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Synthesis of Buckminsterfullerene C_{60} functionalised core cross-linked star polymers

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Abstract

Buckminsterfullerene C_{60} core functionalised core cross-linked star (CCS) polymers have been prepared for the first time, using atom transfer radical polymerisation and the arms-first approach. A simple and efficient method is presented which allows the construction of star polymers consisting of a large number of arms and multiple units of C_{60} per core, far in excess of that obtained previously. The C_{60} CCS polymers were characterised by gel permeation chromatography (GPC), UV–vis spectroscopy and cyclic voltammetry (CV). GPC revealed that the C_{60} CCS polymers possess weight average molecular weights (M_w) ranging from 172–411 kDa and up to 30 arms per macromolecule. The average number of molecules of C_{60} per CCS polymer core was found to be dependent on the C_{60}/PMMA ratio employed and was determined by UV–vis spectroscopy to range up to 6.2. CV revealed that, like pristine C_{60}, the C_{60} CCS polymers possessed three reversible one electron reductions. However, the reduction potentials were positively shifted, implying that the electron affinity of these macromolecules is higher than pristine C_{60}.

Keywords: Fullerene C_{60}; Star polymer; Cyclic voltammetry

1. Introduction

In the twenty years since fullerenes were first reported by Kroto and co-workers [1] a large range of novel fullerene-based macromolecular architectures [2] with potential applicability to advanced materials have been developed. These polymer–fullerene hybrids can be prepared via a variety of synthetic methodologies and enhance the solubility, tractability and processibility of fullerenes [3]. Functionalised star polymers with fullerene as the central core have been particularly well studied as a result of their potential use as porous membranes [4] and light emitting devices [5]. Star polymers incorporating fullerenes have been prepared via three distinct strategies: (i) the addition of linear polymer chains to unfunctionalised fullerenes via radical [6–10], nucleophilic addition [11–13] or insertion [14,15]; (ii) the addition of linear polymer chains to multisubstituted fullerenes [16,17], and (iii) polymerisation of vinylic monomers using charged [18] or functionalised fullerenes as initiators [19].

The large variety of methods available for the synthesis of fullerene functionalised star polymers has enabled the development of macromolecules comprised of a wide range of polymer types, however, the number of arms per molecule is generally low (≤10) as a result of steric crowding around the fullerene core or charge delocalisation encountered during reaction [20]. For example, the nucleophilic addition of an excess of living carbanionic polymer with C_{60} results in the formation of a 6-arm star polymer. This limit of six grafts is realised as a result of delocalisation of each carbanion over one of the six pyracyclene units from which the fullerene is comprised. Therefore, as a result of the involvement of all the unreacted double bonds in delocalisation of the six

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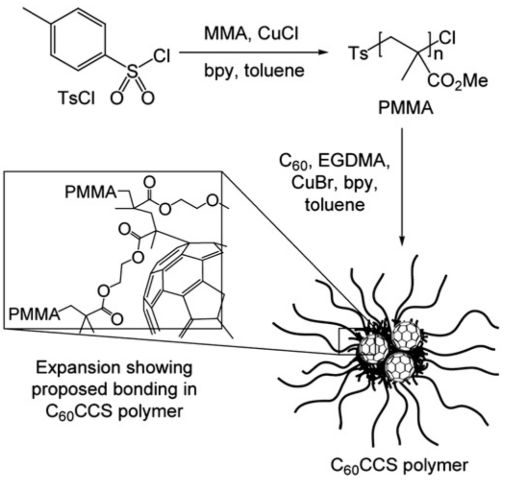
carbanions none of them are susceptible to further carbanionic polymer addition [11]. A further limitation associated with the aforementioned methods is that each macromolecule possesses only one molecule of C_{60} present as the central core.

As part of ongoing studies into unique star polymer architectures we were interested in the incorporation of fullerenes into the core of core cross-linked star (CCS) polymers as such structures would be capable of having a large number of arms and multiple units of C_{60} per core. Unlike star polymers [6–15] prepared by the addition of living linear polymers to C_{60}, the C_{60} present in the core of the CCS polymers would be surrounded by a cross-linked polymer sheath, creating a sterically isolated nano-environment with potentially interesting properties, such as unusual redox, photophysical or stabilising properties. For example, fullerene dendrimers in which the C_{60} is shielded by the dendritic arms, kinetically stabilise chemically generated fullerene anions [21] and delay fullerene triplet quenching as a result of a decrease of dioxygen diffusion rates [22]. CCS polymers have been prepared using a variety of living radical polymerisation methodologies [23–25] and ring-opening polymerisation [26] via either the core or, more commonly, arms-first approach. The arms-first approach involves the preparation of living linear polymers (the arms) which are then reacted with a cross-linker that forms the core of the CCS polymer. In this current investigation CCS polymers functionalised with fullerene C_{60} at the polymer core were prepared via atom transfer radical polymerisation (ATRP) of living poly(methyl methacrylate) (PMMA) and ethylene glycol dimethacrylate (EGDMA) in the presence of C_{60}. The incorporation of C_{60} into the macromolecular architecture was evidenced and quantified by UV–vis spectroscopy. The redox properties on the C_{60} functionalised CCS polymers were investigated via electrochemistry.

2. Results and discussion

In this study C_{60} functionalised CCS polymers were prepared via the arms-first approach involving the synthesis of living linear PMMA followed by cross-linking with EGDMA in the presence of C_{60}. Initially, living PMMA ($M_w = 11.9$ kDa, polydispersity index (PDI) = 1.07) was prepared via ATRP of methyl methacrylate (MMA) using *p*-toluenesulfonyl chloride (TsCl) as the initiator (Scheme 1).

Reaction of living PMMA with EGDMA and C_{60} (1:2 C_{60}:PMMA mole ratio) under standard CCS polymer formation conditions afforded pure C_{60} functionalised CCS polymer **P1a** ($M_w = 372$ kDa, PDI = 1.15, 65%) after fractional precipitation. The mechanism of the reaction can be considered as a combination of strategies in which the living PMMA reacts with the cross-linker via ATRP and then reacts with C_{60} through atom transfer radical addition (ATRA) to afford a C_{60} functionalised macromolecular architecture consisting of a C_{60} molecule complete with a delocalised radical. Given the stabilised nature of this radical it is unlikely that it would initiate further ATRP with available cross-linker, but would rather, undergo dimerisation with any free radical species present in the reaction mixture; however, dimerisation of C_{60} radicals is disfavoured as a result of the formation of a sterically strained species in which two C_{60} molecules are joined through a single bond [7]. As a result of previous studies investigating the ATRA of living polystyrene to C_{60} it is expected that only two or four covalent linkages are formed with the C_{60} molecules present in the CCS polymer core [6–9]. In parallel, a blank CCS polymer **P2** ($M_w = 490$ kDa, PDI = 1.20, 64%) was prepared using identical conditions, but without the addition of C_{60}, enabling comparisons to be drawn between the functionalised and unfunctionalised CCS polymers.



Scheme 1. Synthesis of C_{60} functionalised CCS polymer, including expansion showing proposed bonding of C_{60} to the cross-linked core.

The C_{60} CCS polymer **P1a** and blank CCS polymer **P2** exhibited identical solubility in aprotic organic solvents; however, **P1a** was light brown in colour as a result of the incorporation of C_{60} into the core of the polymers architecture. Gel permeation chromatography multi-angle laser light scattering (GPC-MALLS) coupled with online refractive index (RI) and UV–vis ($\lambda = 330$ nm) analysis of the unfractionated C_{60} CCS polymer **P1a** (Fig. 1(a)) and blank CCS polymer **P2** (Fig. 1(b)) revealed similar RI profiles for both polymers, with the exception of a small amount (<2%) of high molecular weight star–star coupled product present in **P1a**. The major difference between the CCS polymers was observed in their respective UV–vis traces, for which the C_{60} CCS polymer **P1a** possessed a strong absorption at 330 nm resulting from the C_{60} incorporated into the core of the polymer. In comparison the blank CCS polymer **P2** possessed negligible absorption at this wavelength. RI and UV–vis traces of the fractionated C_{60} CCS polymer **P1a** are also presented in Fig. 1(c).

Incorporation of C_{60} into the CCS polymer **P1a** was quantified via UV–vis spectroscopic analysis at $\lambda = 330$ nm, as it was determined that the absorption of the linear PMMA arms and EGDMA core was negligible at this wavelength. As the covalent attachment of polymer to the C_{60} potentially disrupts the conjugation across one or more pyracyclene units on the C_{60} it was necessary to prepare a reference polymer with a known amount of C_{60} attached to the polymer to mimic the substitution pattern of the C_{60} present in the C_{60} CCS polymer. Although the C_{60} covalently attached to the CCS polymer

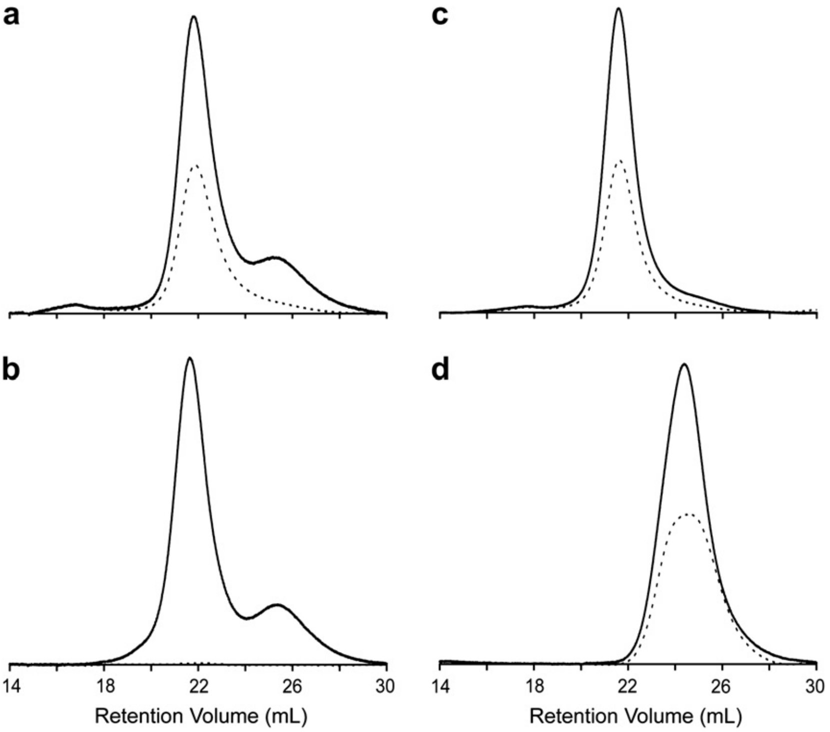
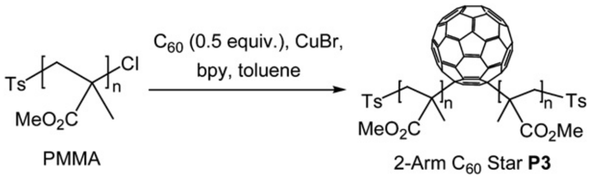


Fig. 1. GPC chromatograms consisting of normalised RI (—) and $\lambda = 330$ nm UV–vis (---) traces: (a) unfractionated C_{60} CCS polymer **P1a**; (b) unfractionated blank CCS polymer **P2**; (c) fractionated C_{60} CCS polymer **P1a**; (d) 2-arm C_{60} star polymer **P3**. GPC-MALLS was conducted in tetrahydrofuran at a flow rate of 1 mL min^{-1}.

core could potentially possess 2 or 4 substituents [6–10] it is evident that a two arm C_{60} star polymer provides a closer structural approximation than pristine C_{60}. A well-defined 2-arm C_{60} functionalised star polymer [7,8] was synthesised for this purpose to determine the effect that modification of the C_{60} has upon its absorption coefficient at $\lambda = 330$ nm. ATRA of living PMMA with C_{60} in a mole ratio of 2:1 afforded exclusively the desired 2-arm star polymer **P3** (Scheme 2). GPC-MALLS of the C_{60} star polymer ($M_w = 24.6$ kDa, PDI = 1.08) coupled with UV–vis analysis (Fig. 1(d)) revealed a strong absorption at $\lambda = 330$ nm corresponding to the C_{60} moiety present in the polymer.

UV–vis spectra of the C_{60} CCS polymer **P1a**, blank CCS polymer **P2**, pristine C_{60} and the C_{60} star polymer **P3** recorded in dichloromethane are presented in Fig. 2. Pristine C_{60} has two strong absorption maxima centred at $\lambda = 258$ and 330 nm corresponding to $6^1T_{1u}-1^1A_g$ and $3^1T_{1u}-1^1A_g$ transitions, respectively [27], which can also be observed at slightly shifted wavelengths ($\lambda = 257$ and 327 nm) in the UV–vis spectra of polymers **P1a** and **P3**. The broadening of the absorption bands corresponding to C_{60} in the polymers can be attributed to the range of weight distributed derivatives that these materials are comprised of and the nature of the complex and coordination of C_{60} [28]. In comparison, the blank CCS polymer **P2** possessed negligible absorbance at wavelengths >280 nm as a result of the absence of C_{60} in this macromolecule. This observation demonstrates that the



Scheme 2. Synthesis of 2-arm C_{60} star polymer **P3**. A less sterically constrained 1,4-disubstitued derivative was assumed based on previous studies [7,8] involving ATRA of living polymers with C_{60}; however, a 1,2-type derivative cannot be excluded.

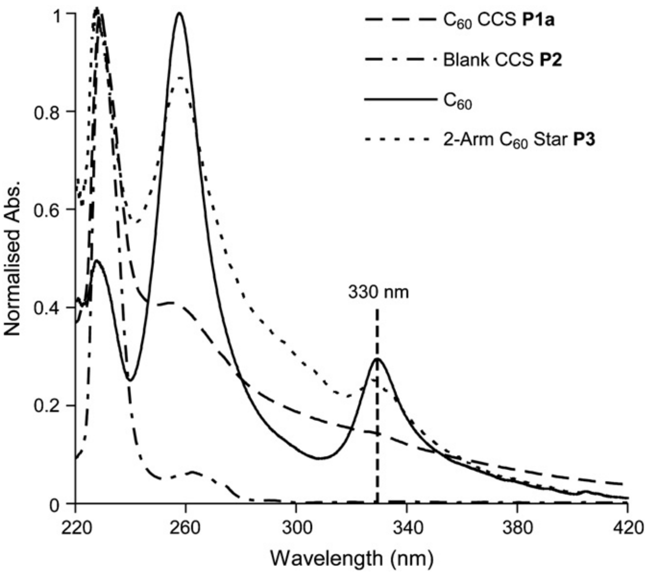


Fig. 2. UV–vis spectra of fractionated C_{60} functionalised CCS polymer **P1a**, fractionated blank CCS polymer **P2**, pristine C_{60} and 2-arm C_{60} star polymer **P3**. Measured in dichloromethane at a scan rate of 1 nm s^{-1}.

C_{60} moieties rather than the PMMA arms or EGDMA core contribute to the absorption profile of the polymers **P1a** and **P3** [29]. The absorption coefficient of pristine C_{60} and the star polymer **P3** in dichloromethane at $\lambda = 330$ nm were determined to be 31 020 and 27 370 $dm^2\,mol^{-1}$, respectively. As expected, the absorbance of C_{60} is slightly reduced by the saturation of one of the double bonds (58π electrons), leading to a lower absorption coefficient for the star polymer. Given the structural similarity of the covalently bonded C_{60} in the star polymer **P3** and the CCS polymer **P1a** it was proposed that the absorption coefficient for the star polymer would provide a more accurate determination of the amount of C_{60} present in the core of the CCS polymer. Using the absorption coefficient obtained for **P3**, the average number of C_{60} molecules present in the core of each molecule of C_{60} CCS polymer **P1a** was determined to be 6.2 (based on a statistical distribution), which corresponds to a 49% incorporation (based upon the maximum theoretical loading [30]) and a 1.2 wt% of C_{60} (0.012 g (or 17 μmol) of C_{60}/g polymer).

The redox properties of the polymers **P1a**, **P2** and **P3** were examined by cyclic voltammetry (CV) and compared to pristine C_{60} (Fig. 3). The C_{60} CCS polymer **P1a** and star polymer **P3** were found to possess three reversible one electron reductions as is the case for C_{60} [31]. As expected, the blank CCS polymer **P2** possessed no redox properties (a weak feature at −1.2 V is attributed to residual dioxygen). The numerical values obtained from the CV experiments are summarised in Table 1. The reduction potentials of polymers **P1a** and **P3** were generally close to those of C_{60}; however, there is an anodic shift of 0.02–0.06 V for **P1a**, and a cathodic shift of 0.04–0.06 V for **P3**. The cathodic shift is expected, based on the shift of reduction potential in response to disubstitution of C_{60} [8,32]. The anodic shift of reduction potentials observed for **P1a** is unexpected given the higher level of substitution of the C_{60} and this may be due to differences in solvation. Anodic shifts of 0.22 V are obtained for the $C_{60}^{0/-}$ couple as the solvent is changed from dichloromethane to *N*,*N*-dimethylformamide [31] and the polymer sheath about

Table 1
Half-wave potentials of redox couples in dichloromethane containing 0.2 M tetrabutylammonium hexafluorophosphate

Sample	$E_{1/2}$ (V) *vs* Fc^+/Fc[a]		
	E^1_{red} (V)	E^2_{red} (V)	E^3_{red} (V)
C_{60}	−1.03	−1.42	−1.87
C_{60} CCS **P1a**	−0.97	−1.38	−1.82
C_{60} star **P3**	−1.05	−1.48	−1.91

[a] All potentials were measured in volts versus the Fc^+/Fc couple. Initial potential and scan rate were 0 V and 0.2 V s^{-1}, respectively. Reported values were obtained from the second scan.

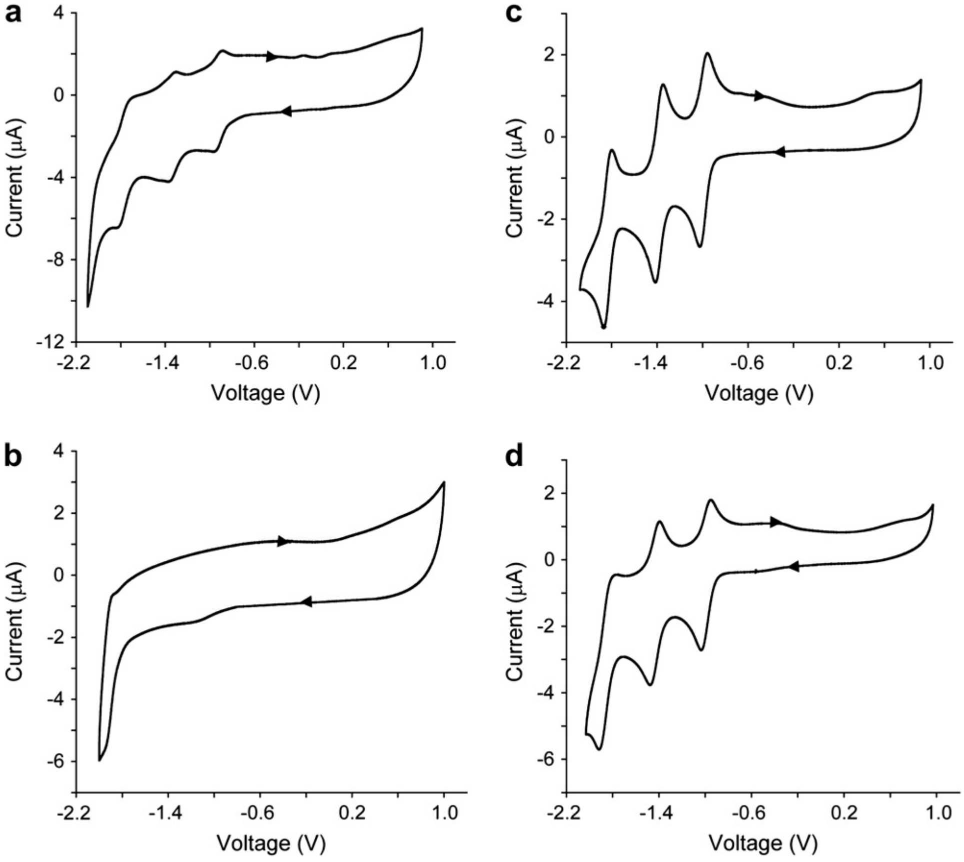


Fig. 3. Cyclic voltammograms of: (a) fractionated C_{60} CCS polymer **P1a**; (b) fractionated blank CCS polymer **P2**; (c) pristine C_{60}; (d) 2-arm C_{60} star polymer **P3**. All potentials were measured in volts versus the ferricenium/ferrocene (Fc^+/Fc) couple using dichloromethane as the solvent and tetrabutylammonium hexafluorophosphate (0.2 M) as the supporting electrolyte. Initial potential and scan rate were 0 V and 0.2 V s^{-1}, respectively. The voltammograms were recorded on the second scan where the arrows indicate the scan direction.

Table 2
Reaction conditions, conversions and characteristics of C_{60} CCS polymers **P1a–e**, blank CCS polymer **P2** and the 2-arm C_{60} star polymer **P3**

Polymer	[PMMA] (mM)	C_{60}/PMMA mole ratio	% Yield	% EGDMA conversion[a]	M_w (kDa)[b]	PDI[b]	R_z[c] (nm)	n (arms)[d]
C_{60} CCS **P1b**	7.03	0.02	80[e] (63)[f]	97	440	1.16	11.1	30
C_{60} CCS **P1c**	7.02	0.04	80[e] (55)[f]	98	411	1.09	10.0	28
C_{60}CCS **P1d**	7.00	0.20	83[e] (57)[f]	96	397	1.08	10.3	27
C_{60} CCS **P1a**	7.05	0.50	77[e] (65)[f]	95	372	1.15	11.6	25
C_{60} CCS **P1e**	7.08	1.00	50[e] (37)[f]	93	172	1.15	8.5	12
Blank CCS **P2**	6.98	–	78[e] (64)[f]	98	490	1.20	10.5	33
2-Arm C_{60} star **P3**	4.01	0.50	86[f]	–	25	1.08	–	2

[a] Determined by GCMS.

[b] Results for fractionated CCS polymers as determined by GPC-MALLS.

[c] Mean radius of gyration as determined by MALLS.

[d] Calculated from the equation: n (number of arms) $= (M_{w\text{- (CCS polymer)}} - (\text{Mol. wt.(C60)} \times \text{calculated loading}))/((15 \times \text{Mol. wt.(EGDMA)} \times (\%\ \text{Conversion}_{(\text{EGDMA})}/100)) + M_{w(\text{arms})})$.

[e] Determined from GPC coupled with RI detection.

[f] Isolated yield after fractional precipitation.

the C_{60} of **P1a** may provide a more polar environment (Scheme 1). It is noted, however, that the solvent dependence of the redox potentials for C_{60} are less pronounced as the charge on the molecule is increased, an observation not apparent for **P1a**.

In order to determine the effect of the reactant C_{60}/PMMA mole ratio on the extent of C_{60} incorporation and characteristics of the resulting CCS polymers the concentration of PMMA and the EGDMA/PMMA mole ratio were kept constant at 7 mM and 15:1, respectively, whilst the C_{60}/PMMA mole ratio was varied from 0.02 to 1.00. The resulting C_{60} functionalised CCS polymers (**P1b–e**) were isolated after fractional precipitation (37–65%) as tan to brown coloured solids and analysed by GPC-MALLS (Table 2) and UV–vis spectroscopy (Table 3).

The M_w of the C_{60} CCS polymers **P1a–e** was found to decrease slightly with an increase in C_{60}/PMMA mole ratio, whereas the yield remained relatively constant, with the exception of **P1e** (Table 2). Compared to the blank CCS polymer **P2**, the introduction of C_{60} into the reaction mixture (up to a C_{60}/PMMA mole ratio of 0.50) had no adverse effects upon the formation of the C_{60} CCS polymers, although at a C_{60}/PMMA mole ratio of 1.00 the high content of C_{60} was found to impede formation of the CCS polymer (**P1e**) resulting in a lower yield and M_w. The incorporation of C_{60} into the CCS polymers **P1a–e** had no noticeable effect on the mean radius of gyration with both functionalised and unfunctionalised polymers having similar values. At all C_{60}/PMMA mole ratios employed low polydispersity C_{60} CCS polymers were prepared that possessed ≥12 arms. However, it should be noted that although macromolecules with a large number of arms can be prepared, the average number of arms per C_{60} molecule decreases from 60 to 3.5 as the C_{60}/PMMA mole ratio increases, thus **P1a**, **P1d** and **P1e** have a ratio of arms to C_{60} comparable with star polymers synthesised by the addition of living linear polymers (via ATRA or nucleophilic addition) to C_{60} to form C_{60} core-type star polymers [6–13].

Table 3
Incorporation of C_{60} into the CCS polymer **P1a–e** as determined by UV–vis spectroscopy

C_{60} CCS polymer	Theoretical loading[a]	Calculated loading[b]	% Incorporation[c]	Weight% C_{60}[d]
P1b	0.6	0.5	83	0.1
P1c	1.1	0.8	77	0.1
P1d	5.4	4.0	74	0.7
P1a	12.6	6.2	49	1.2
P1e	11.7	3.5	30	1.5

[a] Theoretical loading (molecules of C_{60} per molecule of CCS polymer) = n (number of arms) × C_{60}/PMMA mole ratio.

[b] Determined from absorbance of CCS polymer at $\lambda = 330$ nm using the absorption coefficient (27 370 $\text{dm}^2\ \text{mol}^{-1}$) obtained for the star polymer **P3**.

[c] % Incorporation = 100 × (calculated loading/theoretical loading).

[d] Weight% $C_{60} = 100 \times ((720.64\ \text{g mol}^{-1} \times \text{calculated loading})/M_w$ CCS polymer).

For all the C_{60} CCS polymers prepared the calculated loading was less than the theoretical loading and the % incorporation of C_{60} was found to decrease with increasing C_{60}/PMMA mole ratio (Table 3). When C_{60}/PMMA mole ratios of >0.20 were employed the resulting polymers possessed between 3.5 and 6.2 molecules of C_{60} per macromolecule (based upon a statistical distribution), which is considerably greater than that obtained previously when synthesising C_{60} core-type star polymers.

3. Conclusions

In summary, a range of novel C_{60} core functionalised CCS polymers have been prepared with a large number of arms and multiple molecules of C_{60} per CCS polymer core. These macromolecules have similar redox properties to pristine C_{60}; however, they possess higher electron affinities as evidenced from the positive shift in reduction potentials.

Appendix. Supplementary data

Experimental details for the synthesis of the polymers and determination of C_{60} content, and differential scanning calorimetry (DSC) results (**P1a** and **P2**). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2008.01.001.

References

[1] Kroto HW, Heath JR, O'Brien S, Curl RF, Smalley RE. Nature 1985;318:162.
[2] Giacalone F, Martin N. Chem Rev 2006;106:5136.
[3] (a) Hirsch A. The chemistry of fullerenes. Stuttgart: Georg Thieme Verlag; 1994;
(b) Geckler KE, Samal S. Polym Int 1999;48:743.
[4] François B, Ederlé Y, Mathis C. Synth Met 1999;103:2362.
[5] Park JH, Park OO, Kim J, Yu J-W, Kim JK, Kim YC. Curr Appl Phys 2004;4:659.
[6] Audouin F, Nunige S, Nuffer R, Mathis C. Synth Met 2001;121:1149.
[7] Audouin F, Nuffer R, Mathis C. J Polym Sci Part A Polym Chem 2004;42:3456.
[8] Okamura H, Terauchi T, Minoda M, Fukuda T, Komatsu K. Macromolecules 1997;30:5279.
[9] (a) Okamura H, Ide N, Minoda M, Komatsu K, Fukuda T. Macromolecules 1998;31:1859;
(b) Okamura H, Takemura T, Tsunooka M, Shirai M. Polym Bull 2004;52:381.
[10] (a) Cao T, Webber SE. Macromolecules 1995;28:3741;
(b) Jiang G, Zheng Q. J Appl Polym Sci 2005;97:2182.
[11] (a) Ederlé Y, Mathis C. Macromolecules 1997;30:2546. and 4262;
(b) Ederlé Y, Nuffer R, Mathis C. Synth Met 1999;103:2348;
(c) Mathis C, Audouin F, Nuffer R. Fullerenes, Nanotubes Carbon Nanostruct 2004;12:341.
[12] Delpeux S, Béguin F, Manolova N, Rashkov I. Eur Polym J 1999;35:1619.
[13] Ederlé Y, Mathis C, Nuffer R. Synth Met 1997;86:2287.
[14] Delpeux S, Béguin F, Benoit R, Erre R, Manolova N, Rashkov I. Eur Polym J 1998;34:905.
[15] Xu H, Sun Q, Lee PPS, Kwok HS, Tang BZ. Thin Solid Films 2000;363:1446.
[16] Goswami TH, Nandan B, Alam S, Mathur GN. Polymer 2003;44:3209.
[17] (a) Chiang LY, Wang LY, Tseng S-M, Wu J-S, Hsieh K-H. J Chem Soc Chem Commun 1994:2675;
(b) Ma C-CM, Sung S-C, Wang F-Y, Chiang LY, Wanng LY, Chiang C-L. J Polym Sci Part B Polym Phys 2001;39:2436.
[18] Wang J, Javahery G, Petrie S, Bohme DK. J Am Chem Soc 1992;114:9665.
[19] (a) Jing H, Dianbao C, Ling X, Qufeng L, Xiongke J, Yifeng Z. J Appl Polym Sci 2002;86:3001;
(b) Hua J, Yang W, Zhu Y, Guo Z, Yang H, Xu L, et al. Mater Lett 2005;59:644;
(c) He J-D, Wang J, Li S-D, Cheung MK. J Appl Polym Sci 2001;81:1286.
[20] Mignard E, Hiorns RC, François B. Macromolecules 2002;35:6132.
[21] Kunieda R, Fujitsuka M, Ito O, Ito M, Murata Y, Komatsu K. J Phys Chem B 2002;106:7193.
[22] Rio Y, Accorsi G, Nierengarten H, Bourgogne C, Strub J-M, Dorsselaer AV, et al. Tetrahedron 2003;59:3833.
[23] (a) Abrol S, Kambouris PA, Looney MG, Solomon DH. Macromol Rapid Commun 1997;18:755;
(b) Solomon DH, Abrol S, Kambouris PA, Looney MG. WO9831789; 1998.
[24] (a) Solomon DH, Qiao GG, Abrol S. WO99/58588; 1999.
(b) Xia J, Zhang X, Matyjasewski K. Macromolecules 1999;32:4482;
(c) Gurr PA, Qiao GG, Solomon DH, Harton SE, Spontak RJ. Macromolecules 2003;36:5650.
[25] (a) Lord HT, Quinn JF, Angus SD, Whittaker MR, Stenzel MH, Davis TP. J Mater Chem 2003;13:2819;
(b) Moad G, Mayadunne RTA, Rizzardo E, Skidmore M, Thang SH. Macromol Symp 2003;192:1;
(c) Zheng G, Pan C. Polymer 2005;46:2802.
[26] (a) Wiltshire JT, Qiao GG. Macromolecules 2006;39:4282;
(b) Wiltshire JT, Qiao GG. Macromolecules 2006;39:9018.
[27] Leach S. Chem Phys 1992;160:451.
[28] (a) Schröder C. Fullerene Sci Technol 2001;9:281;
(b) Konarev DV, Semkin VN, Lyubovskaya RN, Graja A. Synth Met 1997;88:225.
[29] Chu C-C, Wang L, Ho T-I. Macromol Rapid Commun 2005;26:1179.
[30] The theoretical loading assumes that for each arm incorporated into the CCS polymer the amount of C_{60} incorporated will be directly related to the C_{60}/PMMA ratio. For example, at a ratio of 0.5 it is assumed that one molecule of C_{60} would be incorporated for every two arms incorporated.
[31] Dubois D, Moninot G, Kutner W, Jones MT, Kadish KM. J Phys Chem 1992;96:7137.
[32] (a) Keshavarz- KM, Knight B, Srdanov G, Wudl F. J Am Chem Soc 1995;117:11371;
(b) Okamura H, Murata Y, Minoda M, Komatsu K, Miyamoto T, Wan TSM. J Org Chem 1996;61:8500;
(c) Komatsu K, Murata Y, Takimoto N, Mori S, Sugita N, Wan TSM. J Org Chem 1994;59:6101;
(d) Prato M, Maggini M, Giacometti C, Scorrano G, Sandonà G, Farnia G. Tetrahedron 1996;52:5221.