000	
PIBr			44,000	1.06			32,000	
PIBr	4	70[d]	49,000	1.15				
$(PS_a)_2C_{60}(PI)_n$				1.10	55,000	1.10	47,000	0.9
$(PS_a)_2C_{60}(PI)_n$		25	101,000		116,000	1.10	74,000	1.7

[a] Number of mole of PS_bBr (PIBr) added per mole of $(PS_a)_2C_{60}$.

[b] Weight % of unreacted PS_bBr and asymmetric or mikto-arm stars calculated from the RI detector response; n, number of grafts added onto the di-adduct.

[c] $I_{RI}=M_{w\ RI}/M_{n\ RI}$ and $I_{UV320}=M_{w\ UV320}/M_{n\ UV320}$.

[d] 10–20% of the di-adduct $(PS_a)_2C_{60}$ have not added a PI chain and a small amount of mono-adduct is included in the RI peak attributed to PI.

For the three examples reported, two PS_b were added to $(PS_a)_2C_{60}$ leading to an asymmetric star $(PS_a)_2C_{60}(PS_b)_2$.

3.1.2. Mikto-arm stars $(PS)_2C_{60}(PI)_2$

As isoprene cannot be polymerized by ATRP, we turned to anionic polymerization to produce a Br-terminated polyisoprene that may be converted to a macro-radical using ATRA conditions. For that a ‘living’ PILi was reacted with a large excess of dibromoparaxylene and the coupling compound $PI–CH_2–Ph–CH_2–PI$ was separated from $PI–CH_2–Ph–CH_2Br$ (later referred to as PIBr) by polymer fractionation. In a second step, PIBr was reacted with a di-adduct $(PS)_2C_{60}$. Fig. 3 shows the SEC analysis of the product obtained (curve 2) upon reacting a four-fold excess of PIBr ($M_{w\ LS}=32{,}000$ g/mol, peak b) with a di-adduct $(PS)_2C_{60}$ ($M_{w\ LS}=20{,}000$ g/mol, curve 1) for 5 days in

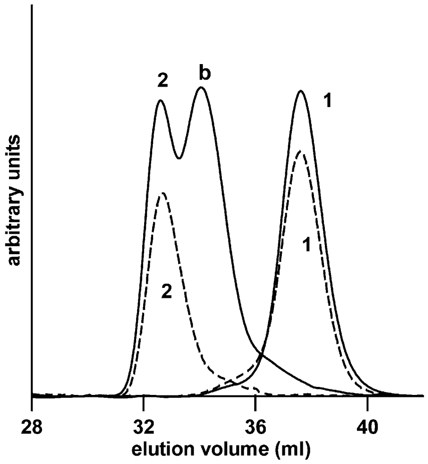


Fig. 1. RI traces (solid line) and UV traces at 320 nm (dotted line) of a di-adduct $(PS_a)_2C_{60}$ ($M_n=14{,}000$, curve 1) and the product (curve 2) obtained after reaction with a four-fold excess of PS_bBr ($M_n=40{,}000$, peak b).

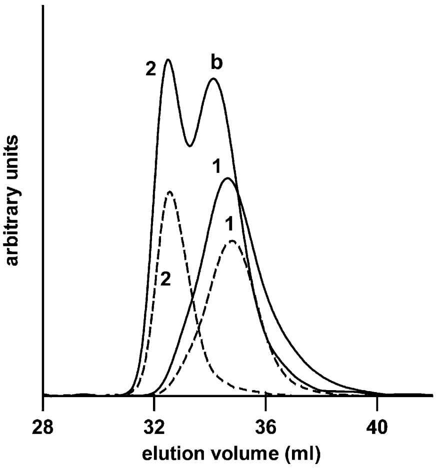


Fig. 2. RI traces (solid line) and UV traces at 320 nm (dotted line) of a di-adduct $(PS_a)_2C_{60}$ ($M_n=31{,}000$, curve 1) and the product (curve 2) obtained after reaction with a four-fold excess of PS_bBr ($M_n=40{,}000$, peak b).

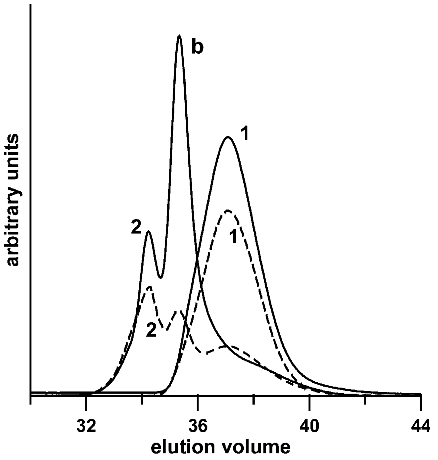


Fig. 3. RI traces (solid line) and UV traces at 320 nm (dotted line) of a di-adduct $(PS)_2C_{60}$ ($M_{\mathrm{n\ SEC}}=16{,}000$, $M_{\mathrm{w\ SEC}}=20{,}000$, curve 1) and the product (curve 2) obtained after reaction with PI–CH_2–Ph–CH_2Br ($M_{\mathrm{n\ SEC}}=44{,}000$—using a PS calibration, $M_{\mathrm{w\ LS}}=32{,}000$, peak *b*).

toluene at 100–110 °C in a sealed glass tube in the presence of CuBr (5/PIBr) and 2,2′-bipyridine (10/PIBr). The molar masses of the products determined by SEC and LS are reported in the last entry of Table 1. The RI trace (solid line) of the reaction products indicates that most of the di-adduct has reacted (the amount of unreacted $(PS)_2C_{60}$ can be estimated around 20%) with PIBr (peak *b*) to form a compound having an apparent molar mass $M_{\mathrm{n\ RI}}=$ 101,000 g/mol (the SEC was calibrated with PS standards). That proves that PI arms were attached to the fullerene core of the $(PS)_2C_{60}$ ($M_{\mathrm{n\ RI}}=16{,}000$ g/mol). Using the apparent molar mass of PIBr determined by SEC ($M_{\mathrm{n\ RI}}=44{,}000$ g/mol) and considering that SEC does not underestimate notably the molar mass of the resulting mikto-arm star since the added PI chains are much longer than the two PS arms already grafted onto the C_{60}, we can assume that two additional PI chains were attached to the fullerene. The same conclusion can be drawn from the actual molar masses determined by LS. The response of the UV at 320 nm is not proportional to the amount of polymer as for each product it depends on the concentration of fullerene: i.e. on the total amount of polymer grafted per C_{60}. So, the response of the di-adduct is much higher than that of the corresponding mikto-arm star. Nevertheless, the UV_{320} trace (curve 2, dotted line) confirms that part of the di-adduct has not added any PI chain and that molecules containing C_{60} are present in the peak *b* consisting mainly of the excess of PIBr. This observation is coherent with the formation of a small amount of a mikto-arm star where the fullerene core bears two PS chains and only one PI chain. This difference between the grafting of PS–CH_2–CH(Ph)Br obtained by ATRP and PI–CH_2–Ph–CH_2Br onto a $(PS)_2C_{60}$ by ATRA can be attributed to the slight difference in the terminal group. Such difference may affect both the addition mechanism and the kinetics.

3.1.3. Mikto-arm stars $PMMAC_{60}(PS)_x$; $x=2$ or 3

Methyl methacrylate can be polymerized via ATRP to obtain Br-terminated chains [14,15,19,20]. After purification, these latter can be converted to macro-radicals in toluene at 100–110 °C using the usual CuBr/2,2′-bipyridine system. If that is realized in the presence of C_{60}, the addition of one chain onto the fullerene occurs as can be seen from the example given in Fig. 4. Indeed, as expected PMMABr is not detected by an UV detector set at 320 nm (Fig. 4(a)), but after reaction a fullerene-containing product with the same molar mass as the starting PMMABr is detected (Fig. 4(b)). No higher adducts could be obtained whatever the stoichiometry PMMABr/C_{60} (1–6) or the reaction time (60–140 h). In addition, the area corresponding to the UV_{320} peak was always lower than that expected for a pure mono-adduct, indicating that some ungrafted chains are still present. That may reflect, at least partially, the fact that not all of the PMMA chains prepared by ATRP have a terminal Br [25,26]. This difference with the grafting of PSBr chains by ATRA points again to a different addition mechanism resulting from the difference of reactivity of the two types of radicals.

Further addition by ATRA of PSBr chains onto a mono-adduct $PMMAC_{60}$ should lead to another type of mikto-arm stars. The results (Table 2) of two such reactions, where a $PMMAC_{60}$ ($M_{\mathrm{w\ LS}}=33{,}000$ g/mol) was reacted for 5 days in toluene at 100–110 °C in the presence of CuBr (3/PSBr) and 2,2′-bipyridine (6/PSBr) with, respectively, 2 and 16 equivalents of PSBr ($M_{\mathrm{w\ LS}}=25{,}000$, peak *b*), are shown in Figs. 5 and 6. From the changes in the UV_{320} traces (dotted lines) it can be seen that in both cases nearly all the $PMMAC_{60}$ has been converted to a higher adduct indicating that addition of PS chains occurred. When the ratio PSBr/$PMMAC_{60}$ was 2 (Fig. 5), the increase of molar mass of the fullerene-containing compound measured by LS corresponds to the formation of a mikto-arm star $PMMA_{33{,}000}$-$C_{60}(PS_{25{,}000})_2$. That is what was expected from the mechanism of grafting of PSBr chains onto fullerene by ATRA. Nevertheless, the RI trace (curve 2) shows that this mikto-arm star represents only about 35% of the compounds, the largest peak *b* containing little fullerene being mainly attributed to unreacted PSBr, PMMA chains that have not added any C_{60} and a small amount of unreacted $PMMAC_{60}$. In the experiment where the ratio PSBr/$PMMAC_{60}$ was 16 (Fig. 6), the main product is unreacted PSBr with probably some PMMA as shown by the RI trace (solid line 2, peak *b*) and as expected from the large excess used. Again, the UV_{320} trace shows that nearly all the $PMMAC_{60}$ was converted to a product of higher molar mass. From the increase of mass measured by LS one can conclude that three PS arms are grafted to form a mikto-arm star bearing 4-arms $PMMA_{33{,}000}C_{60}(PS_{25{,}000})_3$. This grafting of 3 PS chains seems in contradiction with the mechanism of grafting of PSBr onto C_{60} by ATRA where only even numbers of grafts were observed. But, on the other hand we have also observed that we could not exceed

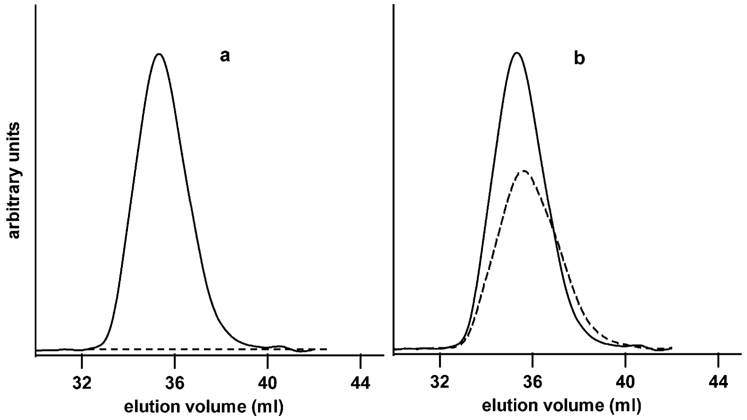


Fig. 4. RI traces (solid line) and UV traces at 320 nm (dotted line) of a PMMABr prepared by ATRA ($M_n = 23{,}000$—using PS calibration, curve a) and the mono-adduct PMMAC$_{60}$ (curve b) formed after reaction with one equivalent of C$_{60}$ at 110 °C for 3 days in toluene in the presence of CuBr/2,2′-bipyridine.

four grafts using ATRA. This limit may result from the high reaction temperature (100–110 °C) needed for these reactions. Indeed, we have recently shown that hexa-adducts $(PS)_6C_{60}$ prepared by grafting of PSLi onto the fullerene transform to lower adducts by cleavage of the PS-C$_{60}$ link if heated at 100–110 °C in toluene [22,23].

3.2. Asymmetric and mikto-arm stars by grafting of 'living' anionic polymers onto C$_{60}$

The maximum number of arms that can be grafted onto C$_{60}$ by reacting this fullerene with PSLi or PILi in a non-polar solvent is 6 [5,18] (Scheme 3). Several years ago we have reported that by controlling the stoichiometry PSLi/C$_{60}$ pure tri- to penta-adducts can be prepared [5]. That means that there still is the possibility to graft onto these adducts, respectively, 3, 2 and 1 additional PS chains of a different molar mass or PI chains by addition of the corresponding 'living' polymers in order to produce asymmetric or mikto-arm stars (Scheme 4).

3.2.1. Asymmetric stars $(PS_a)_xC_{60}(PS_b)_{6-x}$

An example of the preparation of such an asymmetric star is given in Fig. 7 and the data are reported in Table 3.

In a first step a PSLi of molar mass $M_n = 2600$ g/mol (curve 1 in Fig. 7(a)) is reacted in toluene with C$_{60}$ in a ratio 4 to 1. The strong absorption of light by the fullerene core of such low molar mass stars does not allow the use of light scattering to determine the actual mass of these branched architectures. Nevertheless, from the RI data (Fig. 7(a), curve 2) we can deduce that more than 80% of the reaction products (product 2) are tetra-adducts. Indeed, the M_n determined by SEC of the largest adduct corresponds to 3.6 times that of the initial PS arm and that is close to the value expected for a tetra-adduct if one takes into account the diminution of the hydrodynamic radius between a 4-arm star and the linear PS of the same molar mass [24]. But some lower adducts are also present as confirmed by the UV$_{320}$ trace (Fig. 7(b), curve 2).

In a second step, the $(PS_{2600})_4C_{60}$ is reacted with a three-fold excess of a PS$_b$Li of $M_n = 8200$ (peak *b* in Fig. 7(a)). From the UV$_{320}$ trace of the reaction product (Fig. 7(b), curve 3) it can be seen that all the polymers containing fullerene have increased their molar mass indicating that the tetra-adduct as well as the lower ones have added additional PS chains leading to asymmetric stars. The RI trace of the same reaction product (Fig. 7(a), curve 3) shows beside the asymmetric stars a minor peak at the same elution volume as the PS$_{8200}$Li (peak *b*). This product contains no fullerene and its concentration corresponds well to the proportion of

Table 2
SEC and LS characterization of the products obtained upon reacting Br terminated polystyrene obtained by ATRP with a mono-adduct PMMAC$_{60}$ at 110 °C in toluene in the presence of CuBr and 2,2′-bipyridine

Sample	PSBr/[a]PMMAC$_{60}$	% RI[b]	$M_{n\ RI}$	I_{RI}	$M_{n\ UV320}$	I_{UV320}	$M_{w\ LS}$	Added arms (n)
PMMABr			23,000	1.38			25,500	
PMMAC$_{60}$			25,000	1.42	22,000	1.70	33,000	
PSBr			21,000	1.17			25,000	
PSBr	2	65	28,000	1.17	–	–		
PMMAC$_{60}$(PS)$_n$		35	61,500	1.08	60,200	1.39	79,000	1.8
PSBr	16	80	25,000	1.14	–	–		
PMMAC$_{60}$(PS)$_n$		20	76,000	1.07	75,000	1.30	107,000	3.0

[a] Number of mole of PSBr added per mole of PMMAC$_{60}$.

[b] Weight % of unreacted PSBr estimated from the RI detector response; n, number of grafts added onto the mono-adduct.

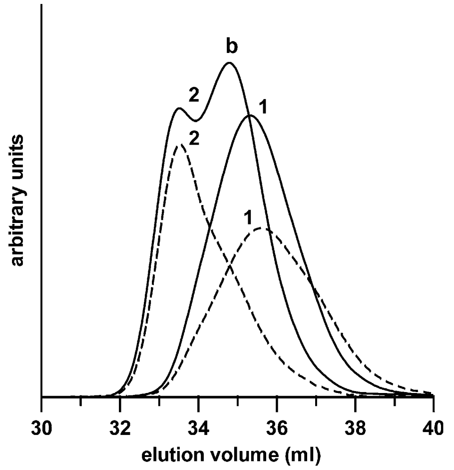


Fig. 5. RI traces (solid line) and UV traces at 320 nm (dotted line) of a mono-adduct (PMMA)C_{60} ($M_n = 25{,}000$—PS calibration, curve 1) and the product (curve 2) obtained after reaction with a two-fold excess of PSBr ($M_n = 21{,}000$, peak *b*).

unreacted $PS_{8200}Li$ expected from the excess used considering that the main reaction is the grafting of two additional arms onto a tetra-adduct. A close scrutiny of the RI (Fig. 7(a), curve 3) and UV_{320} (Fig. 7(b), curve 3) traces reveals that the peak corresponding to the asymmetric stars presents a shoulder on the higher molar mass side. The main product with a molar mass $M_n = 26{,}400$ g/mol can be assigned to an asymmetric star $(PS_{2600})_4C_{60}(PS_{8200})_2$ and the minor compounds responsible for the shoulder to a mixture of asymmetric stars $(PS_{2600})_xC_{60}(PS_{8200})_{6-x}$ ($x < 4$) resulting from the addition of $PS_{8200}Li$ onto the fullerene core of the small amount of $(PS_{2600})_xC_{60}$ with $x < 4$ present in product 2. This last consideration points to the main difficulty of this synthetic route toward asymmetric PS stars with a C_{60} core: the control of the stoichiometry $PSLi/C_{60}$ in the first step.

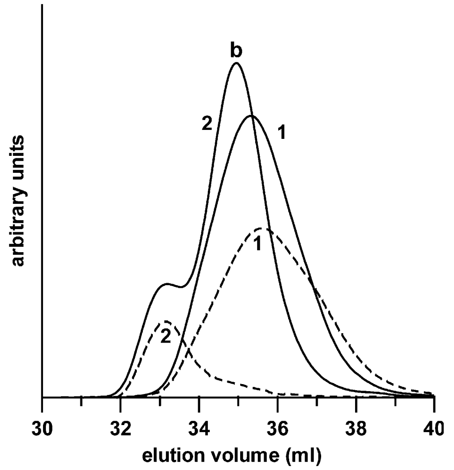
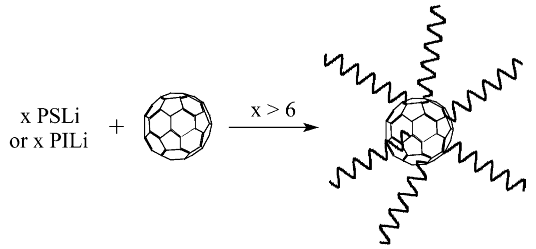


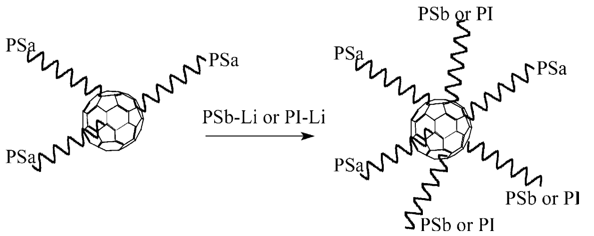
Fig. 6. RI traces (solid line) and UV traces at 320 nm (dotted line) of a mono-adduct (PMMA)C_{60} ($M_n = 25{,}000$—PS calibration, curve 1) and the product (curve 2) obtained after reaction with a 16-fold excess of PSBr ($M_n = 21{,}000$, peak *b*).



Scheme 3. Hexa-adducts obtained by addition of an excess of PSLi or PILi onto C_{60}.

3.2.2. Mikto-arm stars $(PS)_xC_{60}(PI)_{6-x}$

Such mikto-arm stars can be produced following the same procedure as described above except that in the second step PSLi is replaced by PILi. An example is shown in Fig. 8 and the SEC analysis of the various polymers is given in Table 4. The arms grafted onto the C_{60} core are long enough to allow the determination of the actual molar masses of the stars by light scattering, the concentration of fullerene becoming low enough to neglect its light absorption. From these data we can conclude that 3.8 arms are attached in the first step where four $PS_{18{,}000}Li$ were reacted with one C_{60}. The UV_{320} trace (Fig. 8(b), curve 2) shows that a small amount of lower adducts are also present. In addition, comparison of the RI (Fig. 8(a)) and UV_{320} (Fig. 8(b)) traces 3 at an elution volume of about 36 ml indicates that a small amount of 'dead' $PS_{18{,}000}$ is also present in the products. That is a consequence of the difficulty to get C_{60} completely free of impurities able to react with carbanions. From these considerations one can see that product 2 consists mainly of a tetra-adduct. In the second step, $(PS_{18{,}000})_{3.8}C_{60}$ was reacted with a 2.5-fold excess of $PI_{19{,}000}Li$. From the increase of molar mass measured by LS, we can conclude that about 1.9 additional $PI_{19{,}000}$ chains have been added to the fullerene core. The amount of ungrafted $PI_{19{,}000}$ seen in the RI trace (Fig. 8(a), peak *b* in curve 3) agrees well with the grafting of about 80% of the $PI_{19{,}000}Li$ used. That allows to conclude that the main product formed is the mikto-arm star $(PS_{18{,}000})_{3.8}C_{60}(PI_{19{,}000})_2$. Again, the limiting point in the synthesis of PS/PI mikto-arm stars with a fullerene core by this route is the difficulty to adjust exactly the stoichiometry $PSLi/C_{60}$ in the first step.



Scheme 4. 6-arm asymmetric star $(PS_a)_xC_{60}(PS_b)_{6-x}$ or mikto-arm star $(PS_a)_xC_{60}(PI)_{6-x}$ obtained by 'saturation' of a polystyrene star $(PS_a)_xC_{60}$ with an excess of PS_bLi or PILi. The number of arms of the non-saturated star ($x < 6$) is controlled by adjusting the stoichiometry PS_a/C_{60}.

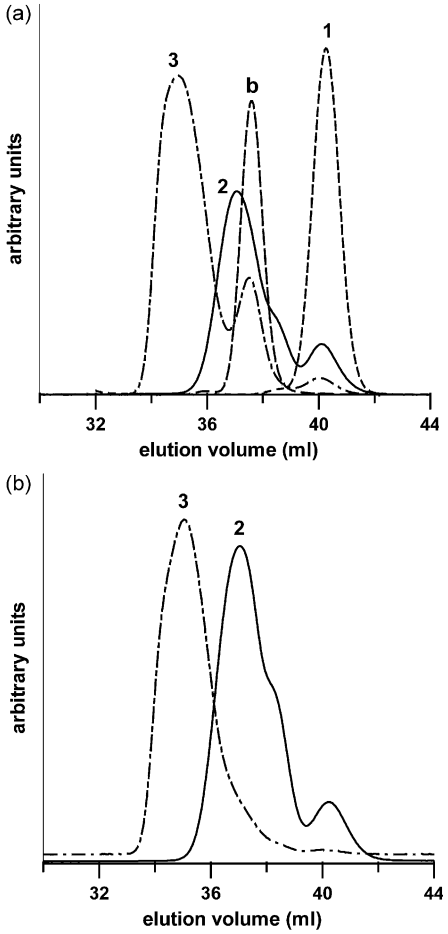


Fig. 7. (a) RI traces of PS_{2600} (curve 1—dotted line), of the 4-arm star $(PS_{2600})_4C_{60}$ (curve 2—solid line) and the asymmetric star $(PS_{2600})_4C_{60}(PS_{8200})_2$ (curve 3—dashed-dotted line) obtained upon reacting the tetra-adduct with an excess of $PS_{8200}Li$ ($M_n=8200$, peak *b*—dashed line). (b) UV traces at 320 nm of the 4-arm star $(PS_{2600})_4C_{60}$ (curve 2—solid line) and the asymmetric star $(PS_{2600})_4C_{60}(PS_{8200})_2$ (curve 3—dashed-dotted line) obtained upon reacting the tetra-adduct with an excess of $PS_{8200}Li$.

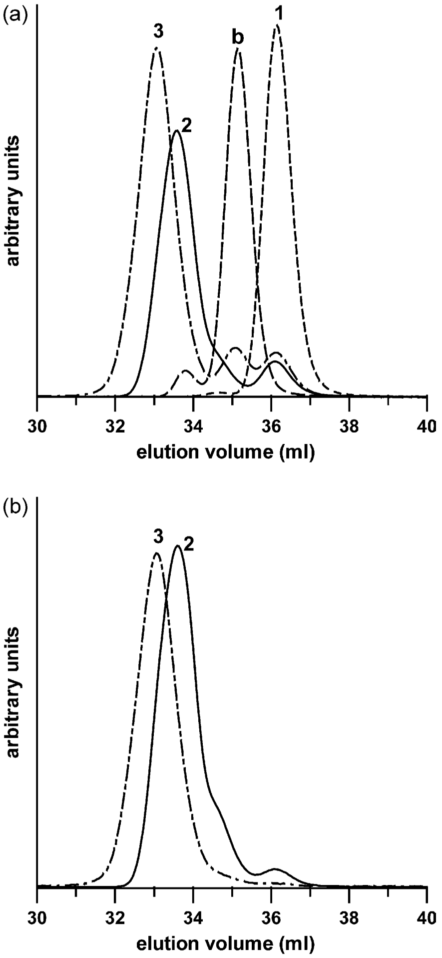


Fig. 8. (a) RI traces of $PS_{18,000}$ ($M_n=16,000$, $M_{w\ LS}=18,000$, curve 1—dotted line), the 4-arm star $(PS_{18,000})_4C_{60}$ (curve 2—solid line) and the mikto-arm star $(PS_{18,000})_4C_{60}(PI_{19,000})_2$ (curve 3—dashed-dotted line) obtained upon reacting the tetra-adduct with an excess of PILi ($M_n=26,800$—PS calibration, $M_{w\ LS}=19,000$, peak *b*—dashed line). (b) UV traces at 320 nm of the the 4-arm star $(PS_{18,000})_4C_{60}$ (curve 2—solid line) and the mikto-arm star $(PS_{18,000})_4C_{60}(PI_{19,000})_2$ (curve 3—dashed-dotted line) obtained upon reacting the tetra-adduct with an excess of PILi ($M_{w\ LS}=19,000$).

4. Conclusion

The good control of the number of polymer chains grafted onto C_{60} using the addition reaction of macro-radicals and 'living' carbanionic PSLi or PILi allows to prepare in a simple way stars with a fullerene core and a controlled number of arms. Pure di-adducts can be produced by grafting PSBr onto the fullerene via an atom transfer radical addition. These di-adducts can be further reacted with PSBr of different molar mass or with PIBr to produce, respectively, asymmetric stars $(PS_a)_2C_{60}(PS_b)_2$ or

Table 3
SEC and LS characterization of the asymmetric star $(PS_a)_4C_{60}(PS_b)_2$ obtained upon reacting a tetra-adduct $(PS_a)_4C_{60}$ with an excess of PS_bLi in toluene at room temperature

Sample	SEC				LS
	M_n	M_w	M_w/M_n	Number of arms[a]	M_w
PS_aLi	2600	2700	1.04		3100
$(PS_a)_xC_{60}$	9000	10,300	1.14	$x=3.6$	–
PS_bLi	8200	8500	1.04		9700
$(PS_a)_xC_{60}(PS_b)_y$	26,400	30,000	1.13	$y=2.2$	–

[a] Even if SEC is unable to give the actual mass of a star we used these data to estimate the number of arms because M_w cannot be determined by LS for such small molar masses due to the strong absorption of light by the C_{60} core (see text).

Table 4
SEC and LS characterization of a mikto-arm star $(PS)_4C_{60}(PI)_2$ obtained upon reacting a tetra-adduct $(PS)_4C_{60}$ with an excess of PILi in toluene at room temperature

Sample	SEC			LS	
	M_n	M_w	M_w/M_n	M_w	Number of arms
PS	16,000	16,600	1.04	18,000	
$(PS)_xC_{60}$	55,000	50,000	1.10	68,000	$x=3.8$
PI	26,800	27,700	1.03	19,000	
$(PS)_xC_{60}(PI)_y$	89,000	82,000	1.09	105,000	$y=1.9$

mikto-arm stars $(PS)_2C_{60}(PI)_2$. The addition of PMMABr onto C_{60} by ATRA leads to mono-adducts that can be further converted to asymmetric stars $PMMAC_{60}(PS)_2$ or $PMMAC_{60}(PS)_3$ by reaction with PSBr. The maximum number of arms of a star produced upon grafting of PSLi or PILi is 6, but lower functionalities can be achieved by a stoichiometric control. These stars $(PS)_xC_{60}$ can further react with PSLi or PILi in order to add $6-x$ more chains and so generate asymmetric $(PS_a)_xC_{60}(PS_b)_{6-x}$ or mikto-arm stars $(PS)_xC_{60}(PI)_{6-x}$.

Beside the two routes described in this paper, asymmetric and mikto-arm stars $(PS_a)_6C_{60}(PS_b)$, $(PS)_6C_{60}(PI)$ and $(PS)_6C_{60}(PMMA)_2$ have also been prepared by using 'living' hexa-adducts $(PS)_6C_{60}^{6-}(Li^+)_6$ to initiate the anionic polymerization of styrene, isoprene and methyl methacrylate [27–30]. Finally, a combination of addition of macroradicals and anionic chains is also conceivable and will be the mater of a forthcoming publication.

Acknowledgements

We would like to thank C. Foussat, O. Gavat, R. Meens and A. Rameau for technical support.

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