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# Thermal degradation in bulk and thin films of 2-, 4-, and 6-arm polystyrene stars with a $C_{60}$ core

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**Abstract**

The thermal stability (TS) of hexa-, tetra-, and di-arm polystyrene (PS) stars with a $C_{60}$ core was studied by thermal gravimetric analysis and mass-spectrometry. The quantitative production of volatile products, their composition and their formation kinetics during heating of ($PS_xC_{60}$) are reported. A bimodal release of styrene is observed. The first release takes place about 100 °C before the depolymerization temperature of styrene and all the $C_{60}$ comes out at this lower temperature. That results from a complete breaking of the weak PS-$C_{60}$ bonds followed by a partial depolymerization of the PS arms initiated by the so formed radicals. The amount of PS 'surviving' this first depolymerization step increases with the length of the arms and its TS is close to that of pure PS. The thermal stability of the $PS_xC_{60}$ stars decreases if the number of arms increases and, from the activation energy of the release of styrene and $C_{60}$, it was possible to estimate the PS-$C_{60}$ bond strength for these three adducts.

*Keywords:* Polymer chemistry; $C_{60}$; Thermal stability

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## 1. Introduction

Two synthetic routes are of special interest for grafting polystyrene (PS) chains onto $C_{60}$: the addition of carbanions or radicals onto the 6–6 bonds on the fullerene. Star like architectures $(PS)_xC_{60}$ can be prepared by reacting $C_{60}$ with polystyryl-lithium in non-polar solvents [1–5] and the maximum number of chains that can be grafted onto the fullerene using this chemistry is six [5,6]. Macro-radicals also add to $C_{60}$ and we have shown that pure di- and tetra-adducts can be obtained through atom transfer radical addition (ATRA) by reacting PS-Br with the fullerene in the presence of CuBr and bipyridine [7,8]. Thermal stability (TS) is one of the basic properties of all materials and it is of interest to get a better understanding of how the incorporation of $C_{60}$ in these materials affects their stability. Several reports indicate that the incorporation of $C_{60}$ in polymers increases their thermal stability [9–12] and previous work showed in contrary a decrease of TS when the PS chains are attached to the fullerene [13–18]. This apparent contradiction can be explained if one remembers that the thermal decomposition of PS results from a depolymerization reaction initiated by radicals formed by bond breaking upon heating. The presence of a very good radical acceptor like pristine $C_{60}$ reduces the depolymerization process and increases the TS. If the fullerene is covalently bonded to a polymer chain the situation becomes totally different. A study of the thermal stability of $(PS)_6C_{60}$ in solution has shown that the link between the $C_{60}$ and the PS chain is weaker than the carbon–carbon bond in the PS chain [19,20]. So, one can expect that the breaking of the chain-$C_{60}$ bond occurs at a lower temperature leading to a reduction of the TS of the materials. Having at our disposal well defined fullerene containing materials such as 2-, 4- and 6-arm polystyrene stars with a $C_{60}$ core, we decided to study in detail their thermal stability using both thermal gravimetric analysis (TGA) and mass spectroscopy (MS).

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## 2. Experimental section

### 2.1. Synthesis and characterization of the polystyrene stars with a $C_{60}$ core

Pure 6-arm stars were synthesized by addition onto $C_{60}$ of polystyryl-lithium (PS-Li) prepared by anionic polymerization in toluene using *sec*-butyl-lithium as initiator. This method, described earlier [4,5], allows to tailor the length of the polystyrene (PS) grafts and leads to perfectly controlled hexa-adducts [5,6]. To prepare 4- and 2-arm PS stars, we turned to an atom transfer radical addition (ATRA) [21] PS macro-radicals generated in toluene at 110 °C in the presence of CuBr/2,2′-bipyridine from PS-Br add to the fullerene. Due to a peculiar mechanism, pure di-adducts are obtained if the ratio PS-Br/$C_{60}$ is lower than 2 and pure tetra-adducts are produced if the excess of PS-Br is larger than 4 [8]. Furthermore, the PS-Br being prepared by atom transfer radical polymerization (ATRP) [21], the length of the arms of these 4- and 2-arm stars is also controlled. The 'parent' PS-Li and PS-Br as well as the stars of various functionalities were characterized by multiple detector size exclusion chromatography (SEC) using a set of five $300\times7.5\ mm^2$ PL Gel columns from Polymer Laboratories ($4\times10\ \mu m^2$ Mixed-B and one 500 Å) connected in series and THF as the eluent. Beside a refractive index (RI) detector (Shimadzu RID10A) and a UV–vis detector (Shimadzu SPD10A), an on-line light scattering detector (MALLS DAWN DSP from Wyatt Technology) was also used to determine the actual molar mass of such branched macromolecules. The main characteristics of the stars and their arms are given in Table 1.

### 2.2. Thermal gravimetric analysis (TGA)

The TGA measurements were run under nitrogen on a METTLER TC15-TG50 between room temperature and 800 °C with a heating rate of 10°/min. The amount of sample used in the experiments was comprised between 10 and 25 mg.

### 2.3. Mass-spectrometry

Polymer films with a thickness ranging from 1 to 600 nm were deposited, from $(PS)_xC_{60}$/toluene solutions (about 0.05 wt%) onto a metal substrate (an oxidized tantalum foil strip-heater equipped with a thermocouple), using a microsyringe. The film thickness was controlled by the volume of the solution deposited. For example, a dry film with an average thickness of 10 nm is formed upon depositing 1 μl of a 0.05 wt% solution on the substrate having an area of $0.5\ cm^2$. The substrate with the applied sample was then introduced into the vacuum chamber of a magnetic mass-spectrometer (MX-1320) and heated at a rate of about $10\ K\ s^{-1}$. The thermal degradation (TD) kinetics of the $(PS)_xC_{60}$ stars was studied by measuring the temperature dependence of selected mass spectrum peaks obtained under ionization by electron impact energy of 7 eV. The peaks selected were 104 amu for the styrene monomer and 720 amu for $C_{60}$. At each temperature $T$, the mass spectral peak height h is proportional to the formation rate $dN/dt$ of the volatile product i.e. $h = k dN/dt$ ($N$ being the number of molecules released, $t$ the time and $k$ a constant). The plot $\ln(h)$ versus $1/T$ K gives a straight line which slope corresponds to $E/R$ ($E$ being the activation energy and $R = 8.3145\ J\ mol^{-1}\ K^{-1}$ the molar gas constant). We also recorded simultaneously the total ion current (TiC) during

Table 1
Characteristics of the 6-arm ($S_6$), 4-arm ($S_4$) and 2-arm ($S_2$) polystyrene stars and the results of their thermal degradation followed by TGA and MS

| Sample | $M_n$ arm | $M_w/M_n$ | $\%C_{60}$[a] from $M_w^*$ | $\%C_{60}$[b] from TGA | $\%C_{60}$[c] from MS | Method used | $R = I_2/I_1$[d] | Zip[e] |
|---|---|---|---|---|---|---|---|---|
| $S_6$-1 | 1300 | | 8.5 | 11.3 | | TGA | 0.9 | 7 |
| $S_6$-2 | 1400 | | 7.9 | | | MS | 0.61[f] | 9 |
| $S_6$-3 | 2300 | | 5.0 | 7.3 | | TGA | 1.2 | 10 |
| $S_6$-4 | 3400 | 1.03 | 3.4 | 3.2 | | TGA | 1.7 | 12 |
| $S_6$-4 | 3400 | 1.03 | 3.4 | | 2.5 | MS | 1.2[f] | 15 |
| $S_6$-5 | 5400 | | 2.2 | 2.0 | | TGA | 3.2 | 12 |
| $S_6$-6 | 8800 | 1.05 | 1.3 | 1.6 | | TGA | 7.0 | 11 |
| $S_6$-6 | 8800 | 1.05 | 1.3 | | | MS | 3.2[f] | 20 |
| $S_6$-7 | 10,500 | | 1.1 | 1.6 | | TGA | 5.9 | 15 |
| $S_6$-8 | 29,000 | | 0.4 | 0.8 | | TGA | 11.5 | 22 |
| $S_6$-9 | 33,500 | 1.04 | 0.4 | – | 1.1 | MS | 25 | 13 |
| $S_4$-1 | 22,000 | 1.3 | 0.5 | 1.0 | | TGA | 16 | 12 |
| $S_4$-1 | 22,000 | 1.3 | 0.5 | | 0.6 | MS | 11[f] | 18 |
| $S_2$-1 | 17,000 | 1.3 | 0.7 | 1.3 | | TGA | 24 | 7 |
| $S_2$-1 | 17,000 | 1.3 | 0.7 | | 1.9 | NIS | 15.5[f] | 11 |

[a] Percent of $C_{60}$ calculated from the molar mass of the star $M_w$*.

[b] Percent of $C_{60}$ calculated from the amount of sample remaining above 500 °C

[c] Percent of $C_{60}$ estimated from MS using a calibration (see text).

[d] $I_1$ and $I_2$ are, respectively, the amounts of the sample released at the 'low' and 'high' degradation temperature.

[e] Average number of styrene molecules released by the breaking of one PS-$C_{60}$ bond: $Zip = DP_{arm}/(1+R)$ where $DP_{arm}$ is the degree of polymerisation of the polystyrene arm of the stars.

[f] $R$ measured by MS on thick films (see text).

the TD process. The TiC kinetics provides information over the global amount of volatile compounds released as a classical thermal gravimetric analysis.

## 3. Results

### 3.1. Thermal gravimetric analysis

Stars with a $C_{60}$ core and, respectively, 6, 4 and 2 polystyrene arms of molar masses ranging from 1000–40,000 g/mol have been studied by thermal gravimetric analysis between room temperature and 800 °C. As it is known that the depolymerization of polystyrene is complete above 450 °C and that the fullerenes are stable at much higher temperatures, the weight percent of $C_{60}$ in the stars may be estimated from the amount of sample remaining at $T > 450$ °C. These values reported in Table 1 are in good agreement with the fullerene content calculated from the molar mass of the arms taking into account the functionality of the star.

The results concerning 6-arm stars of various molar masses are given in Fig. 1. In all cases the thermal stability of the $C_{60}$ containing stars is reduced as compared to linear polystyrene. For stars with PS arms of low molar masses (around 2000 g/mol) about half of the weight is lost around 350 °C whereas PS shows no weight loss before 400 °C. The thermal stability of the stars seems to increases with increasing molar mass of the PS arms to approach the stability of PS for very long arms. The derivatives of the variation of weight as a function of temperature (Fig. 2) are bimodal curves indicating that the thermal degradation of $(PS)_xC_{60}$ occurs in two steps. The first, at a temperature around 350 °C, is specific for these stars with a fullerene core and has to be connected with the presence of PS-$C_{60}$ bonds in these samples. The second degradation step at around 425 °C corresponds to the classical depolymerization of PS promoted by the formation of radicals through random breaking of C–C bonds in the PS chain. The weight percent of the sample released at the lowest temperature is very much dependent on the molar mass of the PS arm. In order to quantify this effect we have determined from the curves shown in Fig. 2 the ratio ($R$) of the amount of sample released at around 425 °C over that lost at around 350 °C. The values of $R$ are reported in Table 1. A straight line is obtained if one plots log $R$ as a function of log $M_b$ (Fig. 3).

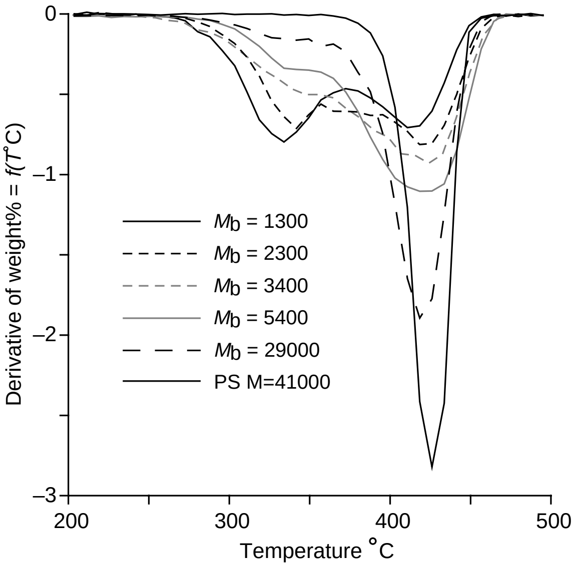


Fig. 2. Derivative of wt% = $f$($T$°C) for $(PS)_6C_{60}$ stars with polystyrene arms ($M_b$) of various length.

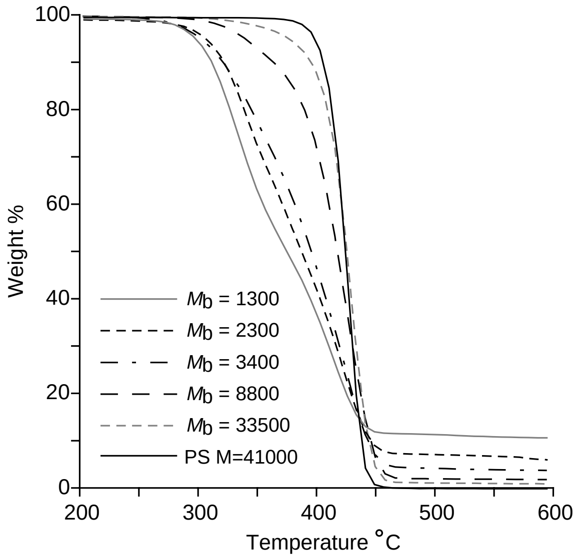


Fig. 1. Thermal degradation of $(PS)_6C_{60}$ stars as a function of the length of the polystyrene arms ($M_b$) measured by TGA.

Fig. 4 shows the TGA results for 6-, 4- and 2-arm PS stars with a $C_{60}$ core and arms of comparable molar masses. Even so, these graphs seems to indicate a slight increase of stability as the number of arms decreases, it is difficult to definitively conclude from these data considering the accuracy of the method.

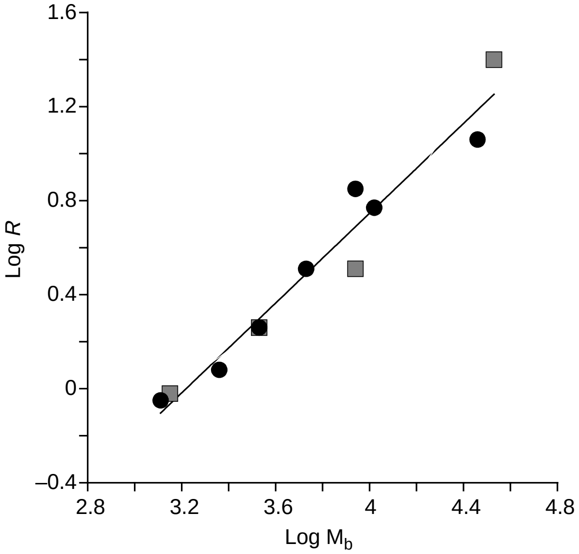


Fig. 3. Variation of $R$ as a function of the molar mass of the arms ($M_b$) of $(PS)_6C_{60}$ stars. $R = I_2/I_1$ where $I_1$ and $I_2$ are the amounts of styrene released, respectively, at the 'low' and 'high' degradation temperature. Circles from TGA and squares from MS.

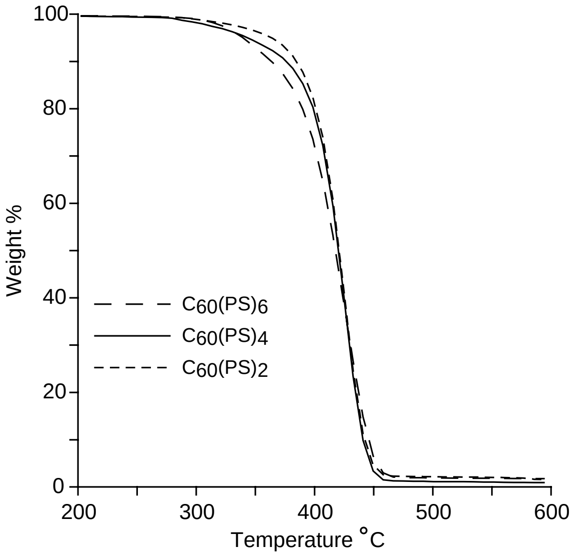


Fig. 4. TGA measurements of the thermal stability of $(PS)_xC_{60}$ stars of comparable molar masses as a function of the number of arms.

### 3.2. Mass spectroscopic analysis

The thermal stability of the 6-, 4- and 2-arm polystyrene stars with a $C_{60}$ core has also been studied by mass spectroscopy up to 600 °C. This method allows to identify the molecules released upon heating and to quantitatively, follow their release kinetics.

Styrene monomer and $[C_{60}]$ fullerene are the main volatile products formed during the thermal degradation of all the $(PS)_xC_{60}$ stars studied. Nevertheless, within the temperature range of 50–150 °C a solvent (toluene) evaporation is always observed regardless of the film thickness and that even if the films were first kept under high vacuum for at least 10 min.

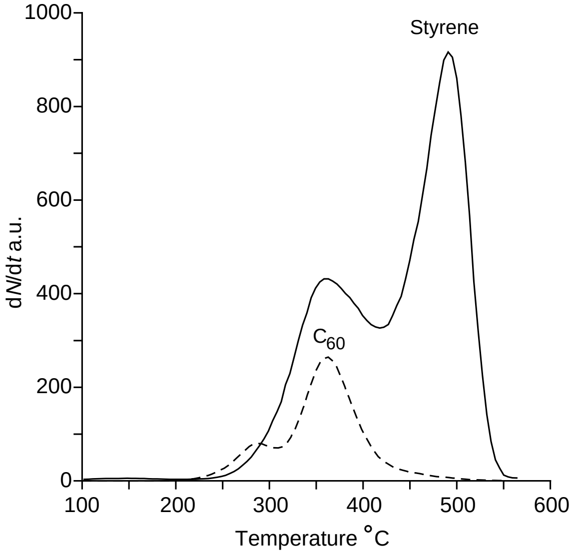


Fig. 5. Variation with temperature of the amount of styrene (solid line) and $C_{60}$ (dotted line) released upon heating a thin film (90 nm) of $(PS)_6C_{60}$ (sample $S_6$-4) at a rate of 10 K s$^{-1}$.

Table 2
Dependence of $R$ on film thickness $\delta$ (nm) for $(PS)_6C_{60}$, $(PS)_4C_{60}$ and $(PS)_2C_{60}$

| Sample | $\delta$ (nm) | | | | | |
|---|---|---|---|---|---|---|
| | 1.5 | 10 | 90 | 180 | 360 | 540 |
| $S_6$-4 | 10 | 4 | 2.2 | 1.9 | 1.5 | 1.2 |
| $S_4$-1 | – | 24 | 16 | – | – | 11 |
| $S_2$-1 | – | 22 | 17 | – | – | 15.5 |

### 3.2.1. Thermal degradation kinetics of 6-arm PS stars

As already reported, the release kinetics of styrene upon heating $(PS)_6C_{60}$ films exhibits a specific and striking bimodal behavior, Fig. 5, which was found to be affected by film thickness [16,17]. The maximum intensity of the first kinetic step is usually observed at $T_1^{\max} \cong 360$ °C and that of the second one at $T_2^{\max} \cong 490$ °C (the corresponding intensities are $I_1$ and $I_2$). Using Arrhenius equation an activation energy and pre-exponential factor were calculated. The activation energy $E_6^{\mathrm{st}}$ for the first release step of styrene and the preexponential factor $\lg A_1^{\mathrm{st}}$ are equal to 110 kJ/mol (with usual error in our measurement for $E$ of $\pm 10$ kJ/mol) and 10 s$^{-1}$. We used the intensity, ratio $R=I_2/I_1$ in order to quantify the effect of the thickness of the films. As illustrated in Table 2 and Fig. 6, the variation of $R$ with film thickness covers a broad range. However, $R$ dependence is also subjected, together with film thickness, to some other factors (see below).

The second kinetic stage for styrene release (at $T_2^{\max} \cong 490$ °C) is due to thermal degradation of the PS chains remaining after the first TD step. The thermal stability of these ‘remaining’ PS chains appears to be decreased as compared to normal PS. Indeed, the $T_2^{\max}$ is about 30 °C lower than the $T_{\max}$ for neat PS thin films ($\sim 520$ °C). That observation points to the presence of some ‘weak’ links on these ‘remaining’ PS.

The $C_{60}$ release takes place completely within the styrene low temperature range, i.e. 200–400 °C, and at the same $T_{C_{60}}^{\max} \cong 360$ °C. The activation energy, estimated from the variation with temperature of the mass spectrum intensity

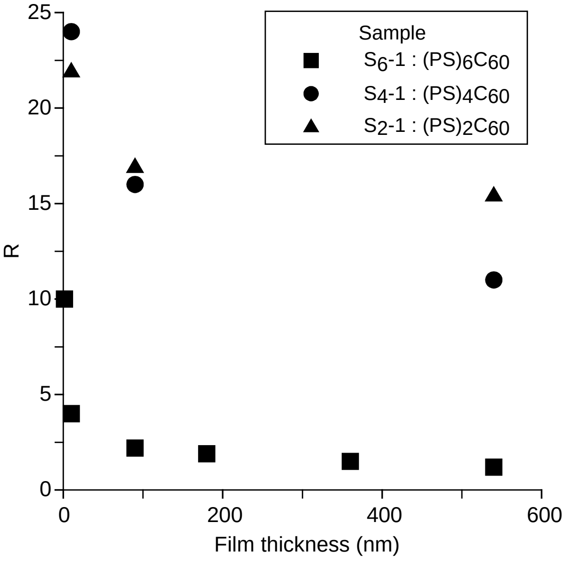


Fig. 6. Variation of $R$ with film thickness in MS measurements on $(PS)_xC_{60}$ stars.

corresponding to $C_{60}$, is $E_6^{C_{60}} \cong 110$ kJ/mol. In addition, it is worthy to note that the $C_{60}$ kinetics often reveals a 'shoulder' at the low temperature side with $T^{max} \sim 300$ °C. This shoulder (not more than 10% of the total amount of released $C_{60}$) is most probably related to the presence of free fullerene molecules in the sample. Indeed, the $C_{60}$ release kinetics for films cast from a toluene solution of a neat PS and $C_{60}$ ($\leq 1$ wt%) displays the same $T^{max}$ ($\approx 300$ °C) and the activation energy of the $C_{60}$ diffusion from these films is equal to 95 kJ/mol.

In order to make a quantitative estimation of the amount of $C_{60}$ released from the stars, the mass spectrometer sensitivity was calibrated with known amounts of $C_{60}$ deposited onto the substrate from toluene solution. The concentrations of fullerene measured by MS (Table 1) are in reasonable agreement with the value calculated from the molar mass of the arm assuming a 6-arm architecture for the stars. This observation confirms that all the $C_{60}$ lose all their grafts at this low temperature decomposition step.

### 3.2.2. Influence of the molar mass of the arms on the thermal degradation kinetics of 6-arm PS stars

As can been seen from Fig. 6, the variation of $R$ with film thickness seems to level off for thick films. So, it is reasonable to compare these 'limit' values with the $R$ determined by TGA on bulk samples of the same stars. From Table 1 it can be seen that the $R$ determined by both TGA and MS on the same sample are in good agreement. The variation of $R$ with the molar mass of the arm found by both methods is also the same as can be seen in Fig. 3.

### 3.2.3. Influence of the star functionality on the thermal degradation kinetics

The typical evolutions of the styrene and $C_{60}$ release kinetics for $(PS)_4C_{60}$ and $(PS)_2C_{60}$ are shown in Figs. 7 and 8. The average activation energies for the release of $C_{60}$, determined under identical experimental conditions as above for the 6-arm stars, are $E_4^{C_{60}} = 145$ kJ/mol and $E_2^{C_{60}} \cong 190$ kJ/mol, respectively, for the 4- and 2-arm stars.

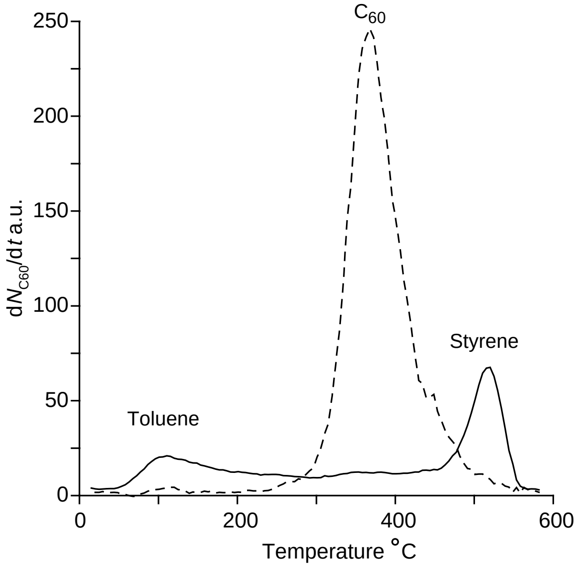


Fig. 7. Variation with temperature of the amount of $C_{60}$ (dotted line) released upon heating a thin film (270 nm) of $(PS)_4C_{60}$ (sample $S_4$-1) at a rate of 10 K s$^{-1}$ as well as the variation of the total ion current TiC (solid line).

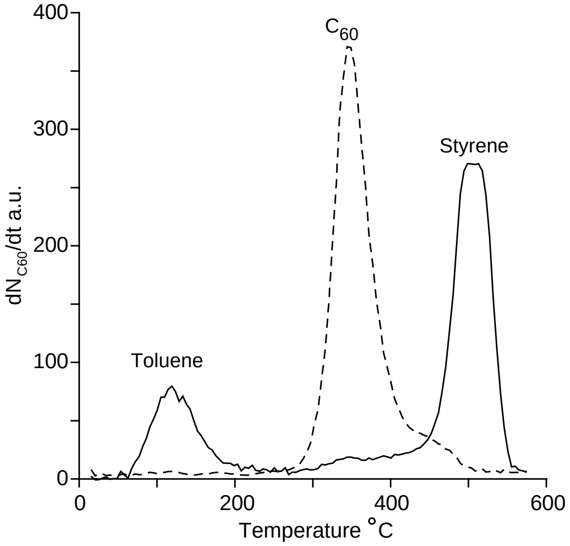


Fig. 8. Variation with temperature of the amount of $C_{60}$ (dotted line) released upon heating a thin film (540 nm) of $(PS)_2C_{60}$ (sample $S_2$-1) at a rate of 10 K s$^{-1}$ as well as the variation of the total ion current (TiC) (solid line).

From the experiments reported in Figs. 7 and 8, the activation energies for the release of styrene during the first thermal degradation stage of $(PS)_4C_{60}$ and $(PS)_2C_{60}$ could also be determined. They are, respectively, equal to $E_4^{st} = 130$ kJ/mol and $E_2^{st} = 155$ kJ/mol.

The variation of $R$ with film thickness $\delta$ for the 2-, 4-arm stars is given in Table 2 and Fig. 6.

## 4. Discussion

The experimental data presented above reveal a deep interrelation between the thermal degradation of the polystyrene stars with a fullerene core and their molecular architecture. The fundamental difference between these compounds and classical polystyrene is that every PS chains is covalently bound to $C_{60}$ and it has been shown that this PS-$C_{60}$ link is weaker than the C–C bonds in the PS chain itself [20]. Thus, the peculiar thermal behavior of these $(PS)_xC_{60}$ results from the presence of a 'weak' bond on the end of every polystyrene chain. Starting from these facts, it becomes possible to analyze the data using the generally accepted mechanism of thermal degradation of polymers (PS, PMMA, PTFE, P-α-MS, etc.) consisting of a free radical induced depolymerizing of the chains. The mechanism involved in the 'low' temperature step proceeds via three elementary reactions.

- Free radical 'initiation', i.e. the rupture of the C–C bond between the PS arms and the fullerene leading to the formation of a radical at the end of each polystyrene chain.
- 'Propagation' of the depolymerization along the chain through this radical via a classical Zip mechanism.

- Termination of the depolymerization by destruction of the radicals.

Such a mechanism (Scheme 1) can explain not only the presence of two steps in the thermal degradation of $(PS)_xC_{60}$, but also the strong influence of the molar mass of the arms on the fraction of styrene released in the 'low' temperature degradation step. The release of styrene at around 350 °C (about 100 °C lower than the normal depolymerization temperature for polystyrene) comes from a partial depolymerization of each PS arm induced by the radical produced by the breaking of its terminal 'weak' PS-$C_{60}$ bond. The 'Zip like propagation' of this depolymerization stops (termination) when the radical is destroyed by recombination or disproportionation. The parts of the PS arms surviving this first depolymerization step behave then as 'normal' polystyrene chains. These latter are afterwards converted to styrene monomer in the 'high' temperature degradation step through the classical depolymerization induced by the radicals formed by homolytical rupture of C–C bonds in the PS chains. In fact, the MS measurements show that this depolymerization occurs at a temperature about 30 °C lower than what is expected for normal polystyrene. This last observation is not unexpected as the termination of the first depolymerization step leads to PS chains with 'weaker' C–C bonds such as head to head bonds –HC(Ph)–CH(PH)–. The respective amounts $I_1$ and $I_2$ of styrene released at the 'low' and 'high' degradation temperature were estimated for the various samples from both TGA and MS experiments and the ratio $R = I_2/I_1$ reported in Table 1.

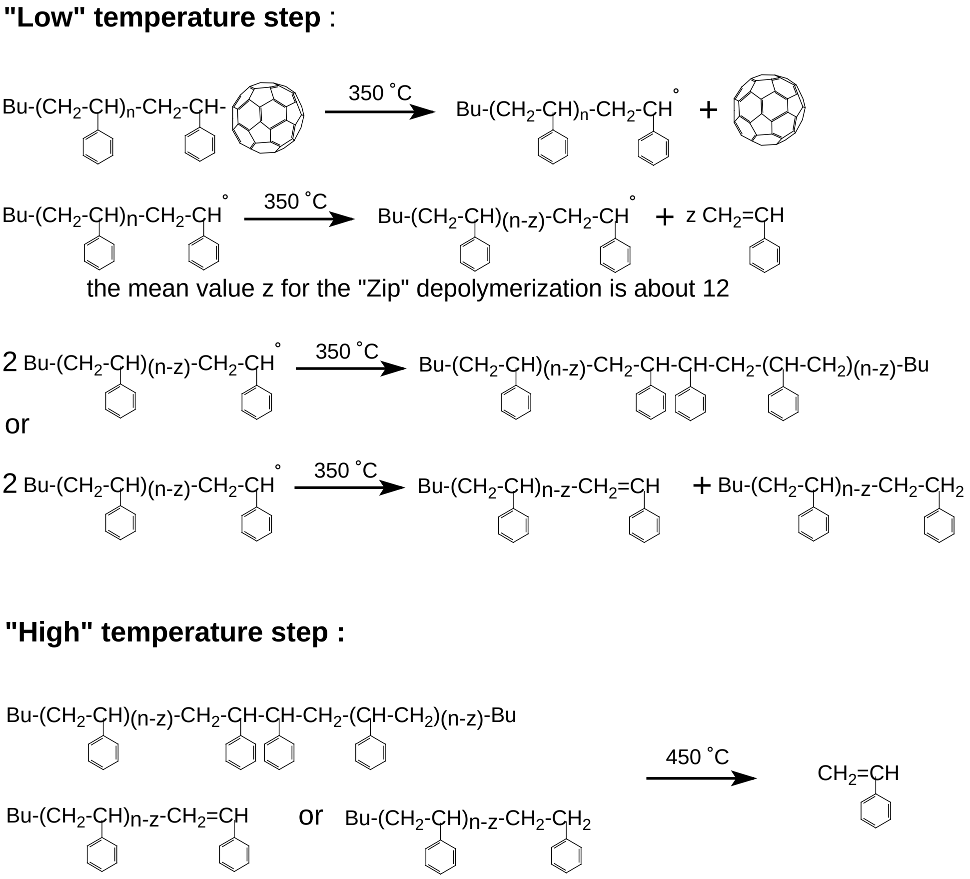
The proportion of styrene released at this 'low' temperature $I_1/(I_1 + I_2)$ is a measure of the efficiency of the depolymerization at that stage. From the values of $R$ and the molar mass of the arms of the corresponding star (Table 1), it becomes possible to calculate the mean number of styrene monomers (named Zip in Table 1) each PS chain has lost. It is interesting to note that each PS arm loses around 12 monomers whatever is its molar mass. That indicates that the efficiency of the depolymerization reaction, i.e. the depolymerization Zip length, is essentially independent from the molar mass of the PS arm grafted onto the fullerene.

The three-step mechanism above makes it also possible to link the activation energy measured experimentally $E_{exp}$ to those of elementary reactions [22]:

$$E_{exp} = \frac{E_i}{2} + E_d - \frac{E_t}{2} \qquad (1)$$

where $E_i$ is the activation energy of a chemical bond rupture, $E_d$ the activation energy of depolymerization, and $E_t$ the activation energy of termination by the radical disproportionation or recombination.

For PS the values of $E_d$ and $E_t$ can be taken from literature: $E_d = 100$ kJ/mol and $E_t = 85$ kJ/mol [23]. $E_i$ is actually a measure of the strength of the chemical bond that is first broken in the macromolecule and it can be calculated from Eq. (1)



Scheme 1. Mechanism proposed for the thermal degradation of $(PS)_xC_{60}$ stars.

Table 3
Comparison of the activation energies (in kJ/mol)

| Sample | $E_i^{st}$ measured | $E_i^{st}$ calculated | $E^{C_{60}}$ measured |
|---|---|---|---|
| $PS_6$-$C_{60}$ | 110 | 105 | 110 |
| $PS_4$-$C_{60}$ | 130 | 145 | 145 |
| $PS_2$-$C_{60}$ | 155 | 200 | 190 |

using the average values of the experimental activation energies determined for the first step of the thermal release of styrene. These latter being, respectively, 110, 145, 155 kJ/mol for $(PS)_6C_{60}$, $(PS)_4C_{60}$, and $(PS)_2C_{60}$, the corresponding values for $E_i^{6,4,2}$ calculated from Eq. (1) are 105, 145, 200 kJ/mol. It is reasonable that these latter values compare well with the corresponding activation energies measured independently from the $C_{60}$ desorption data: $E_6^{C_{60}} \cong 110$, $E_4^{C_{60}} \cong 145$, and $E_2^{C_{60}} \cong 190$ kJ/mol (Table 3). Indeed, the $E_{6,4,2}^{C_{60}}$ are in reality the energies of the 'PS-$C_{60}$' bonds that break first just as the values of $E_i^{st}$ These results show that the strength of the 'PS-$C_{60}$' bonds increase with the decrease of the star functionality confirming earlier independent measurements [20].

The data in Table 3 allow us to plot the activation energy $E_i^{st}$ as a function of the number n of grafted arms (Fig. 9). This dependence can be expressed, in first approximation, as a linear correlation $E_i = -23n + E_i^0$ where $E_i^0$ is the value extrapolated at $n = 0$ ($E_i^0 = 245$ kJ/mol) That result resembles closely an inference made from photoluminescence study on suitable 'PS-stars' (HOMO-LUMO radiative electronic transition) [24]. In this publication, a linear correlation between the number n of arms and an energetic shift of the maximum in the photoluminescence spectrum of the $C_{60}$ core was found: $\Delta E_{(\mathrm{kJ/mol})} = 3.85n$. Thus, it seems that the vibrational (our data) and electronic [24] subsystems response to PS chains grafting onto the $C_{60}$ core proceeds in a similar manner. However, the photoluminescence shift tends toward higher energy and the thermal degradation activation energies on the contrary toward lower energy with the increase of the number of arms.

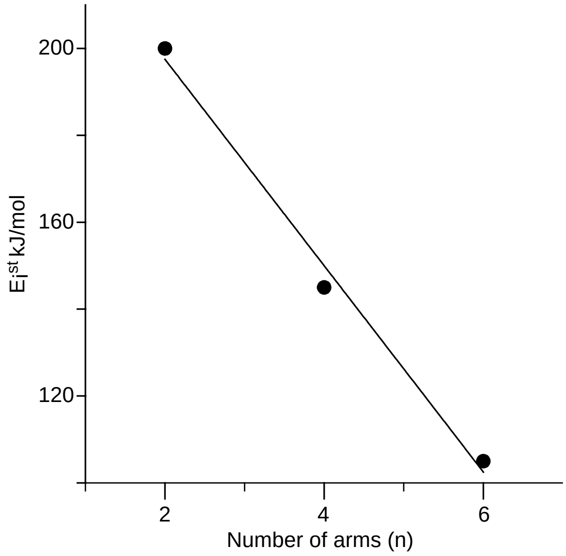


Fig. 9. Variation of the activation energy $E_i^{st}$ of the styrene release at the 'low' temperature step as a function of the number $n$ of arms of a $(PS)_xC_{60}$ star. $E_i = -23n + E_i^0$ where $E_i^0 = 245$ kJ/mol is the value extrapolated at $n = 0$.

## 5. Conclusion

Both experimental methods, TGA and MS, show that the thermal stability of $PS_xC_{60}$ stars is reduced as compared to pure polystyrene. The formation of styrene upon heating follows a bimodal pattern, a given amount of monomer being released at about 100 °C below the normal depolymerization temperature of polystyrene. A mechanism based on the presence of weak PS-$C_{60}$ bonds in these stars with a fullerene core is proposed to account for the various elementary reactions. It is the breaking of these PS-$C_{60}$ bonds at a lower temperature that generates radicals that start a first depolymerization process. Each radical leads to the release of about 10–20 monomer units per PS arm before its destruction by recombination or dismutation. So, the amount of styrene released in this first step will strongly decrease when the length of the PS arms increases as is observed. The part of the PS chains left behind after that first depolymerization step have no longer a weak PS-$C_{60}$ bond and their thermal stability will become close to that of pure PS. In fact, the somewhat lower TS observed experimentally may result from the formation of 'head to head' bonds by recombination of two $PS^{\cdot}$ radicals in the first step. From the kinetics of release measured by MS, the relative strength of the PS-$C_{60}$ bonds for hexa-, tetra-, and di-arm polystyrene stars with a $C_{60}$ core could be estimated. The stability of this link decreases when the number of grafted arms on the fullerene increases such confirming earlier results obtained in solution.

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