# Role of $C_{60}$ in the free radical polymerisation of styrene

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**$C_{60}$ retards the free radical polymerisation of styrene and results in polymers containing stable free radicals.**

The incorporation of $C_{60}$ into macromolecular architectures offers the attractive possibility to combine the unique electronic and magnetic properties of $C_{60}$ with polymeric characteristics such as ease of processability.[1,2] Several approaches have been developed to prepare $C_{60}$-containing polystyrene; these have included the reaction of $C_{60}$ with living polystyrene carbanions yielding polymers with the structure $C_{60}(PS)_x$ (PS = polystyrene) where $x$ = 1 to *ca.* $10^3$, the reaction of linear polystyrenes containing azide functional groups with $C_{60}$,[4] and the reaction of amino-terminated polystyrene with $C_{60}$.[5] Most recently the reactivity of $C_{60}$ towards free radicals[6] has been exploited to obtain $C_{60}$-containing polystyrene using standard free radical polymerisation conditions.[7–9] This offers a convenient route to the preparation of $C_{60}$-containing polymers although both the role of $C_{60}$ in these reactions as well as the structures of the polymers obtained are unclear. Cao and Webber[7] suggested two possible reaction mechanisms each initially invoking the formation of $PSC_{60}^{\bullet}$ from the reaction of $PS^{\bullet}$ with $C_{60}$ followed by either (i) the reaction of $PSC_{60}^{\bullet}$ with a styrene monomer to eventually yield $PSC_{60}PS^{\bullet}$ or (ii) the reaction of $PSC_{60}^{\bullet}$ with a second $PS^{\bullet}$ in a termination step. In contrast, Bunker *et al.*[8] proposed a random copolymer structure while Camp *et al.*[9] speculated that multiple radical addition occurs early in the polymerisation process and that termination is predominantly *via* the coupling of two $C_{60}$ radicals. Here we discuss the role played by $C_{60}$ at low concentrations in free radical polymerisations.

The free radical polymerisation of styrene in the presence of $C_{60}$ was initiated by AIBN in benzene† and the extent of polymerisation was monitored by dilatometry.‡ A control experiment was also performed in which styrene was polymerised under identical conditions in the absence of $C_{60}$. The polymers were purified by dissolution in chloroform and precipitation into methanol; this was repeated until the polymer was free from traces of monomer. The brown $C_{60}$-containing polystyrene was readily soluble in a range of organic solvents. Gel permeation chromatography using a Knauer Instruments chromatograph equipped with dual detectors (differential refractometer and UV-spectrophotometer) was used to establish that $C_{60}$ was incorporated into the polystyrene structure as described elsewhere.[7,8] The molecular weight data for the $C_{60}$-containing polystyrene (run 1. $M_n$ 9670, $M_w$ 16280; run 2: $M_n$ 8490, $M_w$ 13530) were essentially identical to those for the polystyrene obtained under identical polymerisation conditions ($M_n$ 9340, $M_w$ 15450). Fig. 1 shows the extent of monomer conversion as a function of time. It is possible to extract from these data the initial rates of polymerisation ($R_p$): for the control experiment $R_p = 6.1 \times 10^{-6}$ mol dm$^{-3}$ s$^{-1}$ and for the $C_{60}$-containing polymerisation, $R_p = 3.9 \times 10^{-6}$ mol dm$^{-3}$ s$^{-1}$. Thus the retardation effect of $C_{60}$ on the polymerisation is relatively small implying that the rate constant for the reaction of $C_{60}$ with the polystyryl radical is smaller than that of propagation. The concentration of $C_{60}$ in a sample of purified polymer was estimated using the absorption at 350 nm in the UV–VIS spectra[7] to be $1.22 \times 10^{-5}$ mol dm$^{-3}$ which is less than that in the reaction mixture, $5.89 \times 10^{-4}$ mol dm$^{-3}$. We note, however, that the photophysical properties of $C_{60}$ are known to be modified in the polymer[7,8] and this determination of the $C_{60}$ concentration is, therefore, approximate. The view that the $C_{60}$ is not completely consumed during the polymerisation is supported by the kinetic data, Fig. 1, which shows that the retardation of the polymerisation is still apparent at the end of the reaction. Using the measured concentration of $C_{60}$ and the number average molecular weight, the estimated number of polymer chains per $C_{60}$ unit is 114.

The thermal behaviour of the polymers was characterised using differential scanning calorimetry and this revealed that $C_{60}$-containing polystyrene behaved identically to polystyrene prepared in the absence of $C_{60}$; specifically the polymers exhibited a glass transition at 99 °C. Similar behaviour was observed for $C_{60}$-endcapped polystyrenes for which the endcapping did not change the glass transition temperature of the amino-terminated polymer[5] and also for free radically prepared polystyrene containing 1% by mass $C_{60}$.[9] The identical thermal behaviour of polystyrene and $C_{60}$-containing polystyrene suggests that $C_{60}$ may in fact not terminate many chains as has been assumed previously[8,9] but instead probably terminates only 1 or 2. This invoked the possibility of the formation of a stable free radical, $PSC_{60}^{\bullet}$, and to investigate this the electron spin resonance spectrum of the $C_{60}$-polystyrene sample was obtained in benzene, Fig. 2. An intense signal was observed with a $g$-value of 2.0020 and flanked by two satellites corresponding to $^{13}C$ hyperfine interactions of 7.2 and 20.2 G. This spectrum is similar to that described by Morton *et al.*[10] for the radical $Cl_3CC_{60}^{\bullet}$; we note that the third weak satellite described by Morton *et al.*[10] was not observed. The intensity of the EPR spectrum suggests that for every $C_{60}$ radical there are approximately 200 polymer chains. This value is only in approximate agreement with that obtained using UV–VIS spectroscopy. The spectral intensity, however, decayed with time and this was particularly rapid for an open tube sample.

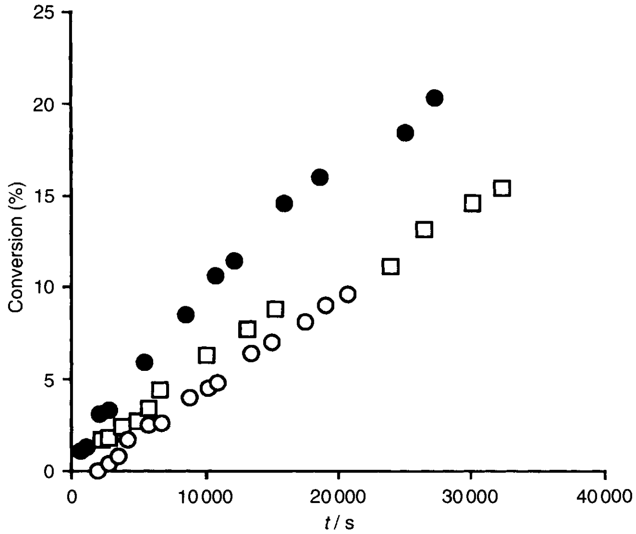

**Fig. 1** Dependence of conversion on time for the AIBN-initiated free radical polymerisation of styrene–$C_{60}$ mixtures (○, □) and of styrene (●)

Storing the polymer as a solid also resulted in a less intense spectrum. Thus it is clear that during the purification and drying procedures radicals are destroyed. To overcome these difficulties, the polymerisation was performed in an EPR tube and the concentration of $C_{60}$ radicals monitored. Unfortunately the spectra obtained were too weak to allow for even a semi-quantitative determination of the radical concentration.

Krusic *et al.*[10–12] have studied the addition of free radicals to $C_{60}$ and proposed that the addition of a single radical gives rise to an unpaired electron which is largely localised on C-1 (Fig. 3) and to a lesser extent on C-3′ and C-5′. The possibility of the extensive delocalisation of the unpaired electron has been excluded. If a similar mechanism is assumed for the addition of a polystyrene chain then the carbon atoms over which the unpaired electron delocalises are too sterically crowded to allow for reaction with a second polystyrene chain. Indeed, Morton *et al.*[10,13] found that free radicals of the form $RC_{60}^{\bullet}$ are obtained providing that R is bulky, for example *tert*-butyl. In contrast, attempts to produce $RC_{60}^{\bullet}$ for smaller radicals, for example methyl, were unsuccessful and the authors proposed that such radicals are highly reactive, immediately reacting with either another radical, the solvent or undergo dimerization. The bulky polystyrene chain in $PSC_{60}^{\bullet}$ prevents the possibility of dimerization, *i.e.* the formation of $PSC_{60}C_{60}PS$, and instead a stable free radical is obtained. However, the attachment of a second polystyrene chain to $PSC_{60}^{\bullet}$ in a position remote from C-1 cannot be discounted and quantitative experiments are planned to investigate this possibility. The primary mode of termination for polystyrene is *via* combination and the similarity of the molecular weight data for the $C_{60}$-containing polystyrene and the control polystyrene, suggests that termination involves the addition of two polymer chains to the $C_{60}$ unit. The addition of more than two chains to a single $C_{60}$ core is unlikely given the thermal behaviour of the $C_{60}$-containing polystyrene. We propose, therefore, that under the conditions used in these experiments that $C_{60}$ retards the free radical polymerisation of styrene and that each $C_{60}$ molecule terminates either 1 or possibly 2 polymer chains. Furthermore, it is the stability of $PSC_{60}^{\bullet}$ which prevents further reaction.

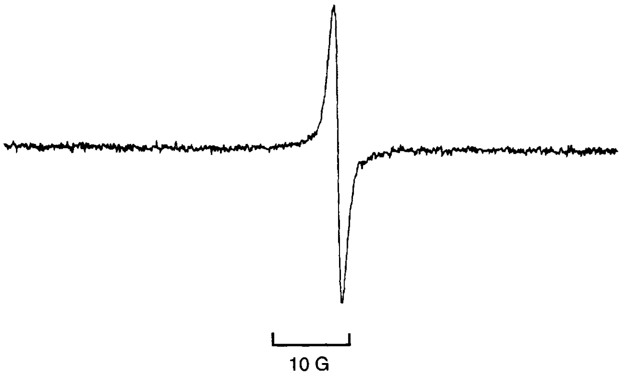

**Fig. 2** EPR spectrum for $C_{60}$-containing polystyrene

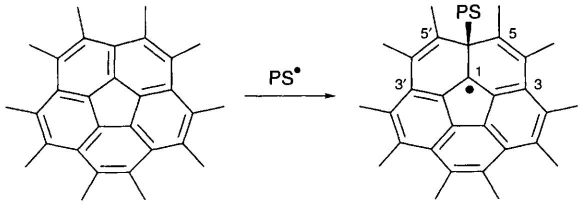

**Fig. 3** Partial structure of $C_{60}$ and $PSC_{60}^{\bullet}$

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## Footnotes

† Styrene (4.2 ml, 36.7 mmol), $C_{60}$ (40.18 mg, $5.58 \times 10^{-2}$ mmol) and benzene (44 ml) were stirred under an argon overpressure for 30 min. The solution was filtered to remove any particulate matter; gravimetric analysis was used to determine the remaining $C_{60}$ in the reaction mixture (20.45 mg, $2.84 \times 10^{-2}$ mmol). AIBN (69.67 mg, $4.24 \times 10^{-1}$ mmol) was added to the reaction mixture and the solution flushed with argon for 20 min. Polymerisation was initiated by heating the mixture to 60 °C.

‡ The dilatometer was calibrated using triply distilled mercury at 25 °C.

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