Fullerene C_{60} Bound to Insoluble Hydrophilic Polymer: Synthesis, Photophysical Behavior, and Generation of Singlet Oxygen in Water Suspensions

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Dedicated to Professor *André M. Braun* on the occasion of his 60th birthday

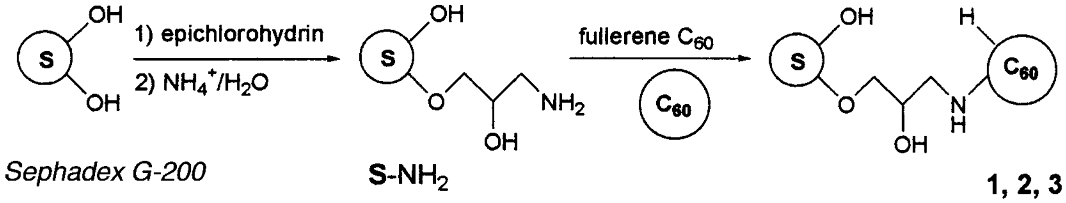
Fullerene C_{60} has been covalently bound to an insoluble hydrophilic polymeric matrix: *Sephadex® G-200*. The new polymeric equivalent of C_{60} swells in H_2O to form gel-like suspensions. The transient photochemical behavior of this polymeric fullerene has been studied in dry and H_2O-suspended samples. Both samples show a transient absorption similar to the absorption of the parent C_{60} solution. There is a lack of triplet-triplet annihilation and of a O_2-quenching process in the dry sample. On the contrary, the O_2-quenching process is very efficient in the H_2O-suspended samples ($k_q(O_2) = (1.9 \pm 0.5) \times 10^8$ dm^3 mol^{-1} s^{-1}) and results in the formation of singlet oxygen, which is detected by its emission at 1270 nm. These results point to this hydrophilic polymeric equivalent of C_{60} as a good candidate for use as a singlet-oxygen solid sensitizer in H_2O suspensions.

Introduction. – Since the discovery of fullerene C_{60}, many efforts have been devoted to obtain polymeric derivatives [1–5] for evaluation of their properties as advanced materials [3]. We prepared one them [5] by a covalent linkage of C_{60} to an insoluble, matrix-like polystyrene cross-linked with 2% divinylbenzene (DVB). The photophysical behavior of the resulting polymeric equivalent of fullerene in the solid state was similar to that of C_{60} in solution: the transient absorption (recorded after exciting with a laser pulse of 355 nm) presented a maximum at 715 nm and a lifetime of $\tau = 40 \pm 5$ μs; this excited state was assigned to the triplet of solid polymeric C_{60} fullerene. Its deactivation by molecular oxygen had a quenching rate constant of $k_q(O_2) = (1.3 \pm 0.4) \times 10^7$ dm^3 mol^{-1} s^{-1}, which is two orders of magnitude smaller than in solution for the parent C_{60}. As the backbone was polystyrene, that polymer could be swollen by hydrophobic organic solvents, but could not be swollen by very polar solvents like H_2O. On the other hand, the generation of singlet oxygen in H_2O by photochemical sensitization is well-documented for soluble sensitizers [6–10], but there are a few references on its sensitization in heterogeneous systems [11–14]. The use of polymeric sensitizers in heterogeneous phase is interesting because the sensitizer can be removed from the reaction mixture by filtration once the photochemical reaction is finished [15].

In this paper, we report the synthesis and characterization of fullerene C_{60} covalently bound to a modified *Sephadex® G-200*, **1**, which is a carbohydrate hydrophilic polymeric matrix, as well as the data for its transient behavior in the solid state obtained by diffuse reflectance laser flash photolysis (DRLFP) [16]. As the new polymeric equivalent is hydrophilic, we have explored its transient behavior in H_2O suspensions and investigated the deactivation by molecular oxygen of the excited state of **1** in a D_2O gel. This deactivation was found to be efficient, resulting in the generation of singlet molecular oxygen, which was characterized by its emission at 1270 nm.

Results and Discussion. – Polymer **1** was prepared according to the *Scheme.*

Scheme



The new hydrophilic polymeric equivalent of C_{60}, **1**, contains 4.45×10^{-3} mol of fullerene C_{60} per gram of polymer. Different loading levels are contained in polymers **2** and **3** (6.66×10^{-3} and 3.61×10^{-3} mol of fullerene C_{60} per gram of polymer, resp.). The ground-state UV/VIS spectra of **S**-NH_2, **1**, **2**, and **3** recorded by diffuse reflectance are shown in *Fig. 1.* The characteristic absorption bands of C_{60} at 220 and 260 nm can be clearly noted for polymers **1**–**3**; in addition, the reflected intensity depends on the amount of C_{60} present in each polymer. Polymers **1**–**3** swell in H_2O to form gel-like suspensions.

The transient behavior of polymers **1**–**3** was studied by DRLFP. *Fig. 2* shows the transient absorption spectra of all three polymers recorded 4.0 μs after exciting the dry solid samples with a short pulse of laser light at 532 nm. Their intensities depend, also, on the loading of C_{60}. The inset in *Fig. 2* shows the decay trace at 740 nm for the excited state of **1**; it follows a mono-exponential decay with deduced lifetime of 41 ± 5 μs. Lifetimes for **2** and **3** are 33 ± 5 and 36 ± 5 μs, respectively. These lifetimes and the position of the maxima are similar to the lifetime and maximum described by us [5] for excited $^3C_{60}$ covalently bound to a hydrophobic cross-linked polystyrene. We assign these signals to the transient absorption of the C_{60} units present in polymers **1**–**3**. As the lifetimes are very similar, one can exclude a relevant contribution, if any, of quenching by the residual NH_2 groups protruding from the backbone. The decay at 740 nm did not modify the kinetics at different oxygen concentrations (N_2-purged, aerated, and O_2-saturated samples), indicating a complete absence of quenching by molecular O_2. In addition, modification of the pulsed laser energy resulted in a parallel modification of the intensity of the transient signals but not in a change in the kinetics, thus excluding the occurrence of the triplet-triplet annihilation process. It seems that the polymeric backbone protects efficiently each C_{60} unit in the dry samples, isolating each from other C_{60} or NH_2 units, as well as from the molecular oxygen.

The situation is different when any of the polymers is swollen in H_2O. They expand their volume to form static gel-like suspensions. *Fig. 3,a*, shows the transient absorption recorded when polymer **1** is excited with a pulsed laser at 532 nm. The first noticeable difference lies in the intensity of the absorption: now, it is much weaker than in the dry sample due to the expanded volume of the wet polymer. The second difference appears when the amount of O_2 present in the solvent is modified: it is observed that the

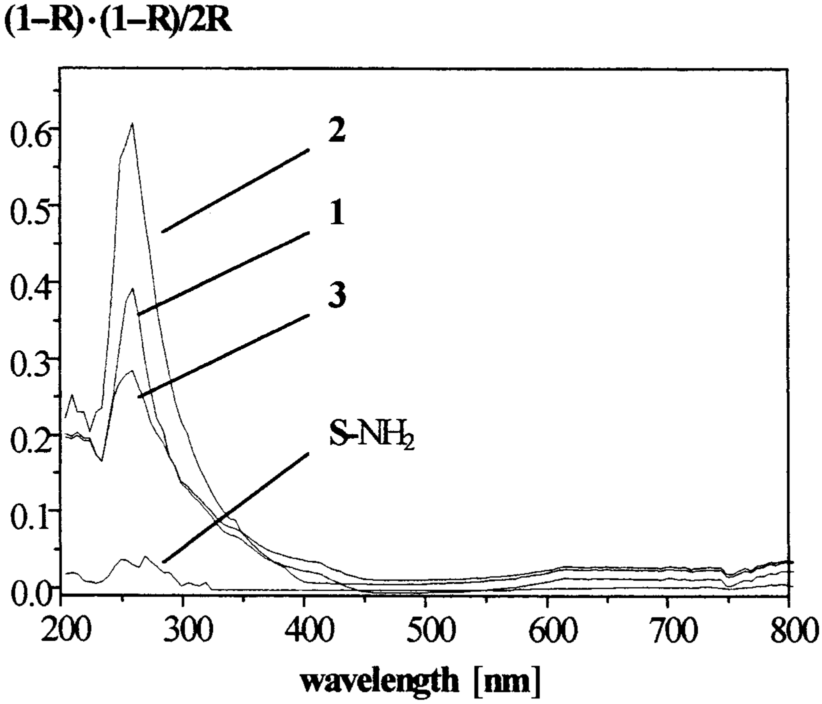


Fig. 1. *Diffuse reflectance UV/VIS ground-state spectra of NH_2-containing polymer* **S**-*NH_2 and fullerene-C_{60}-containing polymers* **1**, **2**, *and* **3**

lifetime of the transient absorption depends on the O_2 concentration. *Fig. 3,b*, shows the decay traces of the C_{60} triplet of **1** at 680 nm for N_2-purged ($\tau = 42 \pm 5$ µs), aerated, and O_2-saturated, H_2O-suspended samples. The deduced rate constant for the quenching of the C_{60} triplet by O_2 is $k_q(O_2) = 1.9 \pm 0.5) \times 10^8$ dm^3 mol^{-1} s^{-1}. Polymers **2** and **3** present similar behavior, and the deduced rate constants for quenching by O_2 are $(1.8 \pm 0.5) \times 10^8$ and $(1.9 \pm 0.5) \times 10^8$ dm^3 mol^{-1} s^{-1}, respectively. The formation of singlet oxygen in this process can be detected through its phosphorescence by monitoring emission at 1270 nm. *Fig. 4* shows the transient emission at this wavelength recorded after excitation of O_2-saturated (*i*), and air saturated (*ii*) suspensions of **1** in D_2O-saturated gel with a pulsed laser at 532 nm. Also shown is the signal recorded after excitation of a N_2-purged gel of unfunctionalized *Sephadex® G-200* suspended in D_2O (*iii*). Aside from the initial points in trace *iii*, which are attributable to scattered emission, there is no other emission detected on the time-scale of the analysis in traces *i* and *ii*. The slow decay in trace *i* is assigned to the emission of the singlet oxygen formed in the O_2-saturated sample. As in *Fig. 3,a*, the signal noise ratio is low due to the large volume occupied by the swollen sample (equivalent to a low 'concentration' of the sensitizing C_{60} units). The intensity emission decreases in trace *ii* for an air-equilibrated sample and, hence, with lower O_2 concentration. The singlet-oxygen lifetime deduced from the slow decays in traces *i* and *ii* is 45 ± 5 µs. The lifetime for singlet oxygen in D_2O is > 60 µs in the presence of soluble sensitizers, but we have proven that it is shorter

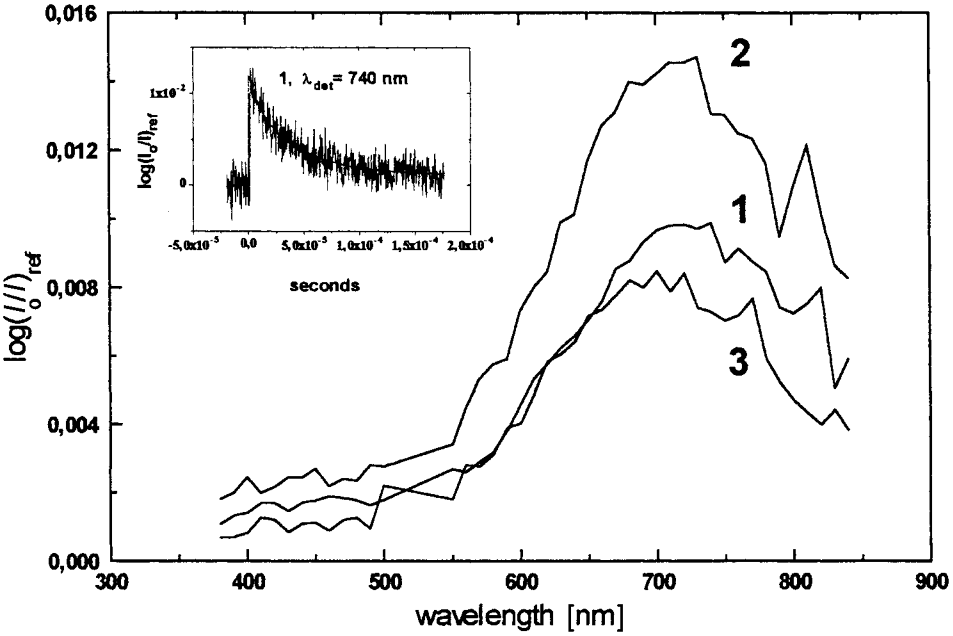


Fig. 2. *Transient absorption spectra of dry, N_2-purged powder of polymers* **1**, **2**, *and* **3**, *4.0×10^{-6} s after laser flash* ($\lambda_{ex} = 532$ nm; intensity 23 mJ/pulse; pulse width, 9 ns). *Inset:* decay trace at $\lambda_{det} = 740$ nm for **1**.

when a hydrophilic polymeric backbone is suspended in the solvent [14]. This is so in the case in polymer **1**: the nondeuterated OH groups present in the polymeric skeleton of *G-200* probably quench the singlet oxygen to reduce its lifetime.

To summarize, we have prepared a new hydrophilic polymeric equivalent of C_{60}, and we have studied its transient photochemical behavior in dry and H_2O-suspended samples. The dry polymer shows a transient absorption similar to the absorption of the parent C_{60} in solution but with the absence of triplet-triplet annihilation and O_2-quenching processes. On the contrary, the O_2-quenching process is very efficient in the H_2O-suspended samples and results in the formation of singlet oxygen, which is detected by its emission at 1270 nm. These results point to this hydrophilic polymeric equivalent of C_{60} as a good candidate for use as a singlet-oxygen solid sensitizer in H_2O suspensions.

Experimental Part

Sephadex® G-200 and all other materials were obtained from commercial sources and used as received. Functionalization of *Sephadex® G-200* with epichlorohydrin was performed as described in [17]. The resulting polymer (0.5 g) was suspended in 75 ml of an aq. soln. of NH_3 (15%) and heated at 70° for 48 h. After filtration, the solid was washed with H_2O (25 ml), AcOH 1% (25 ml), Na_2CO_3 (0.1M, 25 ml), and MeOH (25 ml). The polymeric amine **S**-NH_2 contained 0.58 mmol of NH_2 groups per gram of polymer, determined by elemental analysis of N. Polymer **1** was prepared from **S**-NH_2 according to the well-known addition of amines to fullerenes (described as the 'buckyball fishing process' [3][4]): 150 mg of the amine were refluxed in 25 ml of a 3.43×10^{-4} M soln. of C_{60} in toluene. While reacting, the UV/VIS spectrum of the liquid phase showed a constant decrease in the intensity of the absorption band of the soluble fullerene at 474 nm. After 12 d, the solid was

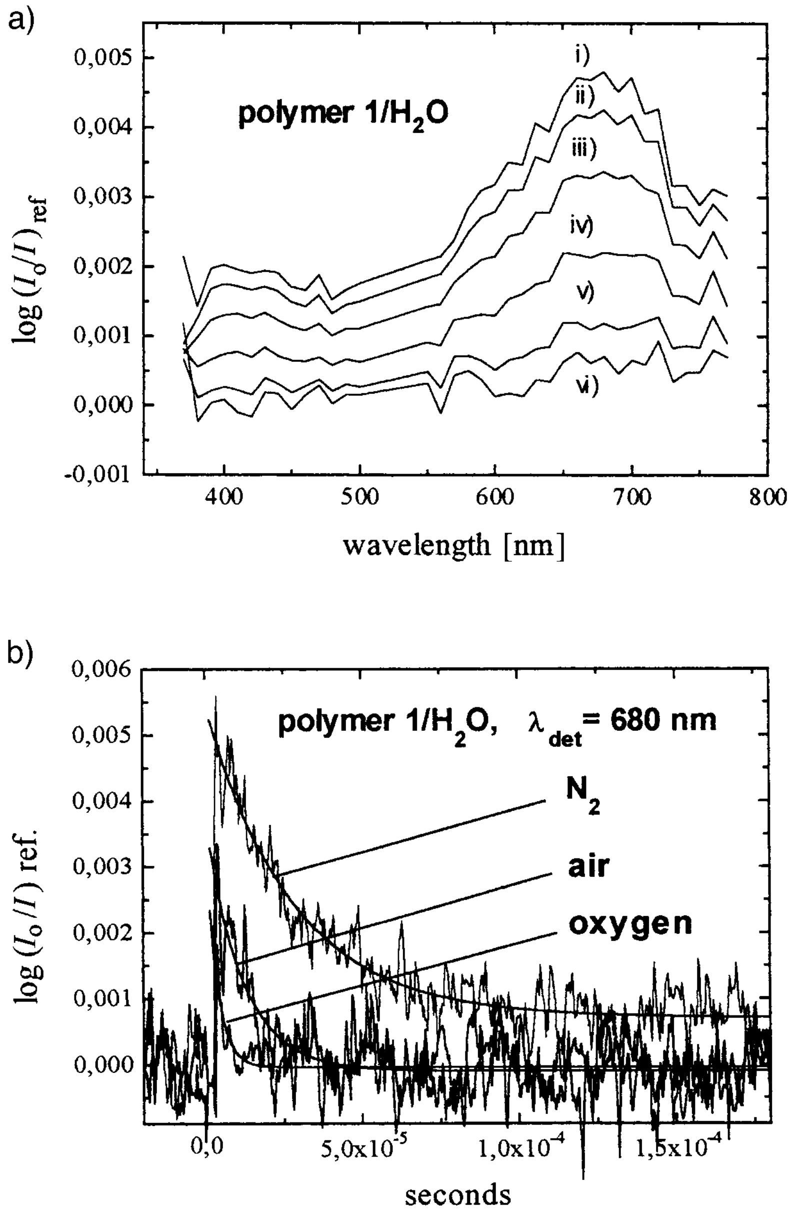


Fig. 3. a) *Transient absorption spectra of a* N_2*-purged suspension of polymer* **1** *in* H_2O ($\lambda_{ex} = 532$ nm; intensity 56 mJ/pulse; pulse width, 9 ns): i) *4.0* $\times$ *10*$^{-6}$ *s after laser flash;* ii) *8.0* $\times$ *10*$^{-6}$ *s after laser flash;* iii) *16.0* $\times$ *10*$^{-6}$ *s after laser flash;* iv) *32.0* $\times$ *10*$^{-6}$ *s after laser flash;* v) *64.0* $\times$ *10*$^{-6}$ *s after laser flash, and* vi) *180.0* $\times$ *10*$^{-6}$ *s after laser flash.* b) *Decay traces at* $\lambda_{det} = 680$ *nm of a* N_2*-purged, air-equilibrated, and* O_2*-saturated suspension of polymer* **1** *in* H_2O

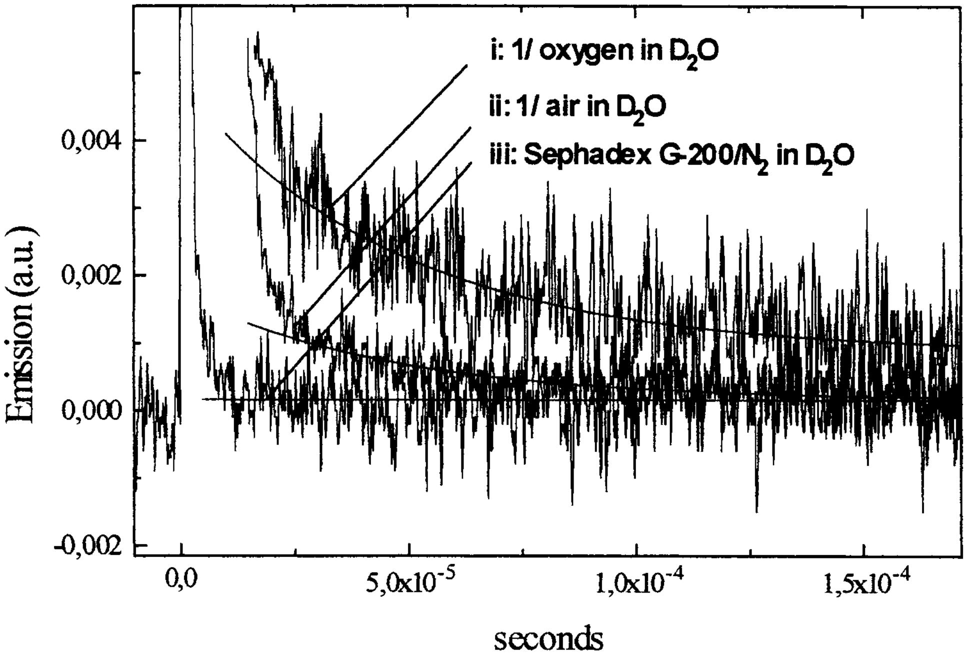


Fig. 4. *Decay traces of emission at 1270 nm after laser-pulsed excitation* (532 nm, 40 mJ/pulse, 9 ns/pulse) *of* i) *O_2-saturated suspension of polymer* **1** *in D_2O,* ii) *air-saturated suspension of polymer* **1** *in D_2O, and* iii) *N_2-purged suspension of* Sephadex® G-200 *in D_2O*

filtered off and washed with toluene/EtOH (2 × 25 ml) and MeOH. We deduced from the absorbance of the filtered liquid phases that polymer **1** contains 4.45×10^{-3} mol of fullerene C_{60} per gram of polymer [5]. Polymers with different loadings of C_{60} were obtained modifying the refluxing time: polymer **2** containing 6.66×10^{-3} mol of fullerene C_{60} per gram was obtained after 14 d, while polymer **3** containing 3.61×10^{-3} mol of fullerene C_{60} per gram was obtained after 10 d.

Laser-flash-photolysis experiments were performed with a *LKS50* instrument from *Applied Photophysics.* The second harmonic (532 nm) of a *Q*-switched Nd:YAG laser (*Spectron Laser Systems*, UK; pulse width, *ca.* 9 ns) was used for laser flash excitation. Emission at 1270 nm from singlet oxygen was measured with a liq. N_2-cooled *Edinburgh EI-P* Ge detector. The excitation beam reached the sample at 45°, while the luminescence was detected from the front face of the sample after passing through two filters: *Spectrogon LP-1000* and *BP-1275-080-B.*

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