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Fullerenes bound to an insoluble polymeric phase: surface photophysical studies using diffuse reflectance laser flash photolysis (DRLFP)

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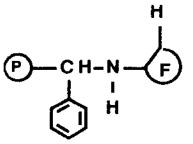
Abstract

Fullerenes C_{60} and C_{70} were covalently bound to an insoluble cross-linked (2% divinylbenzene (DVB)) polystyrene. The transient absorption of the polymeric C_{60} triplet was recorded by diffuse reflectance laser flash photolysis (DRLFP) showing a lifetime similar to that described for the C_{60} triplet dissolved in toluene. The deactivation by molecular O_2 has a quenching constant two orders of magnitude smaller than in solution.

Keywords: Fullerenes; Insoluble polymeric phase; Photophysical studies; Diffuse reflectance laser flash photolysis

1. Introduction

Since the discovery of the fullerenes C_{60} and C_{70}, much effort has been devoted to the full clarification of their properties [1–4]. Some polymeric derivatives have also been studied [5–8] in an attempt to improve the solubility of fullerenes [8] and to design soluble fullerene-containing polymers suitable for the processing of advanced materials [7]. However, to our knowledge, litle information is available on fullerenes covalently linked to insoluble polymers. Such polymers would act as permanent solutions of fullerene, and their properties could be checked as precursors of organic superconducting polymers [9]. In this paper, we report the synthesis and characterization of fullerenes covalently bound to an insoluble, matrix-like, cross-linked (2% divinylbenzene (DVB)) polystyrene (**1**), together with data on its transient behaviour obtained using diffuse reflectance laser flash photolysis (DRLFP).



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Ⓕ : fullerene C_{60} or C_{70}

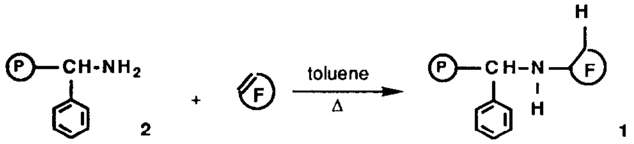
Ⓟ :cross-linked (2%DVB) polystyrene

2. Results and discussion

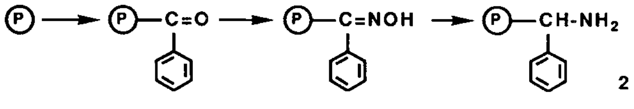
Polymer **1** was prepared from polymer **2** and a commercial mixture (Aldrich) of C_{60} and C_{70} fullerenes (85:15) (Scheme 1) following the well-known addition of amines to fullerenes (described as the ''buckyball fishing process'', with the amine group protruding from the framework of a soluble polymer [7,8]).

In turn, polymer **2** was prepared from commercial cross-linked polystyrene (Dow Chemicals) following the sequence shown in Scheme 2 as already described in Refs. [10] and [11].

Benzoylation of polystyrene was followed by oximation [10] and reduction [11], yielding the insoluble polymeric amine **2** which contains 0.74 meq of R–NH_2 groups per gram



Scheme 1.



Scheme 2.

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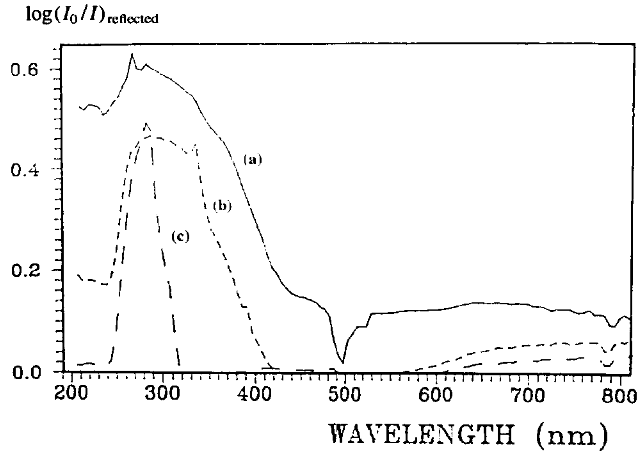

Fig. 1. Diffuse reflectance UV–visible ground state spectra of fullerene-containing polymer 1 (a), amine group-containing polymer 2 (b) and cross-linked (2% DVB) polystyrene (c).

of polymer (equivalent to 8.3 functionalized phenyls out of 100), determined by elemental analysis for nitrogen.

The synthesis of 1 was carried out by stirring, at 120 °C, a suspension of 2 (400 mg) in toluene (22 ml) containing 4 mg of a commercial mixture of C_{60} and C_{70} fullerenes (85:15) (4.7×10^{-3} meq of C_{60} and 0.71×10^{-3} meq of C_{70}). While stirring, the UV–visible spectrum of the liquid phase showed a constant decrease in the intensity of the absorption band of the soluble fullerene at 474 nm. After 40 h, this absorption remained constant, stirring was stopped and the polymer was filtered off and washed with toluene (25 ml, stirring 24 h), toluene–dioxan (1:1) (25 ml, stirring 24 h) and the following mixtures (20 ml each) stirring for 5 min each time: acetone–THF (THF, tetrahydrofuran) (1:1), MeOH–acetone–THF (1:1:1), MeOH–THF (2:1, 1:2, 1:3), THF, THF–ether (2:1, 1:1, 1:2, 1:3) and ether. Only the first portion of the solvents presented signs of soluble residual fullerenes as noted by their UV–visible spectrum. In this way, 345 mg of polymer 1 was obtained; the C : N ratio (elemental analysis) was larger than in polymer 2, and we deduced from the absorbance of the filtered liquid phases that polymer 1 contains 6.7×10^{-3} meq of fullerenes C_{60} and C_{70} per gram of the polymer (equivalent to 0.08 functionalized phenyl groups out of 100).

The new polymer was a brown powder whose IR spectrum (KBr) presented very small differences to the IR spectrum of polymer 2; only the broad band at 3300–3700 cm^{-1} (stretching $-NH_2$) was decreased in intensity; this is in accordance with the low degree of functionalization (0.08%). In contrast, the ground state UV–visible spectrum recorded by diffuse reflectance (Fig. 1(a)) showed relevant differences to a similar spectrum of polymer 2 (Fig. 1(b)); the spectrum was a sum of the absorption band of 2, the three characteristic absorption bands of C_{60} at 220, 260 and 330 nm (shoulder) and the characteristic absorption band of C_{70} at 470 nm (shoulder) [12]. The reason for the difference lies in the methodology used to record both the IR and UV–visible spectra. The IR spectrum records the intensity of the transmitted light through a pellet of KBr polymer, thus analysing the average degree of functionalization. The UV–visible spectrum, however, investigates by diffuse reflectance only the surface of the polymer beads. We have already demonstrated [13–15] that, in the polymers used in solid phase synthesis, up to 1% of the functionalization is located on the surface of the polymer bead which is the more accessible and reactive part. As polymer 1 has been prepared following the concept of solid phase synthesis [16], its UV–visible spectrum shows a "fullerenes-enriched" area.

The transient behaviour of 1 was studied by DRLFP (LKS.50 model, Applied Photophysics Ltd., UK) which also makes use of diffuse reflected light to detect transient absorptions following pulsed excitation of opaque light-scattering substances, such as polymer-pendant fullerene 1 [13,17,18]. Fig. 2 shows the transient absorption of 1; it is centred at 715 nm, and the lifetime deduced at the end of the decay at 715 nm is $\tau = 40 \pm 5$ μs. The lifetime matches that already described for $^3C_{60}$ in toluene [19], and the maximum is blue shifted by 25 nm relative to the transient absorption maximum of $^3C_{60}$ in the same solvent. We believe that the shift is due to the very different "solvation" environment present in 1 (N_2 molecules instead of toluene molecules) and we assign the recorded transient absorption to the triplet state of the polymer-pendant C_{60}. Although the same polymer carries a small amount of C_{70}, we cannot distinguish from the recorded spectrum evidence of a hypothetical transient absorption of $^3C_{70}$.

We also followed the decay of the C_{60} triplet at 715 nm at different oxygen concentrations (Fig. 3, N_2-purged, aerated and oxygen-saturated) and determined the rate constant for the quenching of the C_{60} triplet by oxygen to be $(1.3 \pm 0.4) \times 10^7$ dm^3 mol^{-1} s^{-1}. This value is very small compared with the described $k_q(O_2) = (1.9 \pm 0.2) \times 10^9$ dm^3 mol^{-1} s^{-1} in benzene and $k_q(O_2) = 8.0 \times 10^8$ dm^3 mol^{-1} s^{-1} in an aqueous solution of γ-cyclodextrin–C_{60} complexes

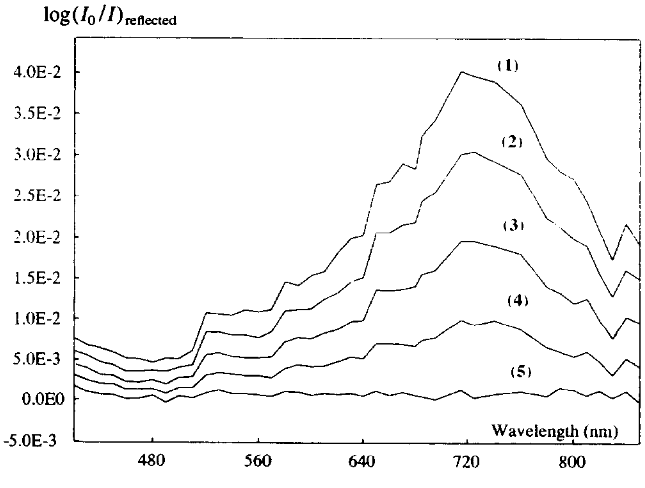

Fig. 2. Transient absorption spectra of dry, nitrogen-purged beads of polymer 1 ($\lambda_{ex} = 355$ nm; intensity, 47 mJ per pulse; pulse width, 9 ns): (1) 4.0×10^{-6} s after laser flash; (2) 12.0×10^{-6} s after laser flash; (3) 26.0×10^{-6} s after laser flash; (4) 52.0×10^{-6} s after laser flash; (5) 180.0×10^{-6} s after laser flash.

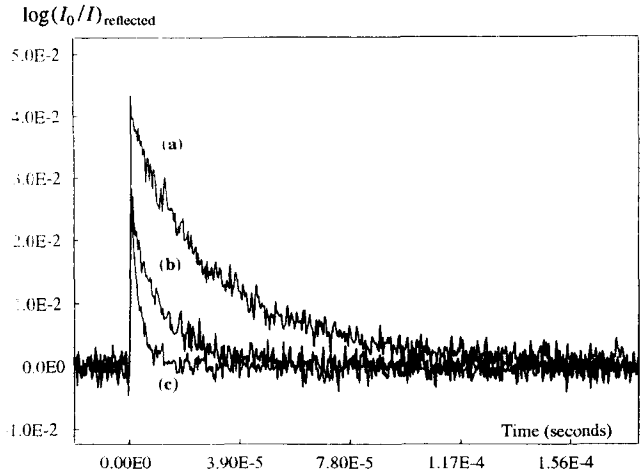

Fig. 3. Decay traces at 715 nm (conditions as in Fig. 2) in N_2-saturated (a), aerated (b) and O_2-saturated (c) polymer 1.

[12]. The reason may be that the polymeric skeleton folds and surrounds the fullerenes protecting them against collision and quenching by O_2. An additional cross-linking provoked by the reaction of one fullerene with two or more amines in polymer **2** could force this folding of the polymeric skeleton.

3. Conclusions

We have covalently linked a mixture of C_{60} and C_{70} fullerenes to an insoluble cross-linked (2% DVB) polystyrene, and have proved by DRLFP that the triplet state of C_{60} is generated after pulsed laser excitation. This triplet state is deactivated by O_2 with a quenching constant two orders of magnitude smaller than in solution. It is well known in solid phase synthesis [20] that these polymers swell in solvents such as benzene, toluene, dioxan, THF, dimethylformamide (DMF), CH_2Cl_2, $CHCl_3$, CCl_4 and CS_2; this opens up the possibility of using many solvents to study the properties of the new fullerene derivatives.

Acknowledgements

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