PAPER www.rsc.org/njc | New Journal of Chemistry

The synthesis of high-content fullerene functionalised polymers through the controlled addition of an amine-tagged fullerene derivative†

Christopher M. Tollan,* Paul R. Birkett and Norman S. Allen

Received (in Durham, UK) 22nd November 2007, Accepted 13th February 2008
First published as an Advance Article on the web 17th March 2008
DOI: 10.1039/b718078k

A method has been developed for synthesising a series of soluble C_{60} containing polymers which have the characteristic photophysical properties of monosubstituted-fullerene derivatives. The strategy employed required that first a suitably derivatised mono-fulleropyrrolidine was prepared and characterised which was then subsequently reacted with an acryloyl chloride functionalised polymer. The amino group of the fulleropyrrolidine reacts with the acyl chloride functional groups of the polymer forming an amide bond. This approach enabled the preparation of several soluble fullerene/acrylic polymers with a controlled and high covalently bonded fullerene content. The resulting fullerene derivatised methacrylate polymers were characterised by UV, infrared and gel permeation chromatography.

Introduction

With the current concern for global warming there has been a considerable effort made to progress the research area of photovoltaic devices.[1] C_{60} is one of very few molecules capable of accepting more than one electron in the gas phase[2] and cyclic voltammetry experiments have shown the presence of six reversible reduction waves[3] indicating that C_{60} is an ideal electron acceptor moiety for incorporation into flexible organic photovoltaic devices.

If the electron accepting and photophysical properties of C_{60} are to be harnessed within a photo-electronic device it must be combined with a polymer that is capable of transferring electrons to it. The first attempts towards achieving this goal used an approach based on the simple blending of pristine C_{60} with a polymeric semiconductor.[4–6] Unfortunately the poor solubility of C_{60}[7] restricts the amount of fullerene that can be blended with a polymer without the occurrence of phase separation. A more sophisticated approach towards the preparation of homogenous fullerene-containing polymer films has made use of blending C_{60} derivatives with polymers in an attempt to overcome the problem of poor solubility of pure C_{60}. By far the most commonly encountered fullerene derivative being used for this purpose is [6,6]-phenyl-C_{61} butyric acid methyl ester (PCBM) which has been blended with polymers such as conjugated poly[2-methyl,5(3,7-dimethyloctyloxy)]-*p*-phenylene vinylene (MDMO-PPV) and arylene-ethynylene/arylene-vinylene hybrid polymers. This strategy has led to the successful preparation of devices with efficiencies of up to 3%.[8,9]

If the efficiency of a device constructed of a polymeric electron donor and fullerene acceptor is to be enhanced beyond 3% it is imperative that soluble polymers with high C_{60} content be obtained. To achieve this covalent attachment of fullerene to a polymer greatly improves solubility. C_{60} has been covalently bound to many different polymers.[1] The most common technique used is to react pristine C_{60} with a functionalised polymer. For example, azido functionalised polymers when reacted with C_{60} result in the formation of aza[60]fulleroids and aziridino[60]fullerene containing polymers.[10–12] Similarly, polymers appended with aldehyde functional groups have been used to produce fulleropyrrolidine containing polymers.[13–15] It is often overlooked, however, that both of these standard fullerene reactions give low yields (20–30%) and produce poly-addition fullerene products which cannot be removed from the final polymer product.[16] Moreover, it is likely that the efficiency of the final device will be reduced due to the presence of C_{60} poly-adducts in the polymer because of the less favourable physicochemical properties of these C_{60} derivatives.

Another strategy which has been employed to incorporate C_{60} into polymers is to functionalise the fullerene in such a way so as to form a monomer. The fullerene monomer can then be polymerised. Polymerisation of C_{60} monomers has usually been done by condensation,[17–19] although examples of addition polymerisation do exist.[20] The wide ranging reactivity of the remaining double bonds on the C_{60} cage is one potential drawback of this approach as further reaction of these double bonds will result in the loss of the required properties of the mono-fullerene adduct.

In an attempt to overcome the problems highlighted above and in order to obtain soluble polymers with the highest possible fullerene content, the strategy used here involved the formation of a suitably functionalised polymer backbone and a functionalised mono-adduct of C_{60}. Both of these materials were easy to prepare using standard techniques. They can be fully characterised, and in the case of the fullerene derivative can be purified. As it is possible to use commonly available monomers for the formation of the polymer backbone there is scope for using current literature to form various types of polymers and copolymers. The polymer and fullerene

---

Department of Chemistry and Materials, Manchester Metropolitan University, All Saints Building, Manchester, UK M15 6BH.
E-mail: c.tollan@googlemail.com; Tel: 01625 533640

† Electronic supplementary information (ESI) available: Spectroscopic data. See DOI: 10.1039/b718078k

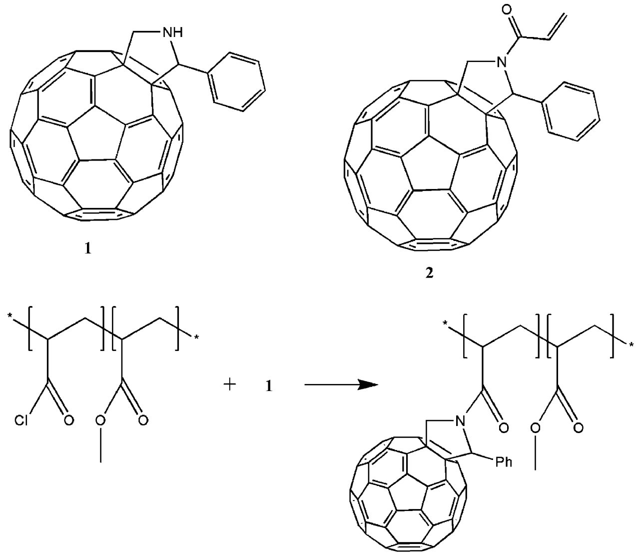

Fig. 1 Diagram of fullerene materials used and a depiction of the reaction scheme used to form the fullerene containing polymers.

adduct were then reacted together to form the target fullerene functionalised polymer (Fig. 1). As shown in this study, by controlling the content of the reactive monomer units in the copolymer it is possible to prepare fullerene-containing polymers with different fullerene contents after reaction of the polymer with the fullerene derivative.

The functionalised polymers used in this study was a series of acryloyl chloride/methyl methacrylate copolymers (Table 1) prepared by free radical polymerization.[21] This polymer was used as the acyl chloride groups were found to be reactive enough to form an amide bond with the amine group on the fullerene derivative in good yield and yet not so reactive that it began to interfere with the fullerene cage. The fullerene adduct used was 2-phenyl fulleropyrrolidine (**1**). The amine group present in the pyrrolidine ring of **1** provides a reactive site for covalent attachment to the polymer after reaction with the acyl chloride group to form an amide functional group on the polymer backbone. A similar reaction was performed between acryloyl chloride and **1** to illustrate the efficacy of the method.

Results and discussion

2-Phenyl fulleropyrrolidine (**1**) was prepared using the standard azomethine cycloaddition route and was obtained in reasonable yield (Fig. 1). The sample obtained was identical in all respects with the published data for **1**.[22]

The acrylic fulleropyrrolidine monomer, **2** (Fig. 1) was synthesis as a model compound for comparison with the fullerene containing polymers. Compound **2** was prepared by the simple reaction of compound **1** with acryloyl chloride and was obtained with a yield of 86% as a brown solid. The UV/Vis spectrum of **2** contained three main UV absorption signals at 207, 254 and 268 nm, respectively, which are signals typical of C_{60} containing materials in which the fullerene cage chromophore is more or less intact. In addition, the lower intensity signal present at 428 nm is known to be characteristic of 6,6-closed fullerene monoadducts and is generally used to confirm that a fullerene mono-adduct has been obtained.[23] A strong signal at 1649 cm^{-1} in the infrared spectrum provided evidence for the presence of the acrylic carbonyl group and the signal observed at 1618 cm^{-1} in the infrared spectrum was assigned to the C=C stretching signal of the acrylic double bond. Moreover, the signal associated with the NH functional group of the starting material **1** at 3328 cm^{-1} was no longer present. The presence of a strong signal at 526 cm^{-1} and several small signals clustered around 580 cm^{-1}, instead of the single signal at 577 cm^{-1} associated with pristine C_{60}, in the infrared spectrum was used to provide further evidence a fullerene monoadduct was obtained.

The ^1H NMR spectrum of the aliphatic protons of compound **2**, present in the pyrrolidine ring show that there is asymmetry within the structure, producing a doublet of doublets due to the positions of the protons over the fullerene cage and the different influences due to the asymmetry of the pyrrolidine ring. The proton at position 2 on the pyrrolidine ring produces a singlet as expected at 6.19 ppm. By contrast, the proton signals due to the methylene group of the pyrrolidine ring are observed as two doublets at 5.71 and 5.89 ppm due to their different chemical environments. The usual monosubstituted aromatic ring signal pattern of two doublets and one triplet corresponding to the five aromatic protons between 7 and 8 ppm was observed. The alkene protons produce two quartets with δ values above 6 ppm in the ^1H NMR spectrum, which is typical for protons in an α,β-unsaturated carbonyl groups.

There are 71 carbon signals in the ^{13}C NMR spectrum as expected for this asymmetric molecule. There are six carbon signals in the ^{13}C NMR spectrum between 128.14 and 129.32 ppm corresponding to the aromatic ring and two carbon signals at 129.93 and 135.14 ppm providing evidence for the

Table 1 Major assignments in the UV and infrared spectra for polymers P1–P4

Polymer Co-monomer ratio	P1 1 : 9	P2 1 : 7	P3 1 : 5	P4 1 : 3
FT-IR (KBr disk), ν/cm^{-1}	2949: C–H stretch aliphatic 1731: C=O stretch acrylate 1149: C–O def. acrylate 527: fullerene monoadduct	2948: C–H stretch aliphatic 1731: C=O stretch acrylate 1148: C–O def. acrylate 526: fullerene monoadduct	2950: C–H stretch aliphatic 1731: C=O stretch acrylate 1148: C–O def. acrylate 527: fullerene monoadduct	2945: C–H stretch aliphatic 1727: C=O stretch acrylate 1143: C–O def. acrylate 526: fullerene monoadduct
UV (hexane), λ_{max}/nm	203 256 327 416 sh	208 257 324 420 sh	211 256 325 421 sh	Insoluble

alkene group. Four signals are found in the sp^3 region of the ^{13}C NMR spectrum and correspond to the carbons of the pyrrolidine ring. All of the remaining signals are in the sp^2 region. One signal is at 164.25 ppm and is due to the carbonyl carbon of the acrylic group. The remaining 58 sp^2 C signals are due to the fullerene cage carbon atoms. The FAB mass spectrum provided further evidence for the formation of **2** as an ion with a mass of 894.3 u was observed. This corresponds well with the molecular mass calculated for the molecular ($M^+ + 1$) ion of the fulleropyrrolidine in question and when taken with the rest of the above evidence demonstrates that the amine group of a fulleropyrrolidine can easily form an amide bond with an acyl chloride.

In order to prepare polymers with different fullerene loadings the amount of acryloyl chloride was varied in the four copolymers prepared. Polymer P1 was formed from a copolymer with the lowest amount of acryloyl chloride groups with an increasing amount of this reactive monomer up to polymer P4 which contained the most and subsequently had the highest incorporation of fullerene. The series of polymers was produced in order to investigate the match between the theoretical amount of fullerene that could be incorporated based on the initial feed ratio of acryloyl chloride/MMA and that which was actually obtained based on TGA results. The reaction between the acyl chloride functionalised polymers and the fullerene adduct (Fig. 1) gave dark red/brown solutions in all cases. There was no evidence of any precipitation indicating reduced solubility of the new fullerene-containing polymers at this stage. Addition of light petroleum (bp 40–60 °C) produced a brown precipitate that, after this purification procedure, had reduced solubility in common organic solvents such as hexane, chloroform and toluene as compared to model compound **2**. This phenomenon has been reported previously in the literature, and in one case the polymers obtained were completely insoluble after the removal of solvent.[24,25] Thin layer chromatography showed the presence of a small amount of starting material as well as the polymer product. The starting material was removed by repeated washing with toluene. After isolation, polymer P4 was insoluble in all solvents except a chlorobenzene–1,4-dioxane (1 : 1) mixture in which it was only slightly soluble. All of the remaining polymers prepared as part of this study were sparingly soluble in hexane and toluene, but had much improved solubility in dichloromethane and chloroform.

The infrared spectrum (Table 1) of the polymers prepared all show a strong signal around 2950 cm^{-1} arising from the C–H stretching vibrations of the aliphatic portions of the molecule. The strength of the aliphatic signal due to the acrylic polymer backbone masks the aromatic signal C–H stretch signal of the phenyl group on the pyrrolidine ring. The signal at around 1730 cm^{-1} is due to the carbonyl bond stretching vibrations of the acrylate and amide groups. The acrylate carbonyl group also gives a signal at 1140 cm^{-1} due to the C–O bond of the ester. The signal due to the fullerene cage and known to be indicative of fullerene monoadducts is present at 526 cm^{-1} in all four of the polymers synthesised. This observation helps to confirm that the C_{60} cage has not undergone any further reactions and that the polymer is appended with fulleropyrrolidine mono-adducts. No N–H signals were present in the infrared spectra of the fullerene polymers indicating that the amine group of the fulleropyrrolidine stating material **1** has formed an amide bond with the acyl chloride groups of the starting polymer.

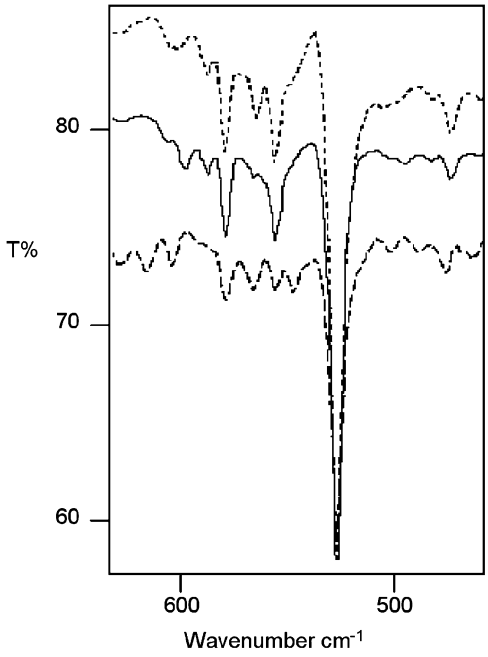

Fig. 2 Infrared spectra of the region between 650 and 450 cm^{-1} for compounds **1** (dashed line) and **2** (solid line) compared with polymer P4 (doted line).

In order to demonstrate that the fullerene cage π bonds do not react under the conditions required to link the fulleropyrrolidine **1** and acyl chloride funtionalised polymer, **1** was also reacted with acryloyl chloride under identical conditions. The product of this reaction (compound **2**) has been characterised above and was obtained smoothly and in high yield thus providing strong evidence that an acyl chloride functionalised polymer should not interfere with the π bonds of the C_{60} cage either. Comparison of the 526 cm^{-1} region of the infrared spectra, associated with fullerene cage vibrations, of model compound **2** and the fullerene-containing polymers formed here are identical. They do, however, differ from the fulleropyrrolidine starting material **1** and therefore provide further strong evidence that the same chemical bond is present between the fullerene and polymer backbone as is found in compound **2** (Fig. 2).

Analysis of the UV spectra (Table 1) of each of the polymers confirms that the fullerene moiety is present due to the three peaks at around 205, 255, and 325 nm which are characteristic of the fullerene group. The standard polymer without the fullerene does not have these three signals present. The shoulder at around 420 nm present in all of the fullerene-containing polymers is characteristic of the presence of mono-C_{60} adducts only.[23] It is noted that a UV spectrum of polymer P4 could not be obtained as it was not sufficiently soluble in appropriate solvents.

The amount of fullerene present in the polymers was in the range of 33 to 44% by weight as determined by TGA. This is a surprising result given that the polymers formed here are also soluble to an extent and fully dissolved in the reaction mixture before isolation. The fullerene content of these polymers also compares well with those found in the literature. There are only two examples of covalent fullerene containing polymers in the literature with higher fullerene content values by weight than the 44% achieved here. In one report a polymer containing 57% C_{60} by weight was obtained.[24] However this was done by direct azide addition to the fullerene surface which as mentioned previously leads to polyaddition to the fullerene surface as well as the desired monoaddition. In a separate study the fullerene content of the polymer formed was found to be 73%. This was done by radical polymerisation which leads to tightly packed and insoluble fullerene clusters with a large amount of branching due to polyaddition on the fullerene surface.[26] In both these cases the polymers were either poorly soluble or insoluble.

The number averaged molecular weight (M_n) of the fullerene containing polymers obtained was in the region of 25 000 to 50 000 and the weight averaged molecular weight (M_w) was in the region of 100 000 to 200 000. These values are similar to those reported in the literature for fullerene acrylic polymers formed by the reaction of an azide with pristine fullerene.[10,11] The polydispersities of the polymers obtained here are around 3.8 (Table 2). These values are similar to those found in the literature for equivalent fullerene containing polymers. Values of 2.1 to 5.2 have been reported.[11,27]

The relative similarity between values for C_{60} wt% (theoretical—based on feed ratio) and C_{60} wt% (TGA) is high. Up to 85% of the initial weight of the fullerene group present in the starting material (compound **1**) has been incorporated into the polymers compared to the highest literature values found (up to 80%[10]). This indicates that a facile reaction has taken place between the amine group of the fullerene and the acyl chloride polymer. The value of 85% was obtained by dividing the theoretical maximum possible amount of fullerene incorporated by the actual amount of fullerene incorporated (based on TGA results). The maximum amount of fullerene that could be incorporated into the polymer is based on complete reaction of all acyl chloride groups with the fulleropyrrolidine starting material and assuming 100% of the feed ratio of acryloyl chloride was incorporated into the polymer (a value of less than 100% here would only result in an increase in the value of 85% incorporation of fullerene). It was necessary to base this value on the feed ratio as the reactive acyl chloride polymer rapidly oxidises on exposure to air and so the actual value of acryloyl chloride groups present in the polymer could not be obtained. This high figure of 85% incorporation of fullerene into the polymer is not a surprising result as the formation of model compound **2** is known to occur with a high yield (86%) and with few by-products being formed as opposed to the large number of by-products formed when using the standard techniques of direct azide or aldehyde and amino acid addition to pristine fullerene.

Table 2 Quantities used and obtained from the synthesis of polymers P1–P4 along with GPC and TGA characterisation data

Polymer	P1	P2	P3	P4
Mass of AC used/g	0.0129	0.0134	0.0128	0.0195
Mass of MMA used/g	0.128	0.100	0.072	0.083
Comonomer ratio (calc. from feed)	1 : 9.0	1 : 6.8	1 : 5.1	1 : 3.8
Mass of initiator used/mg	2.9	2.2	1.6	1.8
Mass of fulleropyrrolidine/g	0.116	0.124	0.113	0.193
Mass of polymer obtained/g	0.21	0.17	0.14	0.19
C_{60} wt% (Theoretical)	39	44	49	54
C_{60} wt% (TGA)	33	34	40	44
M_n/g mol^{-1}	27 854	52 523	25 620	Insoluble
M_w/g mol^{-1}	108 956	200 872	96 651	Insoluble
Polydispersity (M_w/M_n)	3.91	3.82	3.77	Insoluble

Experimental

Materials

Unless otherwise stated in the methods all chemicals were used as received. Chlorobenzene 99%, benzaldehyde 99 + %, and 1,4-dioxane 99% were purchased from Alpha Aesar. C_{60} 99 + % was purchased from Moscow State University. Benzoyl peroxide (with 25% H_2O) was purchased from Merck-Schuchardt. Glycine 99% was purchased from Lancaster Synthesis. Methyl methacrylate 99% and acryloyl chloride 96% were purchased from Aldrich chemicals. Pyridine 99 + % was purchased from BDH. All other solvents were purchased from BDH (general purpose reagents).

Instrumentation

^{1}H and ^{13}C NMR spectra were recorded on a Jeol GSX/Delta 270 MHz Fourier transform spectrometer. FAB + (Fast atom bombardment) mass spectra were obtained on a Finnigan MAT 900 XLT, using 2,5-dihydroxybenzoic acid as matrix. UV-Vis absorption spectra were obtained using a Perkin-Elmer Lambda 40 spectrophotometer. Infrared spectra were recorded on a Nicolet Nexus Fourier transform infrared spectrometer. Fluorescence spectra were recorded on a Perkin Elmer LS55 luminescence spectrometer. Thermogravimetric analysis was carried out on a Netzsche Thermische Analyse TG 209 cell. Gel Permeation Chromatography analysis was carried out at Repsol YPF, Spain. Reactions were monitored by thin-layer chromatography using Merck precoated silica gel (0.25-mm thickness) plates. Flash column chromatography was performed employing silica gel (BDH). Reaction yields were not optimized and refer to pure, isolated products.

Methods

2-Phenyl fulleropyrrolidine 1. The methods used for the synthesis of **1** have been reported previously.[22] (1.20 g, 31%); λ_{max} (hexane)/nm, 213, 255, 309, 323, 429 (6,6 closed); ν_{max} (KBr disk)/cm^{-1}, 3328 (N–H), 3026 (C–H), 2920 (C–H), 526 (fullerene monoadduct); δ_H (270 MHz; $CDCl_3$; Me_4Si) 4.99 (1H, d, H of CH_2), 5.12 (1H, d, H of CH_2), 5.81 (1H, s, H of CHPh on pyrrolidine ring), 7.36 (1H, d, *p*-H phenyl), 7.45 (2H, t, 2 × *m*-H phenyl), 7.80 (2H, d, 2 × *o*-H phenyl), N–H hydrogen not observed; δ_C (68 MHz; CS_2–D_3CCOCD_3 (10 : 1); Me_4Si) 62.31, 73.16, 77.81, 78.27, 128.67 (2C), 128.85, 129.16 (2C), 130.90, 136.34, 136.67, 137.17, 138.31 (2C), 139.97, 140.36, 140.58, 140.62, 141.95, 142.13, 142.28, 142.41, 142.43, 142.44, 142.54, 142.56, 142.63, 142.77 (2C), 142.98, 143.02 (2C), 143.09, 143.13, 143.44, 143.53, 143.57, 144.73, 144.76, 144.96, 144.98, 145.01, 145.06, 145.33, 145.55, 145.61 (2C), 145.64, 145.69, 145.73 (2C), 145.76, 145.84, 145.93, 146.15, 146.31, 146.42, 146.48, 146.52, 146.59, 146.61 (2C), 146.68, 146.67, 146.77, 147.31, 147.49; FAB-MS: *m*/*z* 839 (M^+).

Synthesis of *N*-acrylic 2-phenyl fulleropyrrolidine 2. 2-Phenyl fulleropyrrolidine (1.10 g, 0.0013 mol) was dissolved in dry chloroform (400 cm^3) and allowed to cool in an ice bath. Pyridine (0.20 g, 0.0026 mol) was added to the foregoing solution of **1** in chloroform. Freshly distilled acryloyl chloride (0.13 g, 0.0014 mol) was dissolved in dry, distilled chloroform (50 cm^3) and also allowed to cool in an ice-bath. Once cool the acryloyl chloride solution was added slowly to the cold fulleropyrrolidine solution and the temperature maintained at 0 °C. The reaction mixture was then stirred for 6 h in an ice-bath and allowed to stand at 3 °C overnight. The solution was then washed with iced water (50 cm^3), dilute HCl (3 × 50 cm^3), and water (3 × 50 cm^3). After drying the organic fraction over $MgSO_4$ the solution was concentrated by rotary film evaporation and purified by chromatography (SiO_2; chloroform). The brown fraction containing the product was concentrated by rotary film evaporation to a small volume (30 cm^3). Precipitation of the product from the concentrated solution was achieved by addition of light petroleum (bp 40–60 °C). The resultant dark brown solid was collected by filtration/decanting the solvent and dried under vacuum/air/oven giving *N*-acrylic 2-phenyl fulleropyrrolidine (1.00 g, 86%); λ_{max} (hexane)/nm, 428 (6,6 closed), 268, 254, 207; ν_{max} (KBr disk)/cm^{-1}, 3058 (C–H), 2921 (C–H), 1649 (C=O), 1618 (C=C), 526 (fullerene monoadduct); δ_H (270 MHz; $CDCl_3$; Me_4Si), 5.71 (1H, d, H of CH_2 on pyrrolidine ring), 5.89 (1H, d, H of CH_2 on pyrrolidine ring), 6.19 (1H, s, H of CHPh on pyrrolidine ring), 6.63 (2H, q, terminal alkene H′s), 6.82 (1H, q, alkene H adjacent to carbonyl), 7.42 (1H, d, *p*-H phenyl), 7.52 (2H, t, 2×*m*-H phenyl), 7.81 (2H, d, 2×*o*-H phenyl); δ_C (68 MHz; CS_2–D_3CCOCD_3 (10 : 1); Me_4Si) 59.99, 69.47, 72.28, 76.16, 128.14, 128.75 (2C), 129.02 (2C), 129.32, 129.93, 135.14, 135.88, 136.62, 137.48, 140.21, 140.69, 140.75, 140.85, 140.99 (2C), 142.32, 142.34, 142.48, 142.50, 142,55, 142.57, 142.61 (2C), 142.62, 142.72, 142.78, 142.86, 143.01, 142.20 (2C), 143.25, 143.62, 143.73, 144.18, 144.90, 145.03, 145.12, 145.19, 145.25, 145.75, 145.83 (2C), 145.85 (2C), 145.98, 146.03, 146.10, 146.19, 146.28, 146.48, 146.53, 146.61 (2C), 146.68, 146.77, 146.84, 146.87 (2C), 147.93, 148.00, 152.99, 154.37, 155.22, 156.60, 164.25; FAB-MS: *m*/*z* 894.3 (M^+ + H).

Acryloyl chloride/methyl methacrylate copolymers. The synthesis of a series of acryloyl chloride/methyl methacrylate copolymers (Table 1) was carried out using methods published previously.[21] The content of the polymerisation tubes was used for further reaction without characterisation due to the unstable nature of the acyl chloride groups in air.

***N*-Acrylic 2-phenyl fulleropyrrolidine/methyl methacrylate polymers.** A series (copolymers P1, P2, P3 and P4, Table 1) of fullerene containing acrylic copolymers was synthesised here. The method below used for the synthesis of copolymer P4 is given as an example.

2-Phenyl fulleropyrrolidine (0.19 g, 0.23 mmol) was dissolved in dry chlorobenzene–1,4-dioxane 1 : 1 (200 cm^3) and pyridine (0.039 g, 0.49 mmol) was added. The solution was then purged under nitrogen and cooled to 0 °C. The polymerisation tube prepared above was cooled to 0 °C and then broken directly into the fulleropyrrolidine solution while under nitrogen at 0 °C. The solution was kept at −4 °C overnight with stirring. It was then allowed to warm slowly to 15 °C and left standing for two days. The solution was washed with dilute HCl (3 × 30 cm^3), water (3 × 30 cm^3), and dried over magnesium sulfate. The solvent was removed by rotary film evaporation to a small volume (30 ml) and light petroleum (bp 40–60 °C) was added until precipitation of the polymer was complete. The solid was collected by decanting the solvent which was then washed with toluene.

Conclusions

An acrylic fulleropyrrolidine polymer was formed by the reaction of a well characterised mono-adduct of C_{60} with a functionalised polymer backbone. Infrared spectroscopy contained identical signals which are assigned to the fullerene cage signals observed around 526 cm^{-1} for the polymers and the novel and structurally similar fulleropyrrolidine model compound. This indicates that the amine of the fulleropyrrolidine had reacted with the acyl chloride functionalised polymer backbone. The highest fullerene content obtained for the polymers synthesised was found to be 44% by TGA and compares well with other values reported in the literature. The comparison of the theoretical expected fullerene content against the actual content gave a value of 85%. This is a higher value than those previously reported for reactions where a fullerene moiety is reacted with a pre-formed polymer demonstrating a pertinent method for covalent incorporation of C_{60} into such a polymer. There is also potential in this synthetic strategy for characterisation of the polymer backbone before reaction with the fullerene adduct. The use of a characterised fullerene adduct, a well-defined polymer backbone, and a relatively clean reaction should give greater confidence in the structural integrity of the resulting fullerene polymer and lead to the formation of fullerene-containing polymers with optimised properties.

Acknowledgements

We thank the EPSRC National Mass Spectrometry Service Centre of Swansea University, UK for providing FAB mass spectra. Also thanks goes to Valentine Ruiz of Repsol YPF, Spain for providing GPC data for the polymers synthesised.

References

1. F. Giacalone and N. Martin, *Chem. Rev.*, 2006, **106**, 5136.
2. R. F. Curl and R. E. Smalley, *Science*, 1988, **242**, 1017.
3. Q. Xie, E. Perez-Cordero and L. Echegoyen, *J. Am. Chem. Soc.*, 1992, **114**, 3978.
4. N. S. Sariciftci, L. Smilowitz, A. J. Heeger and F. Wudl, *Science*, 1992, **258**, 1474.
5. C. J. Brabec, V. Dyakonov, N. S. Sariciftci and W. Graupner, *J. Chem. Phys.*, 1998, **109**, 1185.
6. L. Smilowitz, N. S. Sariciftci, R. Wu, C. Gettinger, A. J. Heeger and F. Wudl, *Phys. Rev. B*, 1993, **47**, 13835.
7. R. S. Ruoff, D. S. Tse and R. Malhotra, *J. Phys. Chem.*, 1993, **97**, 3379.

8. H. Hoppe, D. A. M. Egbe and D. Muhlbacher, *J. Mater. Chem.*, 2004, **14**, 3462.
9. S. E. Shaheen, C. J. Brabec and N. S. Sariciftci, *Appl. Phys. Lett.*, 2001, **78**, 841.
10. C. J. Hawker, *Macromolecules*, 1994, **27**, 4836.
11. H. W. Goh, S. H. Goh and G. Q. Xu, *J. Polym. Sci. Part A: Polym. Chem.*, 2002, **40**, 1157.
12. S. Xiao, S. Wang, H. Fang, Y. Li, Z. Shi, C. Du and D. Zhu, *Macromol. Rapid Commun.*, 2001, **22**, 1313.
13. F. Zhang, M. Svensson, M. R. Andersson, M. Maggini, S. Bucella, E. Menna and O. Inganas, *Adv. Mater.*, 2001, **13**, 1871.
14. Y. Obara, K. Takimiya, Y. Aso and T. Otsubo, *Tetrahedron Lett.*, 2001, **47**, 6877.
15. J. Ikemoto, K. Takimiya, Y. Aso, T. Otsubo, M. Fujitsuka and O. Ito, *Org. Lett.*, 2002, **4**, 309.
16. E. Nakamura, H. Isobe, H. Tokuyama and M. Sawamura, *Chem. Commun.*, 1996, 1747.
17. S. Shi, K. C. Khemani, Q. Li and F. Wuld, *J. Am. Chem. Soc.*, 1992, **114**, 10656.
18. T. Benincori, E. Brenna, F. Sannicolo, L. Trimarco, G. Zotti and P. Sozzani, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 648.
19. F. Lu, S. Xiao, Y. Li, H. Liu, H. Li, J. Zhuang, Y. Liu, N. Wang, X. He, X. Li, L. Gan and D. Zhu, *Macromolecules*, 2004, **37**, 7444.
20. X. Zhang, A. B. Sieval, J. C. Hummelen and B. Hessen, *Chem. Commun.*, 2005, 1616.
21. M. Stolbova, N. E. Hudson, R. A. Pethrick, D. C. Sherrington and A. Slark, *J. Macromol. Sci. Phys.*, 2005, **44**, 941.
22. D. G. Zheng, C. W. Li and Y. L. Li, *Synth. Commun.*, 1998, **28**, 2007.
23. D. Guldi, H. Hungerbuhler, I. Carmichael, K. Asmus and M. Maggini, *J. Phys. Chem. A*, 2000, **104**, 8601.
24. M. H. van der Veen, B. Boer, U. Stalmach, K. I. van de Wetering and G. Hadziioannou, *Macromolecules*, 2004, **37**, 3673.
25. D. Taton, S. Angot and Y. Gnanou, *Macromolecules*, 1998, **31**, 6030.
26. W. T. Ford, T. Nishioka and S. C. McCleskey, *Macromolecules*, 2000, **33**, 2413.
27. N. Zhang, S. R. Schricker and F. Wudl, *Chem. Mater.*, 1995, **7**, 441.