Synthesis and Characterization of Star Copolymers Consisting of Fullerene and Conjugated Polyphenylene: 6-*star*-C_{60}[styrene−poly(1,4-phenylene)-*block*-polystyrene] and 6-*star*-C_{60}[polystyrene-*block*-poly(1,4-phenylene)]

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ABSTRACT: The grafting of "living" polystyrene-*block*-poly(1,3-cyclohexadiene)-*block*-styryllithium and poly(1,3-cylclohexadiene)-*block*-polystyryllithium onto C_{60} yielded, respectively, 6-*star*-fullerene[styrene-*block*-poly(1,3-cyclohexadiene)-*block*-polystyrene] and 6-*star*-fullerene[polystyrene-*block*-poly(1,3-cyclohexadiene)]. Selective dehydrogenation of these macromolecules yielded, respectively, 6-*star*-fullerene-[styrene-*block*-poly(1,4-phenylene)-*block*-polystyrene], C_{60}(st−PPP−PS)$_6$, and 6-*star*-fullerene[polystyrene-*block*-poly(1,4-phenylene)], C_{60}(PS−PPP)$_6$. 6-*star*-Fullerene[poly(1,4-phenylene)-*block*-polystyrene] could not be synthesized via this route as fullerene−poly(1,3-cyclohexadiene) bonds were found to form without control and to degrade during aromatization. Star copolymers containing conjugated PPP were characterized by size exclusion chromatography, UV, and fluorescence spectroscopy. Fluorescence quantum yields of C_{60}(st−PPP−PS)$_6$ and C_{60}(PS−PPP)$_6$ in THF were compared and discussed in light of characterizations of PPP−PS−PPP in comparable conditions without or mixed with C_{60}(PS)$_6$.

Introduction

Poly(1,4-phenylene) (PPP) has received considerable attention since the 1950s due to its high thermal stability, chemical resistance,[1] electrical conductivity upon doping,[2] and optoelectronic properties.[3−5] The π-orbital conjugation of PPP, on which these properties depend, demands regular repetition of 1,4-links and is arrested by 1,2-links. While increasing the length of conjugated 1,4-phenylene units increases $\lambda_{\max}$ of the resulting polymer to between 300 and 340 nm, the PPP obtained, with enhanced interchain interactions, becomes crystalline, insoluble and infusible at >6 repeat units.[1,6] With increasing crystallization of PPP segments, there is a concomitant reduction in opto-electrical properties, due to the increasing ease in which thermal relaxation, rather than radiative decay processes, may occur.

Syntheses of PPP are often limited by rapid formation of quasi-crystalline particles of low molecular weight segments of PPP in solution. The literature details various routes leading to PPP (degree of sequential 1,4-phenylene units ≤ 12); nevertheless, the resulting polymers have broad molecular weight distributions, high 1,2-isomer contents, numerous structural defects, and low purities.[1,6,7] To improve the physicochemical properties of PPP and simultaneously prepare a highly conjugated polymer, derivatives have been synthesized which are soluble in common organic solvents.[6] The most convenient route to PPP is the dehydrogenation of poly(1,3-cyclohexadiene) (PCHD) which is tractable.[8−12]

PCHD is at present best synthesized via "living" anionic polymerization. This route has readily permitted syntheses of AB and ABA type copolymers of PCHD and polystyrene (PS).[13] Subsequent dehydrogenation resulted in block copolymers containing relatively long PPP segments (up to 15 units).[14−16] It is known that block copolymers assist in the dispersion of otherwise insoluble component polymers in solvents, and in this case, the high solubility of PS−PPP, relative to PPP, permitted more extensive formation of conjugated PPP segments. Block copolymers can improve mechanical and optoelectronic properties, compared to individual component homopolymers, by forming well-defined macrostructures based on stable, chemically inter-linked macrodomains.[17] PPP−PS has been shown to form micelles in a wide range of organic solvents with PPP "cores" surrounded by PS "shells" ,[18−22] and thin films of PPP−PS−PPP self-organize into a honeycomblike morphology[23] presenting promising photo- and electroluminescence properties.[20,22,24,25]

The synthesis of star copolymers consisting of PCHD, about divinylbenzene[26,27] or trichloromethylsilane[28] cores, has led to the possibility of preparing three-dimensional copolymers containing PPP which may display novel properties. However, the internal structures of such copolymers are poorly defined and may favor intramolecular crystallization of PPP. In contrast, the wide range of macromolecules devised using C_{60} has permitted the preparation of well regulated structures.[29] Of particular interest here is the work of Ederlé and Mathis, which described controlled grafting of up to six "living" anionic polymers onto fullerene[30] or C_{60}. In these systems, the grafted polymers may be isotropically spaced about the C_{60} core, and therefore the interactions between "arms" of the same molecule are limited. It is probable that the properties of such materials may be less dependent on the formation of macroscopic domains than for block copolymers.[17] It has been recognized that C_{60}, being a good electron acceptor, when combined with photoactive conjugated polymers, acting as electron donors, may permit the preparation of photovoltaic

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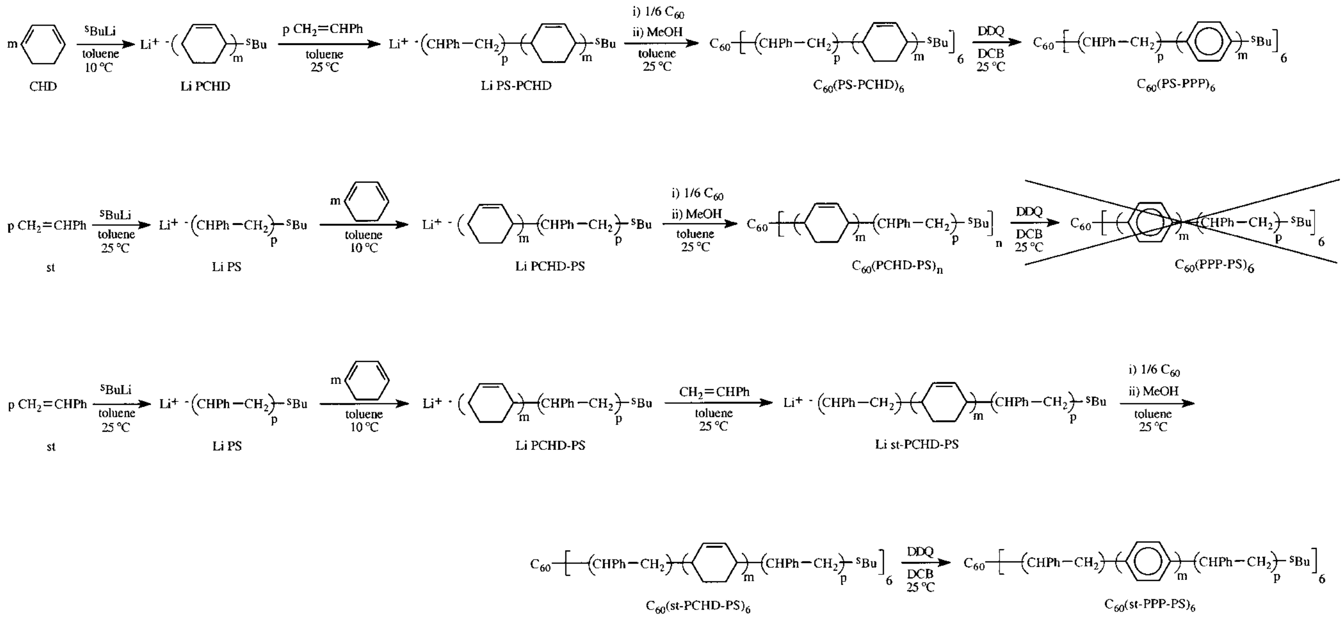
Scheme 1. Representation of Overall Synthetic Routes to Star Copolymers



devices.[31−33] Thus, it was imagined here that "living" PCHD might be grafted onto C_{60} and that subsequent dehydrogenation of the grafted PCHD could yield star copolymers with isotropically spaced PPP segments exhibiting charge-transfer reactions resulting from "photodoped" PPP.

Three types of novel star copolymers were prepared with the aim of forming materials with different macroscopic properties: Scheme 1 shows the synthetic routes to 6-*star*-fullerene[polystyrene-*block*-poly(1,3-cyclohexadiene)], $C_{60}(PS-PCHD)_6$, *n*-*star*-fullerene[poly(1,3-cyclohexadiene)-*block*-polystyrene)], $C_{60}(PCHD-PS)_n$, and 6-*star*-fullerene[styrene-poly(1,3-cyclohexadiene)-*block*-polystyrene], $C_{60}(st-PCHD-PS)_6$, and attempted aromatizations using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in 1,2-dichlorobenzene (DCB) to, respectively, yield 6-*star*-fullerene[polystyrene-*block*-poly(1,4-phenylene)], $C_{60}(PS-PPP)_6$, *n*-*star*-fullerene-[poly(1,4-phenylene)-*block*-polystyrene], $C_{60}(PPP-PS)_n$, and 6-*star*-fullerene[styrene-poly(1,4-phenylene)-*block*-polystyrene], $C_{60}(st-PPP-PS)_6$. It was expected that the outer PS shell of $C_{60}(PPP-PS)_6$ might limit intermolecular aggregation of PPP segments and retain the optoelectronic properties of PPP and C_{60} and that $C_{60}(PS-PPP)_6$ might undergo intermolecular aggregation to form a network of PPP organized in an insulating matrix of PS. It was subsequently discovered that $C_{60}-$PCHD links ruptured during aromatization. Therefore, $C_{60}(st-PCHD-PS)_6$ was prepared to limit this possibility. Fluorescence studies of star copolymers and compared and discussed in light of comparable characteristics of linear PPP−PS−PPP without $C_{60}PS_6$ and mixed with $C_{60}PS_6$.

Experimental Section

General Data. All chemicals were obtained from Aldrich, France unless otherwise noted. sec-Butyllithium (^sBuLi) as a 1.3 M solution in cyclohexane and 1,1-diphenylethylene (DPE) (Fluka, France) were used as received. THF was distilled from over benzophenone and sodium under nitrogen. Toluene was freshly distilled under nitrogen from over molten sodium and stored with ^sBuLi and DPE under nitrogen until used. Polymerizations were performed in flame-dried glass vessels which had been evacuated under high vacuum (ca. $10^{-3}-10^{-4}$ Pa), set with break-seal ampules.[34−36] A known quantity of initiator, ^sBuLi, was added to purified toluene in a break-seal on the vacuum line immediately prior to use. MeOH, st and CHD were distilled into break-seals. The latter two chemicals were initially degassed and distilled twice, first over CaH_2 and then over ^nBuLi. C_{60} (Fluka, France) was washed thrice in THF and dried and sealed under high vacuum. DCB, tetrachloro-1,4-benzoquinone (TCBQ), and DDQ were used as received.

Synthesis of PPP−PS−PPP Precursor Block Copolymers. Two samples of PPP−PS−PPP were prepared as previously described:[24,25] PPP−PS−PPP(1), $M_n \approx 5000$ g mol^{-1}, $M_w/M_n \approx 1.2$, PPP blocks, $M_n \approx 1000$ g mol^{-1}; and PPP−PS−PPP(2), $M_n \approx 32\,700$ g mol^{-1}, $M_w/M_n \approx 1.1$, PPP blocks $M_n \approx 1550$ g mol^{-1}.

Syntheses of Precursor Star Copolymers. The following sample synthesis of $C_{60}(PS-PCHD)_6$ is a standard method. Toluene (30 mL) was distilled via a high vacuum line into a vessel (100 mL) equipped with break-seals containing reagents as shown in Figure 1. The break-seals were placed so that, after delivery of reagents, each could be used later on to easily remove aliquots from the reaction mixture. The vessel was sealed from the vacuum line, a break-seal containing ^sBuLi (4.2×10^{-4} mol) in toluene (20 mL) was broken, and the interior of the vessel rinsed with the solution so as to eliminate impurities on vessel walls which might otherwise have interrupted polymerizations. CHD (0.7 mL, 7.3×10^{-3} mol) was introduced, and a pale yellow color gradually appeared, characteristic of "living" poly(1,3-cyclohexadienyl)lithium. The reaction mixture was stirred at 10 °C (to reduce the possibility of secondary reactions) over a period of 4 days to obtain PCHD molecular weights of ca. 2000 g mol^{-1}. Polymerization times were calculated using known kinetic rates.[16] An aliquot of PCHD was removed for characterization. To prepare poly(1,3-cyclohexadiene)-*block*-polystyryllithium, PCHD−PS Li, styrene (6.1 mL, 5.32×10^{-2} mol) was added via a break-seal. The characteristic orange-red color of "living" polystyryllithium was observed, and the reaction mixture was allowed to warm to room temperature. After 2 h, an aliquot was again recovered for characterization. To form $C_{60}(PS-PPP)_6$, the break-seal containing C_{60} (0.03 g, 4.2×10^{-5} mol, 10% relative to "living" copolymer end groups) was broken, and toluene was distilled into the then open tube; the resulting violet solution was slowly added to "living" PCHD−PS Li to ensure that there was not a relative excess of C_{60}. The reaction mixture was stirred at 25 °C for 24 h. Subsequently, C_{60} core carbanions were "killed" using acidified methanol (a weak solution of HCl in 1 mL of

Table 1. Molecular Weights of Star Macromolecules and Component Polymers Indicated by SEC (RI)

	outermost polymer		copolymer "arms"		macromolecule	
sample	M_n (g mol^{-1})	M_w/M_n	M_n (g mol^{-1})	M_w/M_n	M_n (g mol^{-1})	M_w/M_n
C_{60}(PS−PCHD)$_6$(1)	2170	1.29	76 700	1.19	213000	1.12
C_{60}(PS−PCHD)$_6$(2)	1140	1.05	3010	1.13	17330	1.16
C_{60}(PCHD−PS)$_n$	2290	1.09	4570	1.17	17220	1.8
C_{60}(st−PCHD−PS)$_6$	670	1.2	1420	1.2	10600	1.15

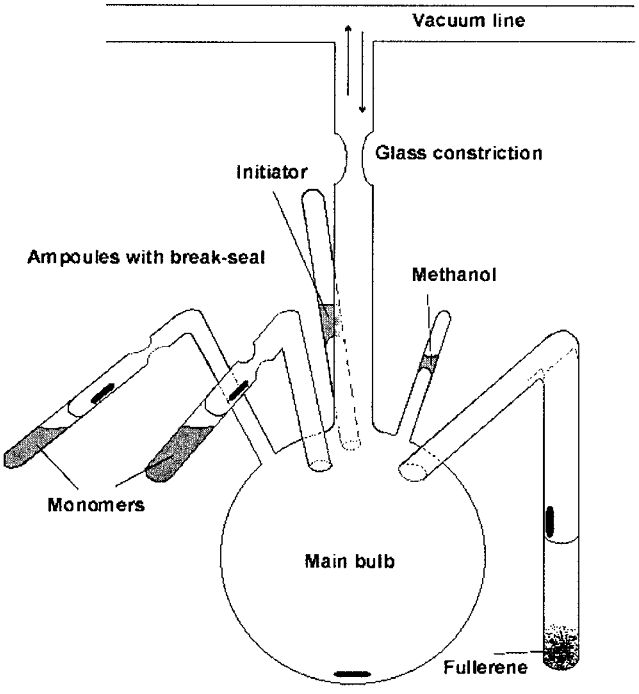


Figure 1. Representative apparatus for synthesis of star copolymers under high vacuum.

methanol) added via a break-seal. When the reaction vessel was broken open, the solution was added dropwise to excess ethanol (ca. 600 mL). Filtration and vacuum-drying at room temperature yielded a light brown powder which was immediately stored in the dark under dry nitrogen atmosphere.

In the attempted synthesis of C_{60}(PCHD−PS)$_6$ and the synthesis of C_{60}(st−PCHD−PS)$_6$, the order of monomer addition was altered along with respective polymerization conditions. Table 1 details SEC-indicated molecular weights of polymer samples removed throughout the reactions.

Aromatization of PCHD in Copolymers. Standard Schlenk techniques were used throughout unless otherwise stated. The following example is a standard method. C_{60}(st−PS−PCHD)$_6$ (0.50 g, containing ca. 3.3 × 10^{-3} mol of CHD units) was placed into a 100 mL Schlenk tube and flushed with nitrogen. DCB (29 mL) was added via syringe and the mixture stirred until the polymer was fully dissolved. DDQ (2.84 g, 12.5 × 10^{-3} mol, 380% with respect to CHD groups) was added and the mixture stirred at 25 °C for 7 h. DDQ was also used, at 25 °C, to dehydrogenate C_{60}(PCHD−PS)$_6$ and C_{60}(PS−PCHD)$_6$(2), whereas TCBQ was used in a similar manner, but at 130 °C, to dehydrogenate C_{60}(PS−PCHD)$_6$(1) and the triblock copolymers previously mentioned. Reactions were followed by UV spectroscopy, and the λ_{max} values are listed in Table 2. Copolymers were recovered as fine, brown powders by repeated filtering and precipitation in an excess of ethanol—to remove byproducts—and then dried under vacuum at 25 °C for 24 h. They were immediately stored in the dark under dry nitrogen.

Star $C_{60}PS_6$. $C_{60}PS_6$(1) ($M_n \approx$ 9300 g mol^{-1}, $M_w/M_n \approx$ 1.1, PS arms, $M_n \approx$ 1550 g mol^{-1}) and $C_{60}PS_6$(2) ($M_n \approx$ 76 000 g mol^{-1}, $M_w/M_n \approx$ 1.1, PS arms, $M_n \approx$ 12 700 g mol^{-1}) were kindly given by Dr. C. Mathis, and the details of their preparation are described elsewhere.[30]

Characterization. SEC. Molecular weight determinations by SEC relative to polystyrene standards were carried out using a bank of 4 columns (HR 0.5, 2, 4 and 6) of 300 mm × 5 μm Styragel at 40 °C, with THF eluent at a flow rate of 1.0 mL min^{-1}, controlled by a Waters 2690 pump equipped with ERMA ERC 7515A refractive index (RI) detector and a Waters 996 multiple wavelength UV−visible photodiode array detector. Samples (ca. 0.1% w/w) were injected in 100 mL volumes. Millennium software permitted estimation of fractional quantities of component polymers. It should be noted that, at 254 nm, both PS and C_{60} have chromophores, but at 320 nm only C_{60} absorbs. PCHD does not have chromophores at these frequencies and therefore was observed only with the RI detector. PPP has active chromophores in the range 300−340 nm depending on the degree of phenyl conjugation. Absolute masses of star copolymers could not be accurately determined by light-scattering techniques due to their relatively low molecular weights.

Table 2. Degrees of Conjugation for PPP-Containing Copolymers As Indicated by UV Spectroscopy

sample	λ_{max} (nm)	n
PPP−PS−PPP(1)	317	6
PPP−PS−PPP(2)	326	8
C_{60}(PS−PPP)$_6$(1)	319	7
C_{60}(PS−PPP)$_6$(2)	320	7
C_{60}(PPP−PS)$_n$	319	7
C_{60}(st−PS−PPP)$_6$	325	8

^{1}H and ^{13}C NMR. Samples were dissolved in $CDCl_3$ and filtered (10 μm filter) prior to characterization. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker Avance spectrometer. Residual hydrogen in deuterated chloroform was used to reference ^{1}H shifts.

Thermal Gravimetric Analysis. Thermally induced degradations of samples were followed under nitrogen atmosphere at 10 °C min^{-1} using a TGA 2950 thermogravimetric analyzer supplied by TA Instruments.

UV−Visible Spectrometry. UV−visible characterizations were performed using a Shimadzu UV-2101 PC from 230 to 800 nm using quartz cells with an optical pathway of 1 cm.

Fluorescence. Fluorescence studies were performed at 25 °C using a Perkin-Elmer LS 50B with quartz cells (1 cm optical pathway) with filtered (10 μm filter) samples. Incident light with wavelength λ_0 was fixed at λ_{max} (determined by the previous apparatus) of the copolymer under study. Emissions were recorded through three passes from 230 to 800 nm with 5 nm excitation and emission windows and a resolution of 0.5 nm. Fluorescence quantum yields, η, of samples were calculated using eq 1 with respect to a reference cell containing quinine sulfate (<10^{-4} M) in sulfuric acid (1.0 M).[37]

$$\eta_x = \eta_r \frac{A_r(\lambda_r)}{A_x(\lambda_x)} \frac{I_r(\lambda_r)}{I_x(\lambda_x)} \frac{n_x^2}{n_r^2} \frac{D_x}{D_r} \tag{1}$$

Subscripts x and r respectively note sample and reference values, $A(\lambda)$ denotes solution absorbance at the excitation wavelength, $I(\lambda)$ is lamp intensity at the incident beam wavelength, n is the refractive index of the solution under analysis, and D is the integral of emissions. Using an incident light of wavelength 360 nm, the absolute quantum yield of the reference solution,[38] η_r, was 0.546; from 345 to 390 nm, η_r was constant to within ±3%, and from 240 to 400 nm, η_r was constant to within ±5%.[37] As emissions were automatically corrected by the instrument, $I_r(\lambda_r)/I_x(\lambda_x)$ equaled 1 in all cases. Refractive indexes of solutions were assumed equivalent to pure solvents: i.e., 1.407 for THF at 25 °C and 1.345 for the reference solution.[39]

Results and Discussion

General Data. To obtain PPP with a high degree of π-orbital conjugation from PCHD requires that PCHD "precursors" have a low content of 1,2-isomers, during aromatization, crystallization of PPP segments is limited, and the number of grafted, defect moieties to PPP segments introduced by dehydrogenation agents[14] are reduced to a minimum.

Anionic Polymerization Leading to Regioregular PCHD. Anionic polymerization of CHD in nonpolar solvents yields PCHD with a high 1,4-isomer content (ca. 90%).[8,11,40,41] The polymerization is however relatively slow, taking several days to reach elevated molecular weights (ca. 10 000),[16] and is subject to a high degree of secondary and chain termination reactions.[15] Indeed, M_w/M_ns, or polydispersities, of PCHDs of weights >5000 were found to be high (ca. 1.3) even at low polymerization temperatures (ca. 10 °C).[15,40] Recently Natori et al. showed that "living" anionic polymerizations of CHD with diamine-based additives, such as 1,4-diazabicyclo[2.2.2]octane, limited secondary reactions and permitted syntheses of high molecular weight PCHD and low values of M_w/M_n.[42−45] However, such additives can also induce a high degree of 1,2-isomer formation.[40,41] As PCHD with a low degree of 1,2-isomerization was required, it was realized that "living" anionic polymerization of CHD, without additives, although time-consuming and demanding high vacuum techniques, would be the most appropriate synthetic route. To retain "living" PCHD, so that subsequent reactions with C_{60} or styrene could be performed, molecular weights were restricted to relatively low values (between 800 and 2000 or 10−25 monomer units). Of the available nonpolar solvents, toluene was preferred as it is a good solvent of C_{60}.

Syntheses of PCHD−PS−PCHD and PPP−PS−PPP Copolymers. The synthesis[46] and dehydrogenation[14,24,25] of PCHD−PS−PCHD triblock copolymers has been extensively studied and will not be discussed in any great detail here. PS−PPP−PS copolymers were not studied, due to their tendency to form dense aggregates in selective solvents providing incomparable values of η.[47]

PPP−PS−PPP(1) and PPP−PS−PPP(2) were synthesized, respectively, by the dehydrogenation of PCHD−PS−PCHD(1) and PCHD−PS−PCHD(2) in DCB using TCBQ. It should be noted that TCBQ has been shown to introduce a low number of pendent chlorophenyl ethers to conjugated PPP.[14]

An aliquot of PCHD was withdrawn during the synthesis of PCHD−PS−PCHD(2) and characterized by ^{1}H NMR. The number-average degree of polymerization of CHD units was calculated by comparing the integrals of peaks from ca. 0.6 to 0.8 ppm, due to six methyl protons of ^{s}BuLi, against those between ca. 5.5 to 5.8 ppm, due to two olefinic protons on PCHD, and was found to be ca. 17. By comparison of the integrals of methylene protons on CHD groups between 1.4 and 2.4 ppm, as will be described elsewhere,[41] it was calculated that there were ca. 12 mol % 1,2-isomers present indicating a number-average of eight CHD units linked in 1,4-fashion. SEC characterization of PCHD−PS−PCHD(2) indicated that the two segments of PCHD each consisted of 19 CHD units, which is in close approximation to that indicated by ^{1}H NMR.

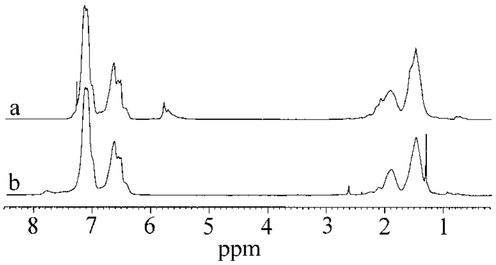


Figure 2. ^{1}H NMR spectra: (a) PCHD−PS−PCHD(2); (b) PPP−PS−PPP(2).

The ^{1}H NMR of the representative PCHD−PS−PCHD(2) is shown in Figure 2a. By comparison of the integrals of PS phenyl protons (ca. 7 ppm) and PCHD olefinic protons, it was deduced that the polymer consisted of 16 mol % CHD groups. Figure 2b shows the ^{1}H NMR of PPP−PS−PPP(2). Most evident is the loss of olefinic protons, indicating a complete dehydrogenation of PCHD segments. However, determination of protons at PPP chains is more difficult due to the high propensity of PPP segments to aggregate in solution,[24] especially at concentrations required for liquid-state NMR. It was for this reason that it was not possible to deduce whether the slight peak at 7.8 ppm was due to protons on PPP or due to grafted chlorophenyl ether moieties. Elemental analysis of PPP−PS−PPP(2) showed it to contain 2.6% Cl; however, this result is ambiguous as it may have resulted from attached and unattached TCBQ, the latter of which were difficult to remove from crystalline PPP or from the remaining DCB.

Thermal gravimetric analysis was shown to be useful in confirming the degree of aromatization of PPP−PS diblock copolymers,[14] and the technique was applied here to determine the molecular weight fraction of PPP in triblock copolymers. PS and PCHD degrade, respectively, at ca. 300 and 150 °C. The latter forms oligophenylenes[46] which are stable up to ca. 450 °C. In contrast, PPP is thermally stable up to ca. 550 °C. PPP−PS−PPP(1) and -(2) were respectively found to contain 47 and 18% w/w of PPP. The latter was, within limits of experimental error, close enough to the ^{1}H NMR determination mentioned above.

Characterization of aromatized triblock copolymers by UV−visible spectrometry confirmed the high degree of aromatization, and consistency of 1,4-isomerization, of PPP chains. PPP has an expected λ_{max} of between 300 and 350 nm, and the number-average degree of conjugation of PP units, n, is directly related to λ_{max} (nm) in the empirically determined equation:[48]

$$\lambda_{max} = \frac{2.08 \times 10^2}{\sqrt{1 - 0.634 \cos\frac{\pi}{n+1}}} \tag{2}$$

For triblock samples, detailed in Table 2, n was between 6 and 8, in agreement with that expected from NMR, TGA, and SEC results. It was interesting to note that the UV coupled SEC indicated the aggregates formed of these samples consistently displayed higher values of λ_{max}. For of aggregates of PPP−PS−PPP(2), the observed value was 342 nm, indicating that the chains consisted of 27 conjugated PP units, and although this cannot be treated as absolute, as eq 2 is inaccurate at high degrees of conjugation, this is the highest recorded value to our knowledge. It would seem correct, on reflection, that aggregates should be formed

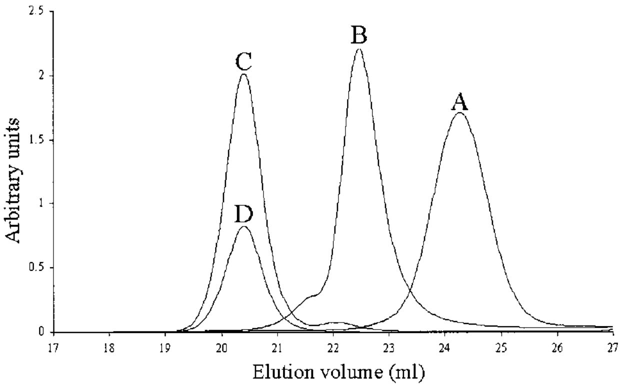


Figure 3. Representative synthesis of $C_{60}(PS-PCHD)_6(2)$ indicated by SEC curves: (A) PCHD (RI); (B) PS−PCHD (RI); (C) $C_{60}(PS-PCHD)_6(2)$ (UV, 254 nm); (D) $C_{60}(PS-PCHD)_6(2)$ (UV, 320 nm).

of PPP−PS−PPP containing the highest degree of PPP conjugation.

Synthesis of $C_{60}(PS-PCHD)_6$. The sequential addition of CHD, styrene and C_{60} to "living" ^{s}BuLi to yield $C_{60}(PS-PCHD)_6$, as described in Scheme 1, was followed by SEC, as detailed in Table 1. Using different ratios of reagents, two star copolymers were formed and labeled $C_{60}(PS-PCHD)_6(1)$ and $C_{60}(PS-PCHD)_6(2)$. The PCHDs were synthesized with relatively low molecular weights for reasons outlined in the previous section. The representative SEC curves recorded for $C_{60}(PS-PCHD)_6$-(2), shown in Figure 3, indicated that all "living" PCHD was consumed in reacting with styrene to yield "living" PCHD−PS and, therefore, a negligible quantity of PCHD was lost to chain transfer and termination reactions.[15] The curves recorded at 254 and 320 nm, after the addition of C_{60}, coincide, giving strong evidence that the formed star copolymers contained PS (and therefore PCHD−PS). It has been shown[30] that a maximum of six "living" anionic polymers may be grafted on to C_{60} in nonpolar media. It is reasonable to assume that mixtures of monofunctional "living" anionic polymers mixed with C_{60} at a respective ratio of greater than 6:1 will yield macromolecules with six "arms" around one C_{60} core. Here, the equivalent ratio used was 10:1, and indeed Figure 3 shows the presence of excess and unreacted PCHD−PS in the final SEC curve. It is known[49] that star polymers exhibit SEC elution volumes greater than would be expected for linear polymers of equivalent mass. The arms of $C_{60}(PS-PCHD)_6(1)$ were indicated to have $M_n = 76\ 700$ g mol^{-1}, but the mass of the resulting polymer was indicated as 213 000 g mol^{-1}. The discrepancy between the apparent and expected mass ($6 \times 76\ 700 + 720 = 460\ 920$ g mol^{-1}) is considerable. It may be explained by the known steric effect of star polymers with respect to linear standards. The copolymer arms of $C_{60}(PS-PCHD)_6(2)$ were indicated to have a mass of around 3010 g mol^{-1}, and therefore, the star copolymer was expected to have a mass around $720 + 6 \times 3010 = 18\ 780$ g mol^{-1}. The number-average molecular weight indicated, 17330, while lower than the expected value due to steric effects of the star molecule, the use of polystyrene standards, and experimental error, was nevertheless surprisingly close to that expected. That the molecular weight distributions of these polymers were low (Table 1), however, gives more compelling evidence that a monopopulation of star polymers was formed. It is evident that the structure of these star copolymers should be more fully examined, and it is intended that a future paper will discuss their characterization using neutron scattering.[50]

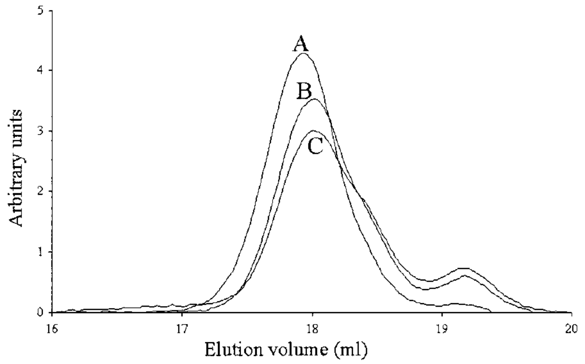


Figure 4. Degradation of $C_{60}PS_6$ against time, using SEC (UV, 320 nm): (A) after 0 min; (B) after 360 min; (C) after 1440 min.

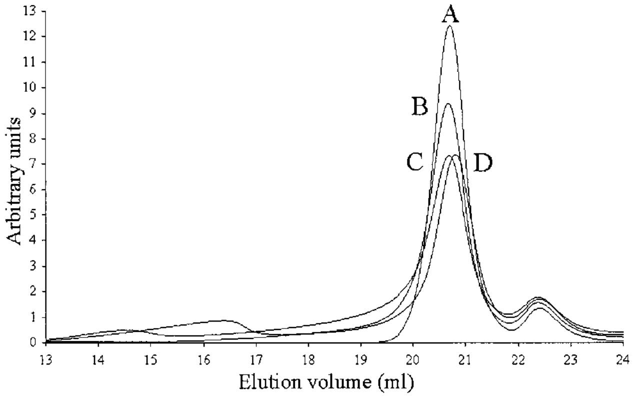


Figure 5. Variation in elution volumes against time for dehydrogenation of $C_{60}(PS-PCHD)_6(2)$ using SEC (RI): (A) after 0 min; (B) after 50 min; (C) after 200 min; (D) after 420 min.

Preparation of $C_{60}(PS-PPP)_6$. An attempt was made to dehydrogenate $C_{60}(PS-PCHD)_6(1)$ in DCB at 130 °C using TCBQ, under conditions similar to those described for the dehydrogenation of PCHD−PS−PCHD.[25] However, there was a near complete degradation of $C_{60}(PS-PCHD)_6(1)$ yielding increasing amounts of aggregates, at high molecular weights, and PCHD−PS "arms" . It is most probable therefore that during this process, dehydrogenated "arms" detached from C_{60} cores.

To further understand the process of degradation, a mixture of $C_{60}PS_6(2)$ and linear PS, the latter equivalent to the molecule weights of the arms of $C_{60}PS_6(2)$, was submitted to continuous heating in refluxing toluene for 24 h, a temperature 20 °C lower than that used to dehydrogenate $C_{60}(PS-PCHD)_6(1)$. Figure 4 indicates that with time, "arms" detached from C_{60}, in agreement with work recently published.[51] The peak at around 19 mL is probably due to $C_{60}PS_m$ in which m is 1, 2, or 3. It was therefore concluded that a stronger dehydrogenation agent, DDQ,[52,53] should be used in place of TCBQ, thus allowing the reaction be carried out at room temperature. SEC curves shown in Figure 5 indicated that the new reaction conditions did not degrade C_{60}-$(PS-PCHD)_6(2)$, although a slight decrease in elution volume appeared due to aromatization and possible intramolecular crystallization of outer PPP chains in THF. It should also be noted that the SEC indicated the formation of a transient network of high molecular weight aggregates, again due to interactions between

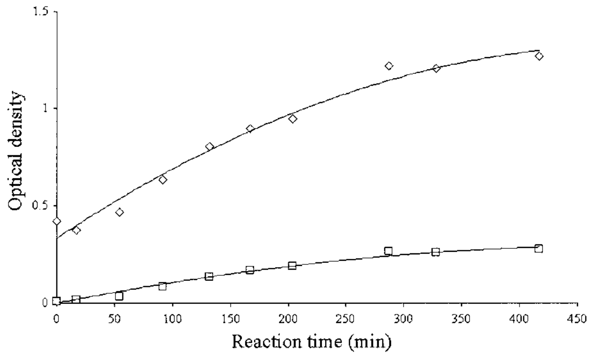


Figure 6. Optical densities of aggregates (◇) and star copolymers (□) during dehydrogenation of $C_{60}(PS-PCHD)_6$ (UV 320 nm).

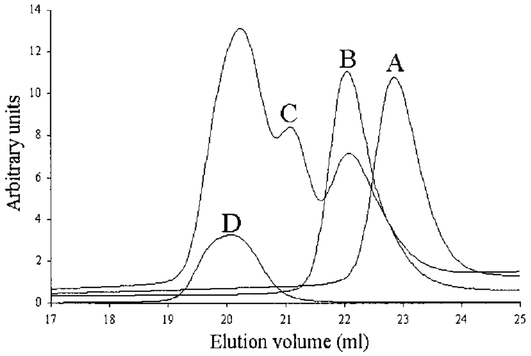


Figure 7. Synthesis of $C_{60}(PCHD-PS)_6$ indicated by SEC curves: (A) PS (RI); (B) PCHD−PS (RI); (C) $C_{60}(PCHD-PS)_6$ (RI); (D) $C_{60}(PCHD-PS)_6(2)$ (UV, 320 nm).

PPP segments.[50] As the dehydrogenation reaction progressed, the relative quantity of aggregates, with lower molecular weights, increased. This was most likely due not to a random dehydrogenation of PCHD but to a stepwise growth of conjugated PPP segments,[14] permitting the formation of more compact aggregates. That, after ca. 350 min of dehydrogenation, the optical density of both aggregates and star copolymers reached a maximum after a steady increase (Figure 6) would tend to support this argument. As to whether the aggregates consisted solely of star copolymers or PPP−PS free "arms" could not be verified by using different SEC detector wavelengths. Both PPP and C_{60} absorb at similar frequencies (and both molecules contain PS). The peak (at around 22.3 mL) due to excess diblock copolymers did not increase, indicating that "arms" were not liberated from star copolymers.

Attempted Synthesis of $C_{60}(PCHD-PS)_6$. C_{60} was coupled with "living" polystyrene-*block*-poly(1,3-cyclohexadienyl)lithium in a manner similar to that previously described for $C_{60}(PS-PCHD)_6$. Table 1 compendiously lists indicated molecular weights. The observed coincidence of RI and UV (320 nm) SEC curves, shown in Figure 7, indicated the formation of star copolymers consisting of PCHD and C_{60}. SEC (RI) also indicated that the M_n of the target copolymer, $C_{60}(PCHD-PS)_6$, was 17 220 g mol^{-1}, lower than that expected (28 140 g mol^{-1}). Again, the same argument may be invoked: the molecular shape of $C_{60}(PCHD-PS)_6$ does not permit comparison against linear PS standards. However, the difference in observed and expected was considerably higher than previously seen for $C_{60}(PS-PCHD)_6$. As a more reliable indicator, the polydispersity of $C_{60}(PCHD-PS)_6$, at 1.8, was considerably higher than those of $C_{60}(PS-PCHD)_6(1)$ and -(2). There are possible reasons for this disparity: first, the $C_{60}(PCHD-PS)_6$ was subject to high and variable degrees of intramolecular crystallization of PCHD segments in the SEC column, but the same phenomenon was not observed for $C_{60}(PS-PCHD)_6$, which was expected to be more susceptible to this process; second, reactions between C_{60} and poly(1,3-cyclohexadienyl)lithium were less favored than those between C_{60} and polystyryllithium. It was observed that the steric bulk and reactivity of carbanions "attacking" C_{60} has an effect on the compositions of resulting star copolymers.[30] While addition of appropriate amounts of PS carbanions to C_{60} can yield $C_{60}PS_6$ copolymers, it is probable that the relatively unstable PCHD carbanions cannot react with C_{60} to such a controlled extent. Indeed, this situation is exacerbated by a reduction in reactivity of C_{60} carbon double bonds with each consecutive grafting of a carbanion.[30] It was most probable that the structure of the star copolymer obtained was $C_{60}(PCHD-PS)_n$ in which n was equal to 4, 5, and 6.

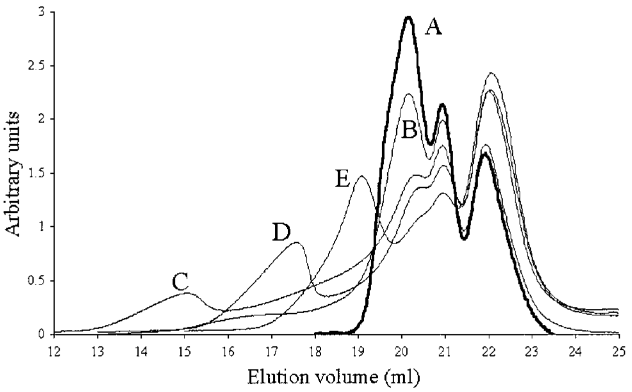


Figure 8. Degradation of $C_{60}(PCHD-PS)_6$ during dehydrogenation characterized by SEC (RI): (A) after 0 min; (B) after 15 min; (C) after 110 min; (D) after 150 min; (E) after 240 min.

Another indicator of the difficulty in reacting poly(1,3-cyclohexadienyl)lithium with C_{60} was shown by the apparition of a second peak in the SEC (RI) characterization of $C_{60}(PCHD-PS)_6$ (Figure 7, curve C) with $M_n \approx 9100$ g mol^{-1}, approximately twice that of the PS−PCHD used. This was also observed by UV (254 nm) and not by UV (320 nm), indicating that the peak was due to a polymer that did not contain C_{60}. It was therefore probably due to PS−PCHD−PCHD−PS. It has been observed that PS carbanions, in the presence of C_{60} and in polar solvents, undergo electron-transfer reactions, forming radicals which may recombine to yield PS−PS.[30,54] In contrast to previous work, in which the transfer of electrons from styryl carbanions was indicated to occur in a polar solvent,[30] the possible transfer of electrons from PCHD carbanions to C_{60} to form PCHD radicals occurred, here, in a nonpolar solvent. This may be indeed be probable as, unlike polystyryl carbanions, carbanions of PCHD readily undergo electron-transfer reactions in nonpolar solvents.[15]

Attempted Preparation of $C_{60}(PPP-PS)_6$. The synthesis of $C_{60}(PPP-PS)_6$ was attempted using DDQ at 25 °C to try to minimize degradation of the precursor star copolymer by thermal affects. The SEC (RI) curves shown in Figure 8 indicated that $C_{60}(PCHD-PS)_n$ degraded during the aromatization reaction. While there was a decrease in the relative amount of star copolymers, there was a concomitant increase in the amount

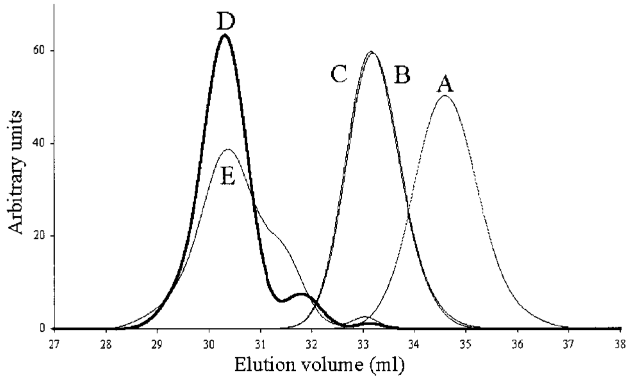


Figure 9. SEC (RI) characterization: (A) PS; (B) PCHD−PS; (C) st−PCHD−PS; (D) C_{60}(st−PCHD−PS)$_6$; (E) C_{60}(st−PPP−PS)$_6$.

of PS−PCHD and, by inference, PS−PPP "arms" . Peaks due to C_{60}(PCHD−PS)$_n$ indicated a steady decrease in molecular weights with time due to the loss of "arms" or, in addition, due to intramolecular crystallization. The aggregates decreased rapidly in size most probably because of the destruction of C_{60}(PPP−PS)$_n$ from which they were formed.

It was concluded that the C_{60}−PCHD bond was considerably weaker than that of C_{60}−PS and that the C_{60}−PCHD and/or C_{60}−PPP bonds were poorly formed and could not withstand dehydrogenation conditions. To permit the formation of a more stable star copolymer containing PPP segments within a protective outer "shell" of PS, a styrene monomer was inserted between the −PCHD−PS "arm" and the C_{60} "core".

Synthesis of C_{60}(st−PCHD−PS)$_6$. Figure 9 indicated that the sequential polymerization of styrene, CHD, styrene, and C_{60} proceeded as expected. While the SEC could not be relied upon to give accurate information concerning molecular weights of the star copolymer obtained, there was corroborative evidence to be drawn by comparing molecular weights. As the M_n of the diblock "arm" indicated was 1420 g mol^{-1}, then C_{60}(st−PCHD−PS)$_6$ was expected to have a mass of $720 + 6 \times 1420 = 9240$ g mol^{-1}, which was of the order of that observed (10 600 g mol^{-1}). That the polydispersity (1.15) was relatively low also indicated that C_{60}(st−PCHD−PS)$_6$ was the major component of the star copolymer formed.

Coinciding peaks, with relatively low surface areas, observed in RI (Figure 9, curve D) and UV (254 nm) curves, indicated the presence of a polymer with $M_n \approx 3100$ g mol^{-1} (ca. twice that of the PS−PCHD "arms"). A comparable peak was not observed in the UV (320 nm) curve, and as was discussed for C_{60}(PCHD−PS)$_6$, the polymer was most probably PS−PCHD−PCHD−PS, formed by the combination of PS−PCHD radicals. As the formation of chain-end radicals of PS in the presence of C_{60} in nonpolar solvents has not been observed, it was inferred that not all "living" 1,3-cyclohexadienyllithium groups were end-capped with styrene. This may be expected considering the low amount of styrene used and the high reactivity of styryllithium to styrene when compared to 1,3-cyclohexadienyllithium.

C_{60}(st−PCHD−PS)$_6$ was characterized by ^{1}H NMR, the result of which is shown in Figure 10. The peaks between ca. 1.0 and 2.5 ppm were due to protons adjacent to unsubstituted carbon atoms of PCHD[41] and backbone carbon atoms of PS. Integration of peaks between ca. 0.5 and 1.0 ppm (due to ^{s}Bu methyl protons), between ca. 5 and 6 ppm (due to olefinic protons on PCHD chains), and from ca. 6.2 to 7.5 ppm (due to phenylic protons on atactic polystyrene) indicated that, for each six methyl protons (assigned 6.0 arbitrary units), there were nine CHD units (18.1 au) and 10 styrene units (51.43 au). These values equated to the presence of PCHD chains of M_n, ca. 720 g mol^{-1}; PS chains of M_n, ca. 1000 g mol^{-1}; and a total theoretical mass for C_{60}(st−PCHD−PS)$_6$ of ca. 11 000 g mol^{-1}. This value corroborated results obtained by SEC, within the limits of experimental error.

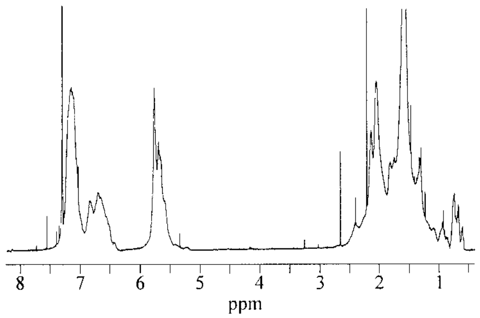


Figure 10. ^{1}H NMR of C_{60}(st−PCHD−PS)$_6$.

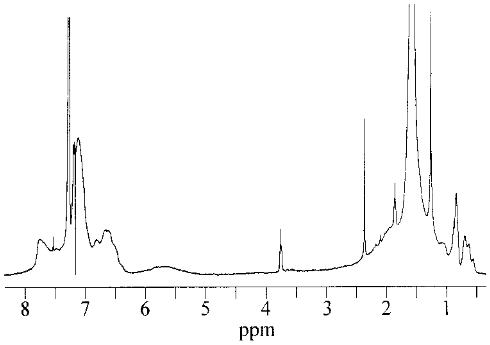


Figure 11. ^{1}H NMR of C_{60}(st−PPP−PS)$_6$ (after 1600 min dehydrogenation). The peak at 3.75 ppm is most likely due an impurity.

Preparation of C_{60}(st−PPP−PS)$_6$. Aromatization of C_{60}(st−PCHD−PS)$_6$ was followed by UV spectroscopy of samples removed after known periods of time. The results, obtained from solutions of concentration 10^{-4} M (UV 320 nm) showed an initial fast increase of the optical density of the solution during the first 600 min. After 1600 min, the optical density of the samples no longer increased. λ_{max}, at 325 nm, indicated the average length of PPP segments to be 8 units, comparable to the values found for triblock copolymers (Table 2), vindicating the use of DDQ rather than TCBQ in forming PPP segments on the star copolymers.

That the SEC curve (E) in Figure 9 of C_{60}(st−PPP−PS)$_6$ approximated to that of C_{60}(st−PCHD−PS)$_6$ indicated that degradation did not occur during dehydrogenation. There was seen however a slight, low molecular weight shoulder to the curve, probably resulting from partial degradation of stars, perhaps due to the loss of "arms" that were bonded to C_{60} via CHD rather than st. It is worth noting that dehydrogenation of C_{60}(st−PCHD−PS)$_6$ did not result in the formation of aggregates to any great extent, and therefore, PS "shells" would seem to have arrested aggregate formation.

C_{60}(st−PPP−PS)$_6$ was characterized by ^{1}H NMR (Figure 11). Integration of peaks at ca. 5 to 6 ppm and between ca. 0.5 to 1.0 ppm indicated that there was approximately 1 CHD group per linear "arm". The ^{1}H

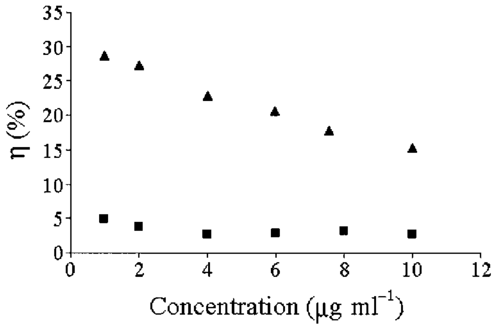


Figure 12. Graph showing variation in η with concentration in THF at 25 °C: $C_{60}(PS-PPP)_6(2)$ at $\lambda_0^{excitation} = 325$ nm (▲) and $C_{60}(st-PPP-PS)_6$ at $\lambda_0^{excitation} = 325$ nm (■).

NMR of $C_{60}(st-PCHD-PS)_6$ indicated there to be nine CHD groups per linear "arm". Therefore, it was deduced that eight out of the nine CHD groups per arm were dehydrogenated. This agreed very well with the results described from UV results (Table 2) in which the λ_{max} accorded to the presence of eight conjugated CHD groups.[48] It could be expected that dehydrogenation of CHD groups nearest the center of the star copolymers would be the most difficult to perform for reasons of steric repulsion, and on an average basis, it is this that is concluded to have occurred. The integral of the peak at ca. 7.7 ppm due to protons on PPP segments, however, did not concur with previous results, and although it may be possible that this peak was due to only a minority of protons on PPP (the others possibly being covered by peaks due to PS), the value obtained was much lower than expected (signifying around two units per chain). This tended to indicate that either the solvent was not fully inserted between chains or that there had been a partial intramolecular crystallization of adjacent PPP arms. A future paper will discuss more fully this problem in the light of neutron scattering results.[50]

Fluorescence Studies of Star, Triblock, and $C_{60}PS_6$ Copolymers. Characterizations of star and triblock copolymers by fluorescence studies were performed using the same temperature, range of concentrations and excitation frequencies accordant to the λ_{max}s of each polymer, thus permitting comparisons to be made between samples.

It was initially observed, as shown in Figure 12, that the quantum yields of the star copolymers $C_{60}(PS-PPP)_6(2)$ and $C_{60}(st-PPP-PS)_6$ were very different, even though the relative amounts of PPP in each star copolymer were of the same order. The value of η resulting from $C_{60}(PS-PPP)_6(2)$ decreased from around 30 to 20% with increasing copolymer concentrations, whereas $C_{60}(st-PPP-PS)_6$ gave rise to a steady curve with η consistently below 5%. With increasing concentrations of $C_{60}(PS-PPP)_6(2)$, the decrease in the value of η may be explained by intercopolymer crystallization of PPP occurring to a greater extent at higher concentrations and limiting fluorescence efficiencies. However, $C_{60}(st-PPP-PS)_6$ was not observed to undergo aggregation, neither under characterization by SEC nor by neutron scattering.[50] The low value of η observed must have therefore have resulted from intracopolymer effects: the results indicated that C_{60} was efficiently quenching the fluorescence of PPP, most likely, by intracopolymer electron transfer. The quenching capabilities of C_{60}, even when substituted by six polymers, are known to remain relatively strong.[55]

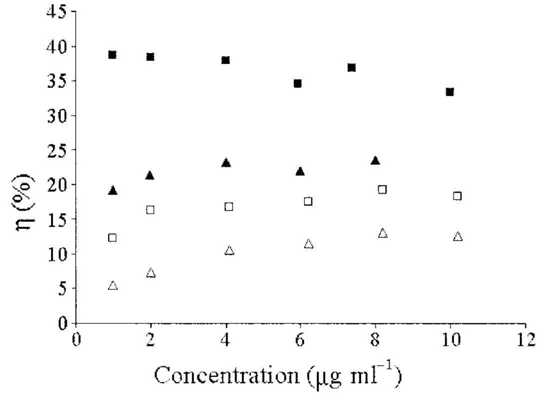


Figure 13. Graph showing variation in η with concentration in THF at 25 °C: PPP−PS−PPP(1) at $\lambda_0^{excitation} = 322$ nm (■), mixture of PPP−PS−PPP(1) and $C_{60}PS_6(1)$ at $\lambda_0^{excitation} = 320$ nm (□), PPP−PS−PPP(2) at $\lambda_0^{excitation} = 331$ nm (▲), and a mixture of PPP−PS−PPP(2) and $C_{60}PS_6(2)$ at $\lambda_0^{excitation} = 330$ nm (△).

It remains possible that intracopolymer crystallization of PPP was occurring within $C_{60}(st-PPP-PS)_6$, reducing the observed fluorescence through thermal relaxation processes. As noted above, the ^1H NMR of $C_{60}(st-PPP-PS)_6$ indicated intramolecular crystallization of PPP "arms" may have occurred. It would be surprising however if intramolecular crystallization of PPP "arms" would not also have occurred for $C_{60}(PS-PPP)_6(2)$, a star copolymer which had PPP segments more available to crystallization than those of $C_{60}(st-PPP-PS)_6$, in which PPP segments are separated by C_{60}. It is apparent though that these star copolymers warrant further attention.

To further characterize the fluorescence of PPP in the presence of C_{60} substituted with 6 PS "arms", additional experiments were performed. First, the fluorescence characteristics of PPP−PS−PPP(1) and PPP−PS−PPP(2) were compared over a similar range of concentrations. They were indicated to contain, respectively, ca. 47% w/w of PPP and 18% w/w of PPP, by TGA. In addition, the fluorescence characteristics of PPP−PS−PPP(1) and PPP−PS−PPP(2), when mixed with $C_{60}PS_6(1)$ and $C_{60}PS_6(2)$, respectively, were studied. In each case, equal concentrations of triblock and star copolymers were mixed.

Figure 13 shows the results of these experiments. PPP−PS−PPP(1) gave rise to the highest values of η, at around 40%. This copolymer contained the highest relative amount of PPP to PS. The value of η descended slightly with increasing concentration, and this may have been due to increasing intermolecular crystallization of PPP chains. In the case of PPP−PS−PPP(2), η remained at around 20%. The result was not untoward, again because of the relative amount of PPP to PS in the copolymer. The value of η increased with increasing concentration, and this indicated that the effects of aggregation observed for PPP−PS−PPP(1) did not occur to such a great extent for PPP−PS−PPP(2). This is quite reasonable when considering the low ratio of PPP to PS in PPP−PS−PPP(2). When $C_{60}PS_6$ samples 1 and 2 were mixed, respectively, with PPP−PS−PPP(1) and -(2), there was a reduction in the fluorescence observed in both solutions. This was due to absorbance of PPP emissions by the $C_{60}PS_6$ molecules—a coincidence of emission and absorbance frequencies was observed, and these results, agreeing with previous work,[55] confirmed that C_{60} retains quenching capabilities even when subject to six grafted polymers. A subsequent point concerns the general increase observed in η, with increasing concentration, for the mixture of PPP−PS−PPP(1), and $C_{60}PS_6$(1) as it was the inverse to that observed for PPP−PS−PPP(1) alone. This indicated that $C_{60}PS_6$ in solution aided dispersion of PPP segments. The presence of $C_{60}PS_6$, withstanding quenching effects, permits higher quantum efficiencies to be obtained from PPP: the tendency of PPP to aggregate and crystallize was reduced by $C_{60}PS_6$.

Conclusion

Star copolymers consisting of C_{60} and monodisperse PPP and PS were prepared using anionic polymerization. Structural control was obtained by varying the order of addition of monomers to the “living” chain ends. However, there were found to be constraints on the structures available: C_{60} was observed to control the limiting number of grafted polymers to six; the relatively slow and unstable polymerization of CHD in a nonpolar solvent, required to prepare PCHD with a high content of 1,4-links, limited the degree of polymerization available; and the substitution of C_{60} by 1,3-cyclohexadienyl anions resulted in copolymers which were either unstable or unable to resist necessary dehydrogenation conditions. The latter restriction was removed by the use of a styrene spacer group between C_{60} and PCHD. The use of a PS “shell” around PPP, themselves spaced about an internal C_{60} core, resulted in materials which consisted of highly conjugated PPP segments yet remained soluble in common organic solvents.

While it is possible that intrastar copolymer crystallization of PPP may have occurred, the separation of PPP segments by C_{60} did result in the formation of highly soluble copolymers. It is evident that further studies of these systems are required to fully determine the nature of interactions between different PPP segments. However, the highly effective quenching of PPP fluorescence emissions in C_{60}(st−PPP−PS)$_6$ was considered indicative of charge transfer from PPP—a known electron “donor”—to C_{60}—a known electron “acceptor”—even across styrene spacer groups.

The photoconductivity indicated to occur in these systems may provide a starting point in the design of photovoltaic devices. However, a combination of C_{60} and PPP will probably require the use of different molecular structures to provide the necessary capabilities of complete electron and hole separation and transfer.

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