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Incorporation of a Photosensitizer Core within Hyperbranched Polyether Polyols: Effect of the Branched Shell on the Core Properties

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ABSTRACT: A photosensitizer core has been covalently incorporated into a hyperbranched polyether polyol structure, using a one-step protocol. Partially deprotonated 2,2′,4,4′-tetrahydroxybenzophenone was used as initiator in the anionic polymerization of glycidol, yielding hyperbranched polyglycerols with benzophenone core in every macromolecule formed. Molecular weights in the range of 1500 to 5800 g/mol and moderate polydispersity ($1.3 < M_w/M_n < 2$) were obtained. Incorporation of the functional core was unequivocally evidenced by MALDI−TOF mass spectroscopy. Further modification via acetylation of the polyglycerol hydroxyl groups afforded polymers of lowered polarity. The photochemical and photophysical behavior of the obtained benzophenone core-containing hyperbranched polyglycerols has been investigated in a variety of solvents and compared with that of the model compound 2,2′,4,4′-tetramethoxybenzophenone. The hyperbranched polymer periphery induced molecular weight-dependent properties in the photoactive core. Although absorption spectra of the polymers show the typical bands of a tetra(alkoxy)benzophenone unit, a dramatic hyperchromic effect of the band assigned to the 2,4-dialkoxybenzoyl chromophore was observed with increasing molecular weight. Steady-state and time-resolved fluorescence measurements evidenced an increase of both the fluorescence quantum yield and the singlet lifetime with the increase of molecular weight. On the other hand, laser flash photolysis (LFP) experiments showed that, as in the case of the reference compound, the lowest-lying triplet of the hyperbranched derivatives in methanol is mainly of the π,π^* nature, while both triplets n,π^* and π,π^* are populated in acetonitrile, which is indicative of easy access of the solvent to the core. However, the quenching rate constant of the aromatic ketone triplet excited-state by naphthalene decreased with the polymer molecular weight, which agrees with the role of the branched shell as a barrier for external quenching. The polymers showed good photostability, i.e., degradation was insignificant upon 1 h of irradiation in methanol.

Introduction

Macromolecular encapsulation in dendrimers has received broad attention in recent years.[1] Particular interest has been focused on encapsulating photoactive, catalytic and redox-active cores, as well as the study of changes in their physical properties within the dendritic structures.[1−7] Detailed studies on dendrimers have revealed that at some critical dendrimer generation, the core is encapsulated by the sterically crowded and densely packed, branched architecture.[8,9] By steric shielding of a functional core from the surrounding environment, several potentially useful properties have been realized, including attenuation of luminescence efficiency in the case of a photoactive core moiety, such as $[Ru(bpy)_3]^{2+}$,[2] as well as azobenzene[3] and silicon phthalocyanine moieties.[4] Dendritic encapsulation also influences the electron transfer to and from an electroactive core, as shown for iron−sulfur clusters,[5] and leads to attenuation of the activity of catalytic functional cores such as manganese(III) porphyrin[6] and bis(oxazoline)s.[7] Dendritic encapsulation of active core moieties has also been proposed to serve as a model for the shielding of active centers in naturally occurring enzymes.[10] In addition, a chromophore at the core of dendritic structures can lead to attractive scaffolds for photocatalysis.[11] The backbone could act as a gatekeeper for substrate access to the photocatalytic center. Size and shape selectivity could be caused by geometrical constraints arising from the different shape and size of substrates, products and transition states. An additional advantage of these macrophotocatalysts is that they can be easily recovered (nanofiltration techniques) and reused.

In contrast to dendrimers, which are prepared in demanding multistep syntheses, hyperbranched polymers offer greater application potential due to their facile one-step synthesis.[12] In general, they possess a certain polydispersity, but, the ring-opening multibranching polymerization (ROMBP) of glycidol (2,3-epoxy-1-propanol) employing slow monomer addition (SMA) affords hyperbranched polyglycerols with controlled molecular weights and moderate polydispersity ($1.2 < M_w/M_n < 1.5$).[13] Well-defined encapsulation of a single core moiety within hyperbranched polymers analogous to the abovementioned dendrimers, however, is a challenge that has scarcely been realized to date. Direct copolymerization using a reactive, modified triphenylamine core[14] or post-polymerization modification of a nitrophenyl ester core, subsequent to the formation of the dendritic structure have been reported.[15]

It should be stressed that firm and unequivocal evidence of the incorporation of a specific core into all species present in the distribution of a hyperbranched structure can only be given

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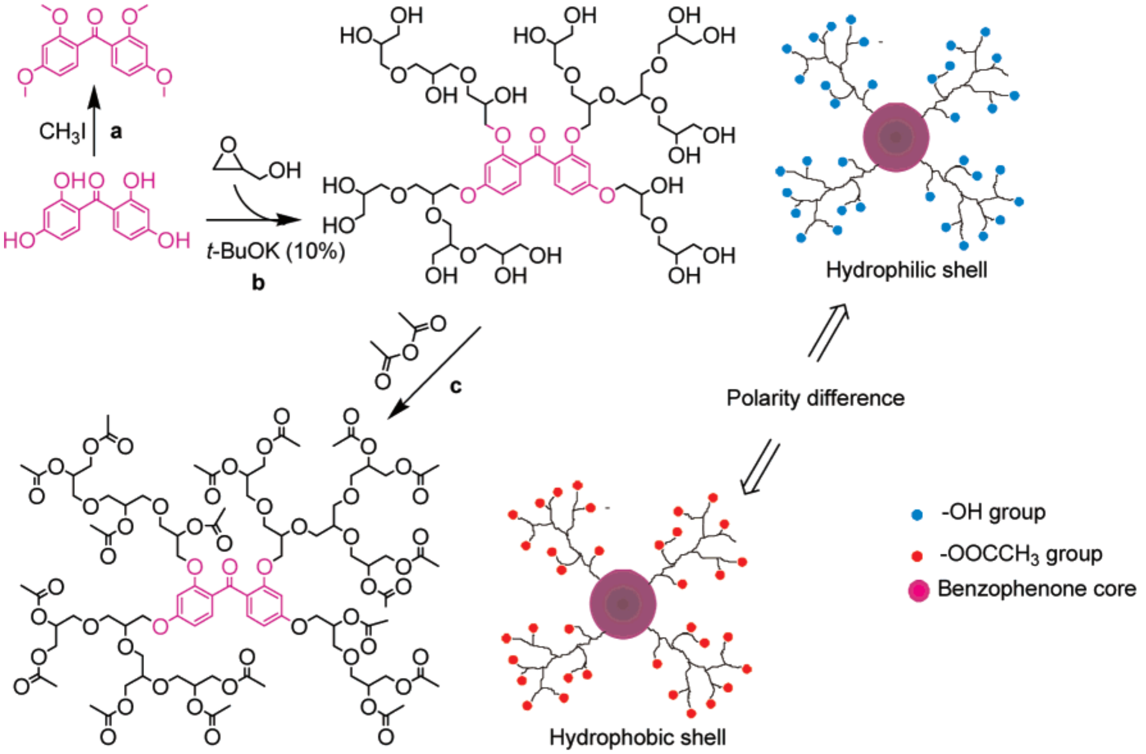
Scheme 1. Synthesis of the Low Molecular Weight Model Compound TMBP from THBP (a) and Synthetic Approach for the Incorporation of the Benzophenone Core within the Hyperbranched Polyglycerols (b) and Peracetylation of Polyglycerol (c)



by mass spectrometry, usually MALDI−TOF mass spectrometry. Clearly, NMR data cannot give conclusive evidence on that point, due to the global nature of this method.

In the present study, we describe two intriguing aspects related to the incorporation of a photoactive core into a hyperbranched polymer structure: (i) the use of a functional benzophenone (2,2′,4,4′-tetrahydroxybenzophenone, **THBP**) as initiator for the polymerization of glycidol and (ii) spectroscopic and spectrometric studies of these compounds demonstrating full covalent incorporation of the benzophenone as a core into hyperbranched polyethers in one-pot procedures. Changing the degree of polymerization of PG, the diameter of the hyperbranched encapsulating polymer periphery has been varied. For some of the samples, additional acetylation was performed subsequent to the polymerization in order to vary the polarity of the polymers. The effect of the branched[16] shell on the photochemical and photophysical properties of the covalently incorporated benzophenone has been studied in a variety of solvents, using steady-state and time-resolved techniques. For comparison, 2,2′,4,4′-tetramethoxybenzophenone (**TMBP**) was used as a low molecular weight model compound. To the best of our knowledge, this is the first practicable and easily accessible route reported to date for the construction of functional polymeric materials based on hyperbranched encapsulation of a functional unit. Until recently, hyperbranched polymers with dendrimer-like properties incorporating covalently a single entity in the core of the polymeric structure were thought to be unachievable.[11]

There are very few reports on dendritic structures used as photocatalysts for conversion of molecules.[11,17] These structures are dendrimers with benzophenone at the core, whose synthesis involves alkylation of the 2,2′,4,4′-tetrahydroxybenzophenone (**THBP**) hydroxyl groups followed by a demanding multistep dendrimer construction protocol. These systems have led to remarkable results as singlet oxygen sensitizers.

Our aim is to obtain easy to synthesize, recoverable, and reusable photocatalysts. With such purpose, we have initiated studies on encapsulation of chromophores using a one-step protocol.

Experimental Section

Polymerizations were carried out according to a reported procedure[12a] via slow monomer addition to 2,2′,4,4′-tetrahydroxybenzophenone (purchased from Acros Organics). This core-initiator was partially (20%) deprotonated using potassium *tert*-butoxide and used directly for the polymerization of glycidol. After completion of the addition, the polymer was dissolved in methanol and precipitated twice in acetone. The precipitated material was dried in vacuum at 80 °C for 2 days. The acetone/methanol fraction was evaporated and the isolated rest was dried as described above. The different polymers were analyzed by ^{1}H and ^{13}C NMR spectroscopy. As an example, NMR data for **TOBP-PG$_{21}$** are as follows: ^{1}H NMR (400 MHz, methanol-d_4): $\delta = 3.42-4.65$ ppm (m, $-CH_2CHO-(CH_2O-)$ hyperbranched polyglycerol backbone), 6.46 (br, 2H), 6.65 (br, 2H), 7.55 (br, 2H); ^{13}C NMR (100 MHz, methanol-d_4) 62.8, 64.4, 64.5, 72.2, 73.9, 79.9, 81.4, 100.9, 107.5, 125.5, 128.9159.7, 160.9, 164.6, 164.7.

TOBP-PG$_{21}$Ac$_{21}$. A 25 mL one-neck flask containing a stirring bar was charged with **TOBP-PG$_{21}$**. Triethylamine (2 equiv relative to the hydroxyl groups of polyglycerol backbone) and acetic acid anhydride (2 equiv) were added. A reflux condenser was attached and the reaction vessel was placed in an oil bath preheated to 120 °C. The reaction mixture was heated with vigorous stirring for 6 h and then cooled to room temperature. Subsequently, the reaction mixture was concentrated in vacuo. The resulting crude product was dissolved in 100 mL of chloroform, and 50 mL of NaOH (10%) was added. The mixture was stirred vigorously at room temperature for 2 h. The organic phase was separated, washed twice with NaOH (10%) and water, dried over Na_2SO_4, and concentrated in vacuum. The crude product was kept under vacuum overnight. Full acetylation of the hydroxyl groups of the benzophenone-cored hyperbranched polyglycerols was achieved, as evidenced from NMR spectroscopic analysis.^{1}H NMR (400 MHz, $CDCl_3$): δ 2.0 (CH_3), 3.2−5.1 ppm (m, $-CH_2CHO-(CH_2O-)$ hyperbranched polyglyc-

Table 1. Characterization Data for TMBP and Hyperbranched Polymers TOBP-PG

compound[a]	M_n(NMR)[b] [g/mol]	M_n(SEC)[c] [g/mol]	M_w/M_n[c]	DB	λ_{abs} (nm)[d] CH_3OH	CH_3CN	dioxane
TMBP[e]	300		1		311	304	302
TOBP-PG$_{21}$	1520	1630	1.5	0.36	311		
TOBP-PG$_{21}$Ac$_{21}$[f]	2120	2650	1.3	0.36	310	303	300
TOBP-PG$_{80}$	5850	6450	1.8	0.40	312		
TOBP-PG$_{80}$Ac$_{80}$[f]	8870	9270	1.5	0.40	309	303	300
TOBP-PG$_{113}$	8340	8740	2	0.45	310		
TOBP-PG$_{113}$Ac$_{113}$[f]	12 900	13 490	1.8	0.45	309	303	300

[a] The subscripts **PG$_x$** denote the degree of polymerization of polyglycerols, while the subscripts **Ac$_y$** denote the number of acetylated hydroxyl groups. [b] Calculated from ^1H NMR spectra. [c] Determined by SEC in dimethylformamide and chloroform for **TOBP-PG** and **TOBP-PGAc**, respectively with PS (polystyrene standards). [d] UV−vis measurements of the polymeric structures were performed in three different solvents: MeOH, CH_3CN, and dioxane, except for non-acetylated polymers, which were only soluble in MeOH. [e] From ref 22. [f] The degree of acetylation of the hydroxyl groups was determined by NMR by comparison with benzophenone signals, showing that it exceeded 95%.

Table 2. Photophysical Characteristics of TMBP and TOBP-PG Samples in MeOH, CH_3CN, and Dioxane[a,b,c]

compound	CH_3OH λ_{em}	Φ_f	τ_f	E_S	CH_3CN λ_{em}	Φ_f	τ_f	E_S	dioxane λ_{em}	Φ_f	τ_f	E_S
TMBP[d]	480	0.004	1.4	75.0	448	0.005	2.0	76.3	453	0.004	2.5	78.0
TOBP-PG$_{21}$	468	0.010	5.0	75.6								
TOBP-PG$_{21}$Ac$_{21}$	455	0.013	2.2	72.3	445	0.010	2.6	71.5	437	0.010	2.8	76.3
TOBP-PG$_{80}$	454	0.025	5.5	71.5								
TOBP-PG$_{80}$Ac$_{80}$	447	0.018	3.6	73.0	438	0.026	3.3	72.0	428	0.026	3.0	73.1
TOBP-PG$_{113}$	451	0.030	6.8	73.6								
TOBP-PG$_{113}$Ac$_{113}$	436	0.028	4.8	73.6	435	0.035	4.0	73.0	422	0.043	4.0	74.0

[a] Fluorescence studies have been performed in three different solvents, except for non-acetylated polymers, which are only soluble in methanol: maximum emission wavelength (λ_{em}), fluorescence quantum yield (Φ_f), fluorescence lifetime (τ_f), and energy of the singlet excited state (E_S). [b] Units: nm (λ_{em}), ns (τ_f), kcal·mol^{-1} (E_S). [c] Fluorescence emission of solutions normalized to the same absorbance (0.3) at $\lambda_{ex} = 355$ nm. [d] From ref 22.

erol backbone); 6.45 (br, 2H), 6.60 (br, 2H), 7.40 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) 19.1, 19.2, 60.9, 67.7, 67.9, 68.1, 68.2, 68.3, 98.0, 98.2, 99.3, 104.3, 114.7, 126.9, 129.1, 130.6, 156.1, 157.1, 157.2, 160.7, 168.4, 168.8.

Model Compound TMBP. A 100 mL two-neck flask equipped with a condenser and stirring bar was charged with 2,2′,4,4′-tetrahydroxybenzophenone (2.0 g, 8.10 mmol) and potassium carbonate (4.5 g, 32.4 mmol), methyl iodide (2.5 mL, 40.5 mmol), and crown ether (0.2 g, 0.8 mmol) and purged with argon. Freshly distilled acetone (30 mL) was added, and the mixture was stirred at reflux for 48 h. The reaction mixture was then cooled to room temperature and filtered. The filtrate was concentrated in vacuum and the residual solid was chromatographed on silica gel with a mixture of hexane/dichloromethane (1:1, v/v). The final product was recrystallized from dichloromethane and hexane, yielding 1.7 g (70%) as white crystalline solid: $R_f = 0.2$. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.68$ (s, 6H), 3.87 (s, 6H), 6.44 (d, 2H, $J = 2.4$ Hz), 6.50 (dd, 2H, $J_1 = 8.6$ Hz, $J_2 = 2$ Hz), 7.71 (d, 2H, $J = 8.8$ Hz). ^{13}C (100 MHz, $CDCl_3$): $\delta = 55.4$, 55.7, 98.5, 104.3, 123.9, 132.5, 160.1, 163.4, 193.0. MS EI (*m/z*): 302 (M^+, 60), 285 (75), 165 (100).

Results and Discussion

The hyperbranched polyethers with photoactive core were prepared from 2,2′,4,4′-tetrahydroxybenzophenone (**THBP**, cf. Scheme 1). Incorporation of the benzophenone core within the hyperbranched PG structure was achieved using similar conditions as those published previously for aliphatic trifunctional initiators.[12a,b,d] **THBP** was partially deprotonated (20%) with potassium *tert*-butoxide, and glycidol was slowly added in the course of several hours. The targeted polymers **TOBP-PGs** were obtained in essentially quantitative yields, and all samples exhibited narrow polydispersity, taking into account that according to theory the expected polydispersity would be $M_w/M_n = 1.25$ for a tetrafunctional initiator.[18] Molecular weights and polydispersities of all polymers are summarized in Table 1. As expected, the materials showed good solubility in MeOH, but were insoluble in less polar organic solvents, due to the polar end groups.

For the subsequent investigation of the photophysical and photochemical properties, a fraction of the samples was peracetylated (**TOBP-PGAc**) in order to modify their solubility. All hyperbranched polyglycerols with BP core were characterized by ^1H and ^{13}C NMR spectroscopy and size-exclusion chromatography (SEC) technique with respect to both the degree of branching (DB) and molecular weight as well as with FT-IR and UV−vis spectroscopy. The obtained data confirm the absence of residual benzophenone initiator. Table 1 summarizes characterization results for all polyglycerols with benzophenone core (**TOBP-PG**) as well as for their acetylated analogs (**TOBP-PGAc**).

Molecular weights were calculated by ^1H NMR, by comparison between the integration of the aromatic signals of the incorporated benzophenone core shifted between 6.40 and 6.75 ppm, which were taken as reference, with the integration of the signals corresponding to the hyperbranched corona (eq 1, Supporting Information). NMR experiments were recorded in methanol-d_4 and chloroform ($CDCl_3$) for **TOBP-PG** and **TOBP-PGAc**, respectively. The degree of branching (DB) values, calculated from ^{13}C NMR, for all hyperbranched samples were in the range of 0.36−0.45. A full assignment of all ^{13}C NMR signals to the four different units (dendritic (D), terminal (T), and linear ($L = L_{13} + L_{14}$)) was achieved as described previously.[12a]

Furthermore, samples of **TOBP-PG** and **TOBP-PGAc** in dimethylformamide and chloroform, respectively, were examined by analytical size-exclusion chromatography (SEC), which was calibrated using polystyrene. This analysis gave molecular weights significantly different to those calculated from ^1H NMR analysis. We attribute this to the different shape and flexibility of the hyperbranched polymers in comparison to the linear polystyrene standards used for calibration.[19] It is also worth mentioning that the molecular weight obtained from NMR data closely matched the expected molecular weight calculated from

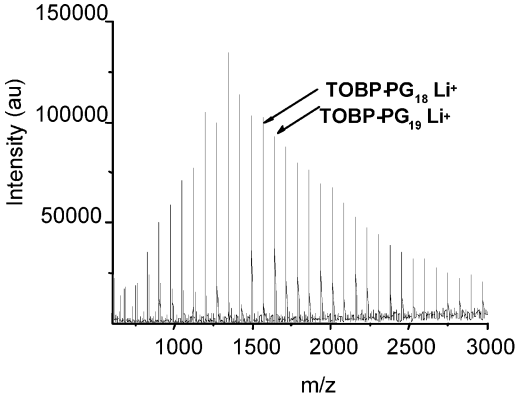


Figure 1. Low molecular weight region of the MALDI-ToF mass spectrum of benzophenone-cored hyperbranched polyglycerol **TOBP-PG$_{21}$**.

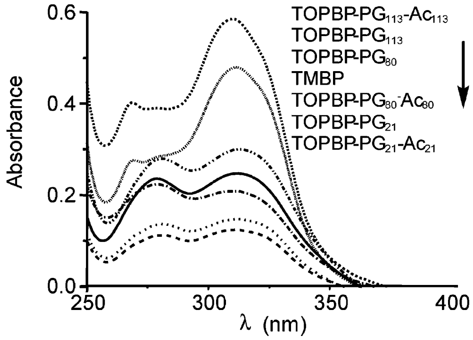


Figure 2. Absorption spectra of 10^{-5} M solutions of **TMBP** and the **TOBP-PGs** in MeOH.

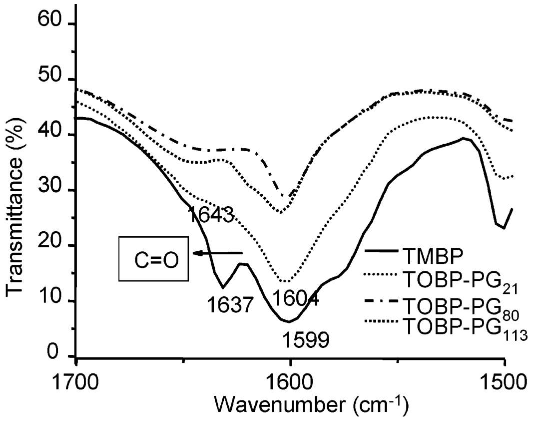


Figure 3. Transmission FTIR absorption spectra of **TMBP** and **TOBP-PGs**.

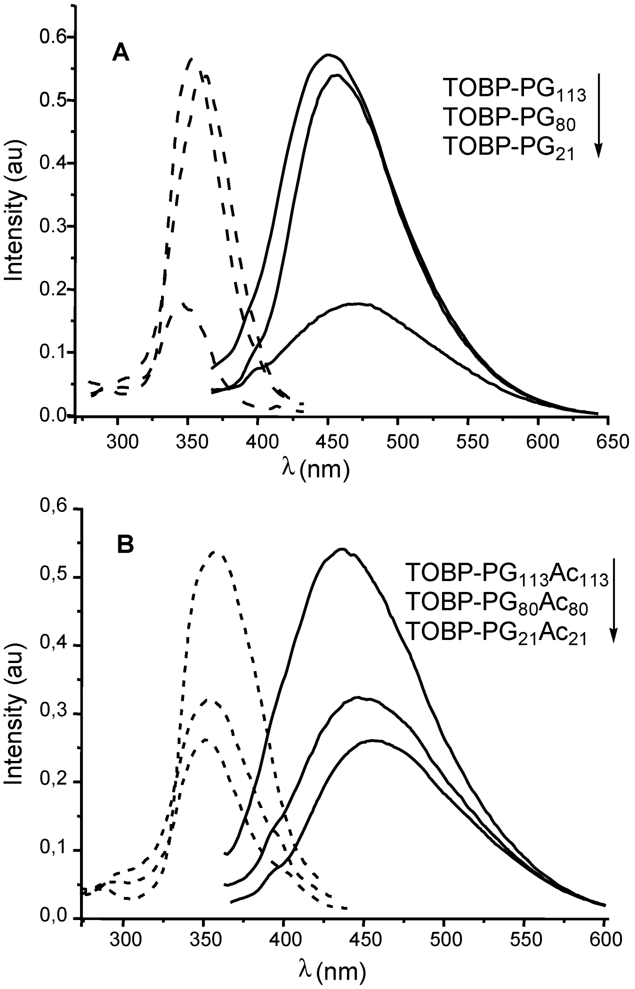


Figure 4. Normalized excitation (left) and emission (right) spectra of **TOBP-PGs** (A) and **TOBP-PGAcs** (B) measured in MeOH.

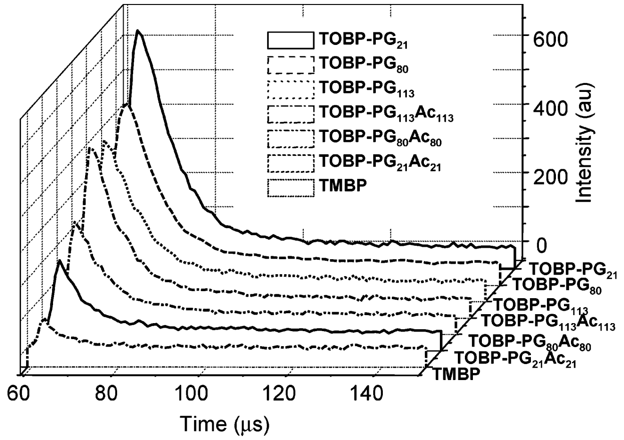


Figure 5. Fluorescence decay traces ($\lambda_{exc} = 355$ nm, λ_{em} = maximum emission wavelength) of **TMBP** and **TOBP-PGAcs** in MeOH.

monomer to core ratio for all BP-cored hyperbranched polyglycerols.

There are several crucial issues for the ensuing discussion of the incorporation of the BP-core into the hyperbranched structure, (i) whether all four hydroxyl groups of **THBP** participate as initiating sites for the polymerization of glycidol and whether (ii) all polymer species of the distribution contain a BP-core. Since the phenolic OH-groups of **THBP** are more acidic than the aliphatic primary and secondary hydroxyl groups of the glycerol units, the core possesses higher reactivity for ether formation than the aliphatic hyperbranched structure. Consequently, this enhanced core reactivity should result in fast and complete alkylation of the four hydroxyl groups of the benzophenone and, therefore, full core incorporation. A comparison of the ^{13}C NMR signals assigned to the carbons bearing hydroxyl groups for **THBP**, **TMBP**, and **TOBP-PG$_{21}$** supports this hypothesis (Figure S1 in ESI). The two resonances at 165.5 and 164.4 ppm in **THBP** shift to higher field upon alkylation, appearing at 163.4 and 160.1 ppm for **TMBP** and as broad bands at ca. 165.0 and 161.1 ppm in the case of **TOBP-PG$_{21}$**. Further confirmation of the branching at all four phenolic OH-groups is obtained from the photophysical studies performed for the hyperbranched materials and the model compound in both ground and excited state (*vide infra*).

Quantitative incorporation of a core into all species of a molecular weight distribution of a hyperbranched polymer can

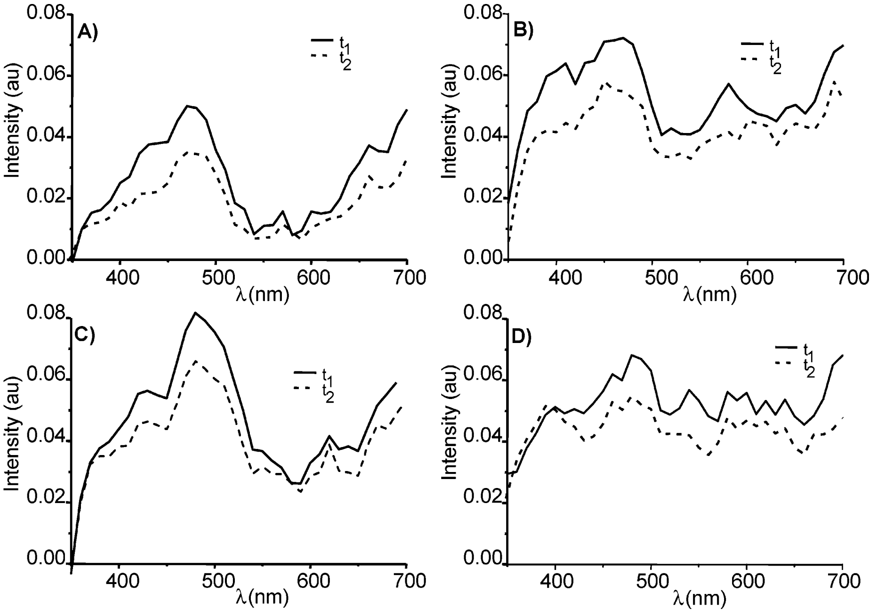


Figure 6. Transient absorption spectra of triplet excited-state of (A) **TMBP** in MeOH, (B) **TMBP** in acetonitrile, (C) **TOBP-PG$_{21}$Ac$_{21}$** in MeOH, and (D) **TOBP-PG$_{21}$Ac$_{21}$** in acetonitrile. The excitation wavelength was 355 nm, and the spectra were obtained $t_1 = 0.07$ μs and $t_2 = 0.81$ μs after the laser pulse.

only be proven unequivocally by suitable mass-spectrometry methods. We have employed MALDI−TOF MS to confirm incorporation of the **THBP** into the hyperbranched polyglycerol samples. Figure 1 shows the central part of the MALDI−TOF mass spectrum of **TOBP-PG$_{21}$** between 500 and 3000 g/mol. The mass differences between the peaks represent the molar mass of glycidol ($M = 74.1$). The mass of each signal in the molecular weight distribution corresponds to the sum of the **THBP** mass ($M = 246.2$) and the mass of the respective number of glycidol repeating units plus one lithium ion ($M = 7.02$). As expected, the molecular weight obtained for **TOBP-PG$_{21}$** from the mass spectrometry measurements closely matches the calculated value. The presence of a single distribution mode, as well as the absence of masses corresponding to non-core-containing PG homopolymers, evidences quantitative incorporation of the benzophenone core. Similar results were obtained for all polymers listed in Table 1.

UV—Visible Studies. The UV−vis absorption spectra of the **TOBP-PG** series and that of the model compound **TMBP** were obtained in solvents of different polarity, such as methanol (Figure 2), acetonitrile and dioxane (see Figure S2 in Supporting Information). It is known that the **TMBP** absorption spectrum exhibits two strong bands, with maxima at $\lambda = 278$ nm ($\log \epsilon = 4.45$) and 312 nm ($\log \epsilon = 4.42$) in methanol, plus a long tail in the lowest-energy region (Figure 2).[20] The band at 312 nm has been assigned to the 2,4-dimethoxybenzoyl chromophore by comparison with absorption spectra of substituted benzophenones.[21] On the other hand, the absorption at longer wavelengths, partially overlapped by the high-intensity band at 312 nm, can be assigned to the carbonyl n,π* transition.[22] The π,π* transition undergoes a small hypsochromic shift in less polar solvents (from 312 nm in methanol to 307 nm in dioxane), in agreement with the π,π* character of this electronic transition (Table 1).

The UV−vis spectra of the **TOBP-PG$_x$Ac$_x$** hyperbranched polymers showed similar features to that for **TMBP** (Figure 2). An insignificant hypsochromic shift (less than 2 nm) of the π,π* transition is observed when the chromophore is encapsulated (Table 1). Therefore, the appreciable bathochromic shift (ca. 10 nm) of the π,π* transition with the solvent polarity for each hyperbranched derivative supports that solvent is present at the photoactive core.

Covalent incorporation of the benzophenone core within the polymer could promote deviations from planarity decreasing resonance stabilization and therefore, increasing the energy of the C=O stretching mode due to the double bond character enhancement[23] (when compared with **TMBP**). Indeed, the carbonyl stretching band located at 1637 cm^{-1} for **TMBP** shifts to 1643 cm^{-1} in the case of the **TOBP-PGs** (Figure 3).

In addition, a systematic increase of the absorbance with the degree of polymerization of PG was observed for the **TOBP-PG** series. This phenomenon has not been detected previously in analogous dendrimers containing the same chromophore, but possessing a long alkyl chain linking the core to a polar dendron structure.[17] There, the absorbance of the dendritic benzophenone is dramatically decreased compared to that of **TMBP** and shows little variation between different dendrimer generations. However, the increase of the chromophore absorbance within the encapsulating hyperbranched polymer should be interpreted with caution, since they are not monodisperse macromolecules.

It is important to stress that the steady-state UV−vis absorption spectra of the **TOBP-PG** series also support the functionalization of all four phenolic groups, since it is known that the absorption band of **TMBP** at 312 nm (in methanol), assigned to the 2,4-dimethoxybenzoyl chromophore, shifts to longer wavelengths for the non-methylated analogoues (329 nm for 2,2′-dihydroxy-4,4′-dimethoxybenzophenone and 348 nm for 2,2′,4,4′-tetrahydroxybenzophenone in methanol).[18] In addition, a large decrease in intensity is observed in the hydroxylated benzophenones, when compared with **TMBP**.

Fluorescence Experiments. The fluorescence spectra of the hyperbranched polymer series (**TOBP-PG$_{21}$**, **TOBP-PG$_{80}$**, and **TOBP-PG$_{113}$**) as well as those of their acetylated derivatives (**TOBP-PG$_{21}$Ac$_{21}$**, **TOBP-PG$_{80}$Ac$_{80}$**, and **TOBP-PG$_{113}$Ac$_{113}$**) were measured in solvents of different polarity, using solutions normalized to the same absorbance (0.3) at λ_{exc} 355 nm (see Figure 4, Figure S1 in the Supporting Information, and Table 2). The excitation spectra (measured at the maximum emission wavelength, λ_{em}) for all compounds confirmed that - as expected

- the emission band is not related to the strong absorption at λ_{max} ca. 300 nm (π,π^* transition) but to a weak absorption located close to 350 nm, partially overlapped by the high-intensity π,π^* band. This absorption can be safely assigned to the n,π^* transition by comparison with that of **TMBP**.[20]

Figure 4 shows the normalized emission and excitation spectra for **TOBP-PGAcs** in methanol, acetonitrile, and dioxane. The intersection between both traces allowed us to locate the 0−0 transitions and to estimate the singlet excited-state energy (E_S). This value is, in general, slightly affected by the solvent and is similar for all the polymers.

It is interesting to note that the incorporation of the chromophore in the hyperbranched structure causes a dramatic and progressive blue shift of the fluorescence emission maximum (up to 44 nm), resulting in a gradual decrease of the Stokes shift with the "thickness" of the branched corona (Figure 4). This observation could be considered as an indication for an increase of rigidity in the direct environment of the chromophore,[24] which could finally result in a decrease of the nonradiative decay rate constant.[25] Indeed, a remarkable enhancement of fluorescence quantum yield (up to 10 times) and lifetime (up to 5 times) with increasing molecular weight was measured (Table 2 and Figure 5).

For comparison, analogous aliphatic polyester-based dendrimers containing a 2,2′-4,4′-tetraalkoxybenzophenone core also show more intense fluorescence (Φ_f up to 0.03) than **TMBP**.[17]

Laser Flash Photolysis Experiments. By understanding of the normal deactivation processes of these fluorescent molecules, peculiar encapsulation effects may be observed. The typical deactivation of the singlet excited-state involves nonradiative deactivation by internal conversion to the ground state (due to quenching with the solvent or energy dissipation through bond rotation or vibrations), and intersystem crossing to the triplet state. In order to detect the T−T absorption of **TOBP-PGs** and **TOBP-PGAcs**, laser flash photolysis (LFP) experiments (Nd:YAG, 10 ns laser pulse, $\lambda_{exc} = 355$ nm) were carried out, using deaerated solutions with the same absorbance (0.3) at the excitation wavelength (see Figure 6, parts C and D, for **TOBP-PG$_{21}$Ac$_{21}$**; spectra of **TMBP** are also included for comparison). In methanol, the transient absorption bands of the **TOBP-PG$_{21}$Ac$_{21}$** samples are located at λ_{max} 470 and 680 nm (Figure 6C). These absorptions could be assigned mainly to a triplet state of π,π^* character by comparison with **TMBP** in methanol (Figure 6A).[26] In contrast, the spectrum obtained in acetonitrile showed the important contribution of both n,π^* (λ_{max} 580 nm) and π,π^* triplets (Figure 6D). Again, this behavior has been previously observed for **TMBP** in acetonitrile (see Figure 6B), This shows that the nature of the populated triplet for **TOBP-PGs** and **TOBP-PGAcs** is only weakly affected by the branched shell, but depends on the type of solvent, which again evidences solvent access to the incorporated chromophore.

Triplet quantum yields (Φ_{isc}) and lifetimes (τ_T) for the **TOBP-PG** series and **TMBP** compound in methanol are summarized in Table 3. The data reveal that Φ_{isc} for the hyperbranched derivatives are generally higher than for **TMBP**, which differ considerably from that of benzophenone (Φ_{isc} close to 1). The decrease of the **TMBP** intersystem crossing in the polar solvent methanol can most likely be attributed to charge-transfer deactivation of the singlet excited-state favored by substitution of electron-donating groups at the aromatic ring, as is obvious from the comparison with the behavior of 4-methoxybenzophenone.[27] Therefore, the higher Φ_{isc} for the **TOBP-PGs** could be a consequence of loss of conjugation within the 2,4-dialkoxybenzoyl moiety in the polymers.

Table 3. Triplet−Triplet Quantum Yield and Lifetime for TMBP and TOBP-PGs in MeOH[a]

compound	Φ_{isc} [b]	τ_T (μs)
TMBP	0.50	1.27
TOBP-PG$_{21}$	0.55	1.42
TOBP-PG$_{80}$	0.63	1.86
TOBP-PG$_{113}$	0.61	0.72
TOBP-PG$_{21}$Ac$_{21}$	0.79	2.30
TOBP-PG$_{80}$Ac$_{80}$	0.57	2.33
TOBP-PG$_{113}$Ac$_{113}$	0.49	2.14

[a] Solutions were normalized to the same absorbance ($A = 0.3$) at $\lambda_{exc} = 355$ nm. [b] Determined by a comparative method, using 4-methoxybenzophenone (see Supporting Information); the extinction coefficient value used for the calculations was that estimated for **TMBP** by the conventional energy-transfer method.

On the other hand, in accordance with the π,π^* nature of the triplet excited state, τ_T for **TMBP** and the **TOBP-PGs** in methanol are longer-lived than that of benzophenone of n,π^* nature ($\tau_T \ll 0.5$ μs), being generally higher for the hyperbranched derivatives.

In order to further investigate the role of the hyperbranched corona, photostability studies of the encapsulated chromophore were performed in both acetonitrile and methanol. The polymer is recovered practically unchanged after 1 h of irradiation time at $\lambda > 320$ nm in methanol, but is chemically modified in acetonitrile. It is known that the efficiency of the photoreduction of aromatic carbonyl compounds by hydrogen-atom donors (as hydrocarbons and alcohols) strongly depends on the electron configuration of the T_1 state. The results on photostability of the polymers agree well with LFP experiments, and the modification of the chromophore in acetonitrile is related to the high abstraction capability of the n,π^* triplet excited state.

To assess the effect of the encapsulation of benzophenone by PG of varying molecular weight, we measured the quenching rate constant of the triplet excited-state of the ketone in the polymers ($k_{q(\mathbf{TOBP-PG})}$)and **TMBP** ($k_{q(\mathbf{TMBP})}$) by naphthalene. The ratio $k_{q(\mathbf{TOBP-PG})}/k_{q(\mathbf{TMBP})}$ decreased with the molecular weight of the polymer (0.27 for **TOBP-PG$_{21}$** and 0.16 for **TOBP-PG$_{113}$**), which indicates some restriction to the access to the core due to the branched shell.

Conclusions

A practical and straightforward strategy for the incorporation in a one-pot procedure of a single photoactive core entity within a hyperbranched polymer is described for the first time. It has been developed using a tetrahydroxyfunctional benzophenone moiety as the initiator-core. A series of hyperbranched polyglycerols with benzophenone core and different molecular weights ($M_n = 1500$ to 5800 g/mol) and moderate polydispersity ($1.3 < M_w/M_n < 2$) has been obtained. The phenolic nature of the hydroxyl groups at benzophenone and the facile deprotonation of this core lead to fast and complete incorporation into the hyperbranched polymers formed. Conclusive evidence for core incorporation has been obtained from MALDI−TOF MS data. To the best of our knowledge, this represents the first example of a hyperbranched polymer with a well-defined photoactive core moiety.

The steady-state UV−vis absorption spectra of the **TOBP-PG** series show that the wavelength of maximum absorbance of the π,π^* transition, assigned to the 2,4-dimethoxybenzoyl chromophore, undergoes an insignificant hypsochromic shift when the chromophore is encapsulated, but is affected by the solvent polarity. This result supports the assumption that the solvent surrounds the photoactive core. In agreement with this model, the nature of the lowest-lying triplet of the tetraalkoxybenzophenone core changes with the polarity of the solvent. However, the remarkable decrease of quenching rate constant of the aromatic ketone triplet excited-state by naphthalene with the extent of the branched corona is an evidence of chromophore encapsulation. This is an interesting result, since this kind of encapsulation of a core function has only been associated with the structurally perfect dendrimers to date.[28]

Fluorescence studies demonstrate that the presence of a hyperbranched polymer "shell" surrounding the chromophore enhances the fluorescence quantum yield by one order of magnitude. It can be speculated that the branched structure leads to a constrained conformation of the chromophore, which could hinder rotation and decrease the available modes of energy dissipation.

Finally, the benzophenone substituted with a hyperbranched PG-corona showed high photostability in methanol; i.e., no transformation was detected after 1 h of irradiation at $\lambda > 320$ nm. Since such polymer-encapsulated benzophenones can be conveniently separated from the reaction media by dialysis or membrane filtration, they are very promising with respect to easily recoverable and reusable photocatalysts.[29]

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Supporting Information Available: Experimental details including materials, chemicals, analytical methods and spectral data (UV−visible, ^{13}C NMR, fluorescence, and excitation data) for **TOBP-PG$_x$Ac$_x$** and a figure showing a partial ^{13}C NMR spectra of the aromatic carbons' region are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) In fact, preliminary results show that the hyperbranched polymer TOBP-PG$_{113}$ behaves as a recoverable and reusable photocatalyst in diazocompounds transformation. Unpublished results.

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