Pergamon

Tetrahedron Letters 44 (2003) 4487–4490

TETRAHEDRON
LETTERS

Synthesis of copolymers alternating oligophenylenevinylene subunits and fullerene moieties

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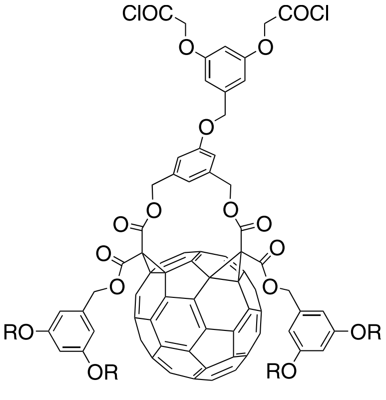
Received 14 April 2003; revised 17 April 2003; accepted 17 April 2003

Abstract—Linear polymers alternating oligophenylenevinylene (OPV) moieties and C_{60} subunits have been prepared in good yields by polycondensation of a bifunctional fullerene derivative with an OPV monomer bearing two alcohol functions. These polymers have been characterized by NMR, UV/vis and their molecular weights determined by size-exclusion chromatography coupled with light scattering. © 2003 Elsevier Science Ltd. All rights reserved.

Compounds combining C_{60} with extended π-conjugated oligomers have received increasing attention in the past few years as these systems can be used for solar energy conversion.[1–3] In particular, it has been shown that the behavior of such hybrid molecules in plastic solar cells allows structure/activity relationships to be obtained for a better understanding of the photovoltaic system.[2] However, for a commercial use, the efficiency of the organic photodiodes has to be improved dramatically and new active compounds with a stronger absorption in the visible range and a better stability towards light are needed. Another important development of this research appears to be the design of new fullerene derivatives easy to process.[1] In this respect, compounds combining the structural characteristics of polymers such as elasticity and film-forming capability with the electronic properties of C_{60}-donor systems are of particular interest.[4] However, the synthesis of structurally well-defined fullerene-containing polymers is difficult owing to the multifunctional character of C_{60} and its chemical reactivity typical of an electron deficient olefin. Actually, radical and anionic polymerizations of fullerenes lead to star-shaped polymers with low fullerene content and/or to non-processible cross-linked polymers.[5] In a recent paper, we have shown that fullerene-containing polymers of high molecular weights can be prepared in good yields by polycondensation of the bifunctional fullerene derivative **1** (Fig. 1) with tetraethyleneglycol.[6] In this paper, we now report polymerization reactions of the fullerene-functionalized diacyl chloride **1** with an oligophenylenevinylene (OPV) monomer bearing two alcohol functions. The resulting linear copolymers alternating OPV moieties and C_{60} subunits represent a new class of macromolecular donor–acceptor systems with potential for photovoltaic applications.

The synthesis of the OPV derivative bearing two alcohol functions is depicted in Schemes 1 and 2. The strategy employed for its preparation is based upon Heck[7] type chemistry. To this end, the key building block **5** was prepared first (Scheme 1). Treatment of tetraethyleneglycol (**2**) with 1 equiv. of *t*-butyldimethylsilyl chloride (TBDMSCl) afforded the mono-protected derivative **3**, which after reaction with tosyl chloride (TsCl) in the presence of pyridine and



1 R = $C_{12}H_{25}$

Figure 1. Bifunctional fullerene derivative **1**.

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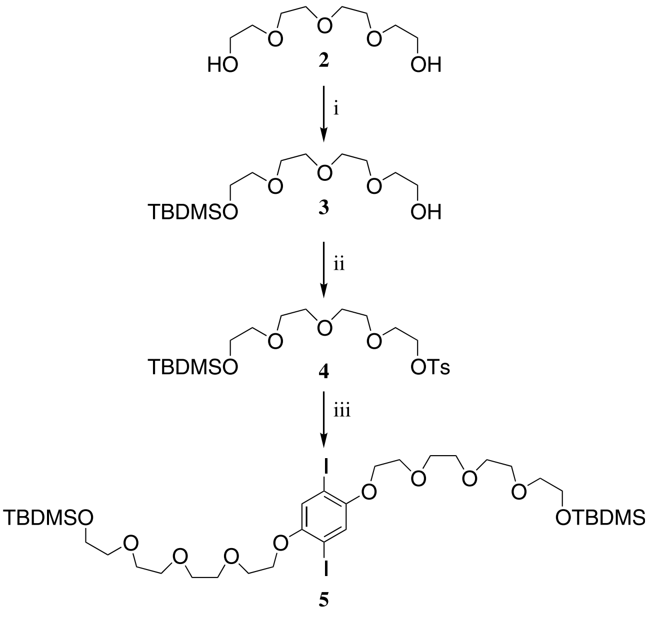
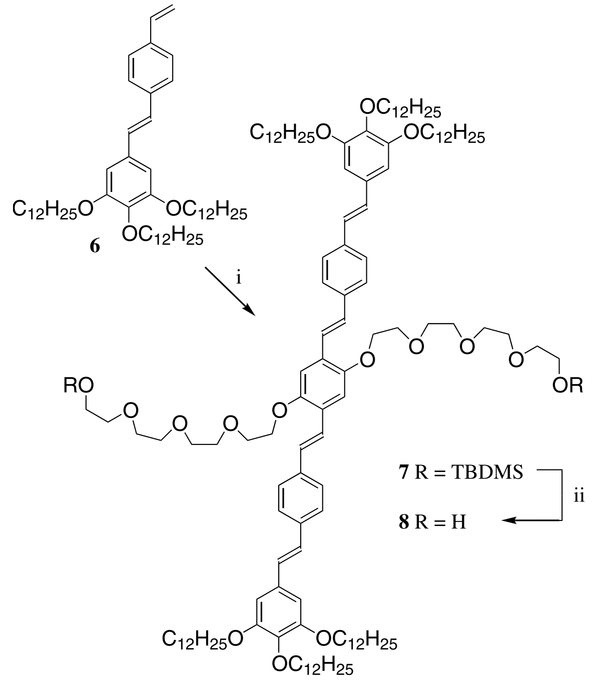
doi:10.1016/S0040-4039(03)00991-2



Scheme 1. *Reagents and conditions*: (i) TBDMSCl (1 equiv.), imidazole, THF, 0°C (48%); (ii) TsCl, pyridine, DMAP, CH_2Cl_2, 0°C (60%); (iii) 2,5-diiodohydroquinone, K_2CO_3, DMF, 80°C (76%).



Scheme 2. *Reagents and conditions*: (i) **5**, $Pd(OAc)_2$, POT, Et_3N, xylene, 80°C (61%), (ii) TBAF, THF, 0°C (90%).

4-dimethylaminopyridine (DMAP) yielded **4**. Subsequent treatment with 2,5-diiodohydroquinone[8] in DMF at 80°C in the presence of K_2CO_3 gave the alkylation product **5** in 76% yield.

Reaction of **5** with styrene **6**[9] (2 equiv.) in Et_3N/xylene in the presence of tri-*o*-tolylphosphine (POT) and a catalytic amount of $Pd(OAc)_2$ afforded the protected monomer **7** in 61% yield (Scheme 2). Finally, treatment with tetra-*n*-butylammonium fluoride (TBAF) in THF gave monomer **8** in 90% yield. The structure and purity of all new compounds were confirmed by ^1H and ^{13}C NMR spectroscopy and elemental analysis. In particular, coupling constants of ca. 17 Hz for the two sets of AB systems corresponding to the vinylic protons in the ^1H NMR spectra of the OPV derivatives **7** and **8** confirmed their all-*E* stereochemistry.

The fullerene-OPV copolymer depicted in Figure 2 was prepared by polycondensation of bifunctional fullerene adduct **1** with monomer **8**. The experimental conditions (temperature, concentration and reaction time) were optimized to improve the yields and to obtain polymers with the highest molecular weight. In a typical procedure, a mixture of **1** (300 mg, 0.134 mmol), **8** (265 mg, 0.134 mmol) and pyridine (65 μl, 0.805 mmol) in CH_2Cl_2 (5 ml) was refluxed for 5 days. At the end of the reaction, the resulting solution was poured in methanol to precipitate the polymer. The dark red powder was filtered and dried. Purification by preparative size exclusion chromatography (SEC) with THF as eluent to remove the low molecular weight materials then afforded **$(C_{60}$-OPV$)_n$** in 65% yield as a dark red solid (366 mg).

Polymer **$(C_{60}$-OPV$)_n$** is well soluble in common organic solvents (THF, CH_2Cl_2, $CHCl_3$, toluene) and was therefore easily characterized. The ^1H NMR spectrum of **$(C_{60}$-OPV$)_n$** recorded in $CDCl_3$ shows the characteristic signals of monomer **1** as well as the typical resonances corresponding to the OPV derivative **8**. It can also be pointed out that the integration is in good agreement with a 1:1 ratio for the two monomeric moieties constituting the polymer. The molecular weight (M_w) of **$(C_{60}$-OPV$)_n$** was determined by analytical SEC coupled with a light scattering (LS) detector. A value of M_w = 63,000 g/mol (polydispersity: $M_w/M_n = 1.1$) was thus obtained revealing that the linear polymeric chains are constituted by 15 OPV moieties and 15 C_{60} subunits on average. It is worth noting that SEC-LS was a particularly interesting tool for the characterization of **$(C_{60}$-OPV$)_n$** since it allows the determination of an absolute molecular weight independently of a calibration curve.[6] Effectively, it has been previously shown that π–π interactions between the C_{60} subunits of fullerene-containing macromolecules and the phenyl moieties of the polystyrene stationary phase lead to an increase of the elution volume. Therefore, the M_w values obtained by analytical SEC using the polystyrene calibration curve as standard are typically underestimated.[6,10]

The UV–vis absorption spectrum of polymer **$(C_{60}$-OPV$)_n$** in CH_2Cl_2 is shown in Figure 3, together with the absorption spectra of the OPV monomer **8** and the fullerene dicarboxylic acid precursor of **1**. Compound **8** shows the characteristic features of OPV derivatives[2,9] and the lowest energy absorption band is observed at $\lambda_{max} = 424$ nm. The spectrum of the fullerene model compound is fully consistent with those of analogous *cis*-2 bis-adducts.[11] As previously observed, it is much less resolved than that of plain C_{60}. In the UV only one

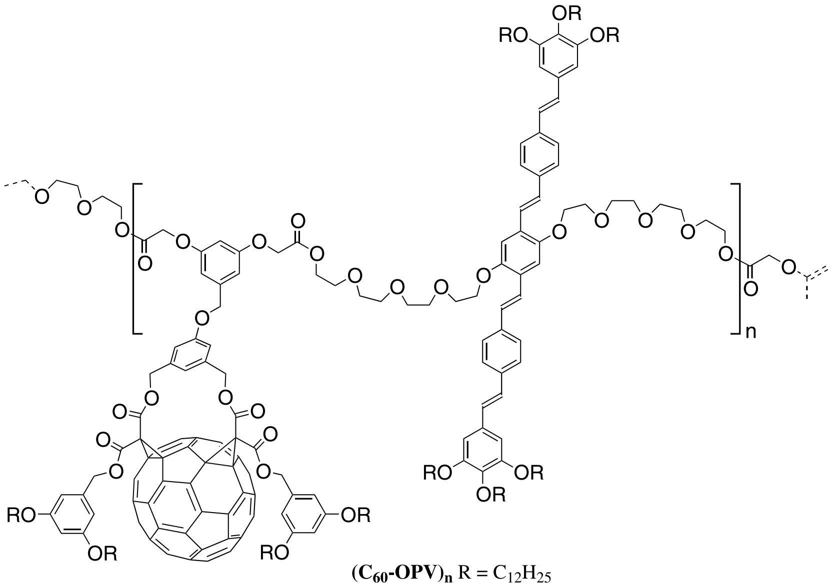


Figure 2. Polymer **$(C_{60}$-OPV$)_n$** alternating OPV moieties and C_{60} units.

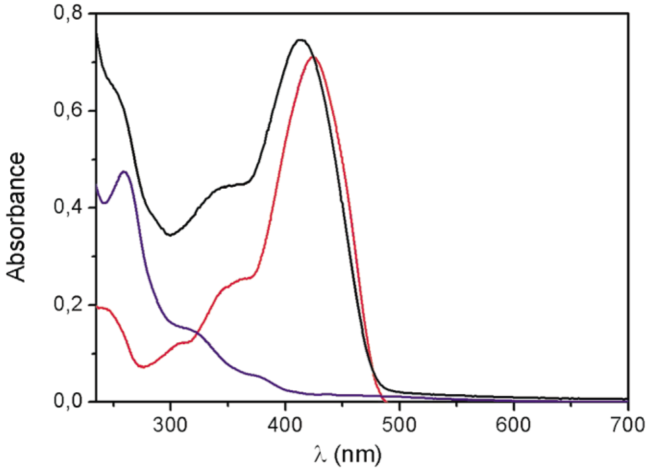


Figure 3. UV–vis spectra of the fullerene dicarboxylic acid precursor of **1** (blue), **8** (red) and **$(C_{60}$-OPV$)_n$** (black) in CH_2Cl_2 solutions at room temperature.

distinct band is present (λ_{max}=258 nm) with two shoulders above 300 nm, compared with the two well distinct bands observed for the parent C_{60} in the same region. In the visible spectral region, the spectrum is very broad and the band corresponding to the lowest allowed singlet transition, which is very sharp and well distinguishable for C_{60}, is barely detectable at 433 nm. The UV–vis spectrum of the polymer displays the characteristic absorption features of both monomeric units. Comparison with the profile obtained upon addition of the spectra of the relative component units shows however some significant differences. In particular, the OPV diagnostic band observed at 424 nm in **8** is seen at 413 nm in the polymer. This blue-shift could suggest the occurrence of some ground state interactions between the two chromophores within the linear polymer chains.

Preliminary luminescence measurements in CH_2Cl_2 solutions show a dramatic quenching of the typical OPV fluorescence by the fullerene unit in **$(C_{60}$-OPV$)_n$** upon selective excitation at the OPV band maximum (413 nm). The latter observation indicates the occurrence of intramolecular photoinduced processes. Detailed photophysical studies are currently under investigation in order to determine the mechanism of this quenching.

In conclusion, linear copolymers alternating OPV moieties and C_{60} subunits have been prepared by reaction of a new OPV monomer with a bifunctional fullerene derivative. The choice of polycondensation conditions for their preparation allowed us to obtain structurally well-defined macromolecules. These C_{60}-OPV polymers present all the characteristic features required for photovoltaic applications and their incorporation in solar cells is now under investigation.

Acknowledgements

This research was supported by ECODEV, the French Ministry of Research (*ACI Jeunes Chercheurs*) and a fellowship from the *CONACyT* to M.G.-N. We further thank L. Oswald for technical help and A. Rameau for molecular weight determination by analytical size exclusion chromatography.

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