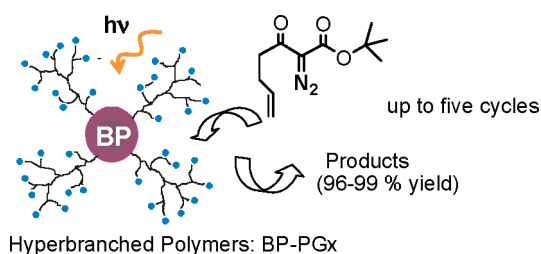## Photocatalysis within Hyperbranched Polyethers with a Benzophenone Core

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Hyperbranched Polymers: BP-PGx

Quenching and product studies have been performed to demonstrate the suitability of hyperbranched polyethers with a tetrafunctionalized benzophenone core as photocatalysts. The triplet photosensitized transformation of an unsaturated diazo compound has been used as the model reaction. The polymer with highest molecular weight led to a similar product distribution even after several catalytic cycles, which evidences its excellent photostability under prolonged irradiation time. We attribute this to the stabilizing effect of the hyperbranched polymer shell.

Recently, it has been reported that covalent encapsulation of photocatalytically active functionalities at the core of the perfectly branched dendrimers gives rise to attractive photocatalysts for the oxidation of sulfides and olefinic compounds via the photosensitized generation of singlet oxygen from ground-state oxygen.[1] In photoactive core-functionalized dendrimers, the photocatalytic site is isolated by the action of the dendritic backbone, which acts as a gatekeeper for substrate access to the photocatalytic center.[2] A unique variation of the product distribution observed in solution can take place by mere geometric constraints arising from the different shape and

SCHEME 1. Synthesis of Hyperbranched Polyether Polymers with Benzophenone Core
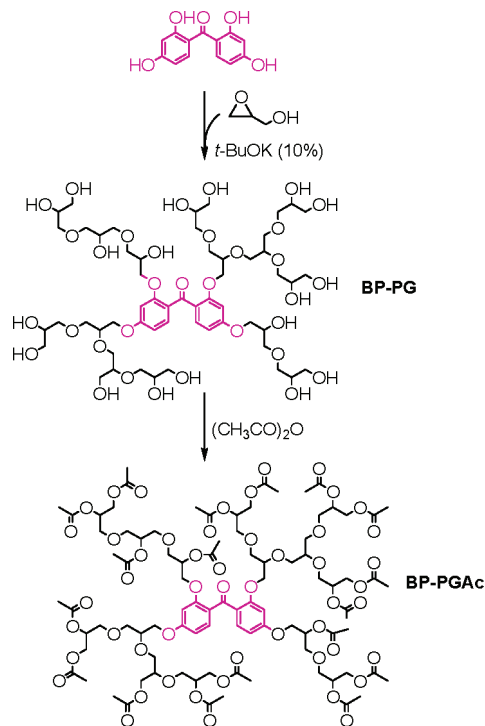
molecular size of substrate, products, or transition states. Other advantages of using dendritic structures, which can be viewed as macrophotocatalysts, arise from their macromolecular size, which enables their recovery using nanofiltration techniques and their further reuse in multiple cycles.[1] However, the highly demanding multistep synthesis and purification of perfect dendrimer systems limits their potential use as macrophotocatalysts, particularly in industrial applications.[3]

In contrast, we have recently reported that the triplet photosensitizer benzophenone can be incorporated at the core of hyperbranched polyether polyols in a one-step protocol by using deprotonated 2,2′,4,4′-tetrahydroxybenzophenone as initiator core in the anionic polymerization of glycidol (Scheme 1).[4] Photoactive hyperbranched polyether polyols (**BP-PGs**) of remarkably narrow polydispersity ($1.3 < M_w/M_n < 2$) are obtained. Further modification by acetylation of the hydroxyl groups affords hyperbranched polymers **BP-PGAcs** of lowered polarity. The branched backbone enhances the very low fluorescence quantum yield of benzophenone by 1 order of magnitude (0.004 for 2,2′,4,4′-tetramethoxybenzophenone, TMBP, and up to 0.030 for the covalently encapsulated benzophenone).[4,5] Laser flash photolysis studies have shown the π,π^* nature of

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(1) Chavan, S. A.; Maes, W.; Gevers, L. E. M.; Wahlen, J.; Vankelecom, I. F. J.; Jacobs, P. A.; Dehaen, W.; De Vos, D. E. *Chem. Eur. J.* **2005**, *11*, 6754. Shiraishi, Y.; Koizumi, H.; Hirai, T. *J. Phys. Chem. B* **2005**, *109*, 8580. Hecht, S.; Vladimirov, N.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2001**, *123*, 18.
(2) Aathimanikandan, S. V.; Sandanaraj, B. S.; Arges, C. G.; Bardeen, C. J.; Thayumanavan, S. *Org. Lett.* **2005**, *7*, 2809.

(3) (a) Alberto, J. *Annu. Rep. Prog. Chem., Sect. C* **2003**, *99*, 177. (b) In the photocatalysis application issue, dendrimers have also been used as photochemical reaction media; see: Kaanumalle, L. S.; Nithyanandhan, J.; Pattabiraman, M.; Jayaraman, N.; Ramamurthy, V. *J. Am. Chem. Soc.* **2004**, *126*, 8999.
(4) Pastor-Pérez, L.; Barriau, E.; Nicoletti, E. B.; Kilbinger, A. F. M.; Pérez-Prieto, J.; Frey, H.; Stiriba, S.-E. *Macromolecules* **2008**, *41*, 1189.
(5) (a) Pastor-Pérez, L.; Wiebe, C.; Pérez-Prieto, J.; Stiriba, S.-E. *J. Org. Chem.* **2007**, *72*, 1541. (b) Full characterization of diazo **1** and photolysis products **2−4** have been recently reported (see ref 5a).

SCHEME 2. Reaction Pathways for the Transformation of Diazo Compound 1

R = C(CH₃)₃
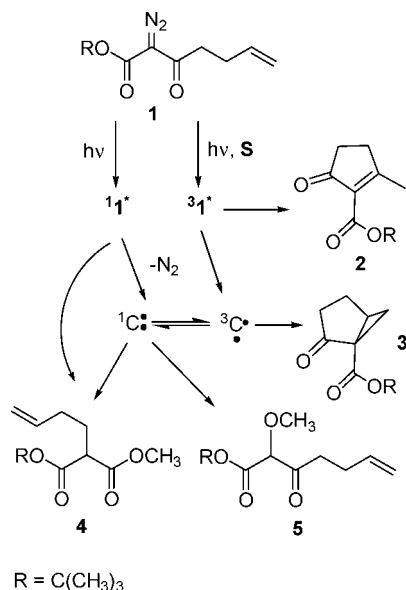
the lowest-lying triplet excited-state of TMBP in methanol. Therefore, it is less prone than benzophenone (BP) to abstract hydrogen from hydrogen donors, such as methanol. As these polymers can be conveniently separated from the reaction medium by dialysis or membrane filtration, they could behave as straightforward prepared, recoverable, and reusable triplet photocatalysts.

Here we report studies performed on the photoinduced transformation of α-diazo carbonyl **1** in the presence of catalytic amounts of various hyperbranched polymers with different molecular weights, namely **BP-PG₂₁** (1520 g/mol), **BP-PG₂₁Ac₂₁** (2120 g/mol), and **BP-PG₁₁₃** (8340 g/mol). The subscript of PG denotes the degree of polymerization, while the subscript of Ac points to the number of acetyl groups achieved after acetylation of the hydroxyl groups. The results demonstrate that hyperbranched polymers covalently incorporating a photoactive functional core can behave as long-lasting photocatalysts.

Direct irradiation[6] of α-diazo-β-keto ester **1** in methanol leads mainly to the Wolff rearrangement product **4**, which arises from the singlet excited-state of the diazo (^{1}**1***) via a concerted or nonconcerted extrusion of nitrogen (^{1}C, singlet carbene as the intermediate); see Scheme 2 and run 1 in Table 1. In addition, the solvent O−H insertion product **5** (a product originating from ^{1}C) and the cyclopropanation product **3** (a product resulting from the triplet carbene, ^{3}C, generated due to spin equilibration of the carbene) are obtained as secondary products.[5b]

In contrast, TMBP-photosensitization[5] gives rise to the diazo triplet (^{3}**1***), which finally affords **3** and 2-methyl-5-oxocycloalk-1-enecarboxylate **2** (Scheme 2 and run 3 in Table 1). The latter compound is only observed in the triplet-photosensitized process; therefore, it has been suggested that it derives from the diazo triplet excited state via a process which does not involve the triplet carbene as intermediate. The complete transformation of **1** in the TMBP-photosensitized process requires considerable irradiation times (5 h when using a 20% of TMBP).

Hence, the photosensitized irradiation of diazo **1** can be used as a model reaction to examine the suitability of hyperbranched

(6) Fien, J.; Kirmse, W. *Angew. Chem., Int. Ed.* **1998**, *37*, 2232.

TABLE 1. Photocatalytic Results[a]

run	sensitizer	mol %	yield[b,c] (%)	2	3	4	5
1	without sensitizer[d]		92		20	64	16
2	without sensitizer[e]		99		25	51	24
3	**TMBP**	25	99	20	78	0	2
4	**BP-PG₂₁**	10	96	13	74	9	4
5	**BP-PG₂₁**	20	99	10	78	9	3
6	**BP-PG₂₁Ac₂₁**	20	97	10	74	10	6
7	**BP-PG₁₁₃**	20	96	14	60	21	5

[a] Deaerated methanol solutions irradiated for 5 h at 400 > λ > 320 nm. [b] Calcultated from ¹H NMR NMR spectra of the crude reaction mixture; the experimental error in these measurements is about 5%. [c] A small amount of the diazo compound is recovered unchanged. [d] Irradiation conditions: Direct irradiation of a deaerated methanol solution during 5 h at λ > 300 nm. [e] Irradiation conditions: Direct irradiation of a deaerated methanol solution during 5 h at λ > 300 nm in the presence of BP-free hyperbranched polymer (20 mol%) of a molecular weight of 5400 g/mol.

polymers PG-BPs to act as photocatalysts, taking into account the following facts: (a) the rate of quenching of the polymers' excited states by **1** could indicate branching effects on substrate diffusion; (b) the change of product distribution after reusing BP-PGs in several cycles would be used as a probe of polymer degradation; (c) in the case of photostable polymers, the product distribution would verify whether the polymer branches play a role in the photocatalyzed transformation of **1**. Combining these data, one obtains information on the branching effect as well as on the convenience and suitability of this type of hyperbranched structures for the encapsulation of a photoactive core as easy to prepare, recoverable, and reuseable photocatalysts in organic synthesis.

The fluorescence quenching of **BP-PG₂₁** and **BP-PG₁₁₃** by diazo compound **1** was studied in methanol, using solutions of the polymer normalized to the same absorbance (0.3) at λ_{exc} 355 nm (see Figure 1). The polymers' singlet excited states were significantly quenched by the diazo compound, with a higher efficiency for the lower molecular weight polymer. The quenching rate constants (4.1×10^{11} M⁻¹ s⁻¹ and 1.8×10^{11} M⁻¹ s⁻¹ for **BP-PG₂₁** and **BP-PG₁₁₃**, respectively) were higher than the diffusion rate constant in methanol (1.2×10^{10} L M⁻¹ s⁻¹) or diethyl ether (3.0×10^{10} L M⁻¹ s⁻¹), which indicated that the fluorescence quenching of these polymers by **1** could have a static contribution in addition to the dynamic quenching process. Consequently, the triplet quantum yield of the polymers should decrease in the presence of increasing amounts of the diazo compound.

The triplet−triplet absorption spectra of the polymers were obtained in deaerated methanol, using a Nd:YAG laser (λ_{exc} at 355 nm, 10 ns laser pulse) and samples with the same absorbance (0.5) at the excitation wavelength (see Figure 2 for **BP-PG₂₁** and **BP-PG₁₁₃**). The transient absorption spectra of the polymers were similar to that of TMBP.

The efficiency in the formation of the polymer triplet excited-state in the presence of different amounts of **1** was followed by measuring the intensity of the triplet absorption spectrum immediately after the laser pulse (topΔA), using λ = 500 nm as the monitoring wavelength. In fact, these data evidenced that the triplet quantum yield decreased linearly with the diazo compound concentration, whose influence was smaller for **BP-PG₁₁₃** (Figure 3) in spite of its higher fluorescence quantum yield and singlet lifetime (0.03 and 6.8 ns vs 0.01 and 5.0 ns for **BP-PG₁₁₃** and **BP-PG₂₁**, respectively).[4] For comparison, the studies were also performed for TMBP (Figure 3).
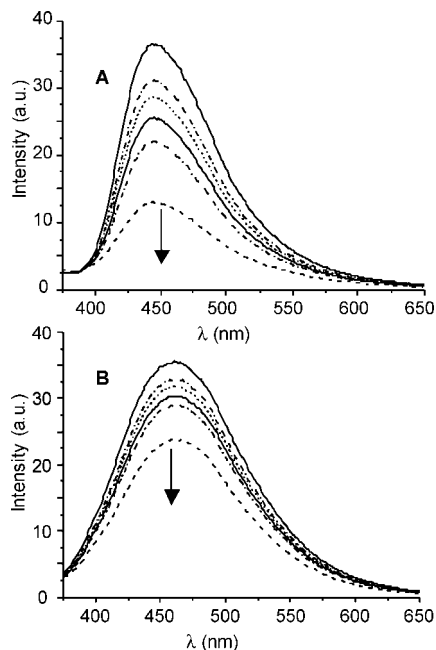
FIGURE 1. Fluorescence spectra of **BP-PG$_{21}$** (A) and **BP-PG$_{113}$** (B) (absorbance 0.3, λ_{exc} = 355 nm) in the presence of increasing amounts of diazo compound **1** (8.7×10^{-5} M, 1.4×10^{-4} M, 2.1×10^{-4} M, 2.9×10^{-4} M, 5.4×10^{-4} M).
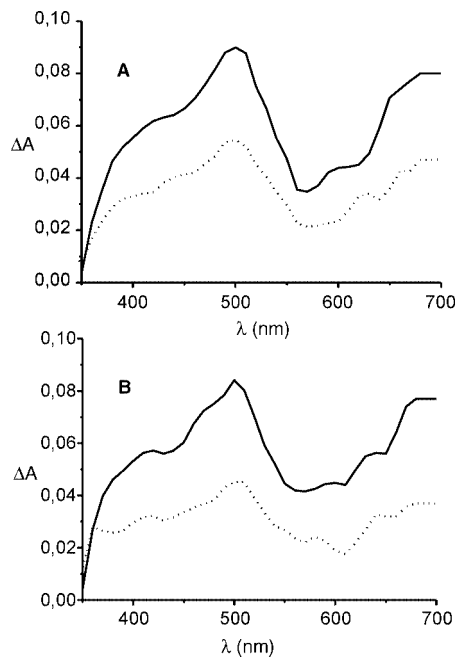
In addition, **1** was also an effective quencher of the polymers' triplet excited states. The kinetic evaluation of the quenching process at room temperature was performed by monitoring the triplet lifetime as a function of the quencher concentration (Figure 4).

The data fit well with eq 1:

$$\tau_0/\tau - 1 = \tau_0 kq[Q] \tag{1}$$

Stern−Volmer plots showed a linear dependence of τ_0/τ - 1 on [**1**] at concentrations up to 0.05 mM (Figure 4). The slopes provided the second-order rate constant of **^{3}BP-PG*** deactivation by the quencher multiplied by its lifetime ($\tau_0 kq$). From the kinetic evaluation, the k_q values found for **BP-PG$_{21}$** and **BP-PG$_{113}$** were 2.1×10^{10} and 1.6×10^{10} M^{-1} s^{-1}, respectively.[7] Therefore, they were close to the diffusion rate constant in methanol or diethyl ether, but k_q was slower for the higher molecular weight polymer, which reflects increasing difficulty for the diazo substrate to approach the photocatalytic center in this polymer. The quenching rate constant of the triplet excited state of TMBP by **1** is much lower ($k_q = 5.4 \times 10^9$, see Figure 4); therefore, the higher values of k_q in the polymers may reflect the close proximity of quencher molecules to the photosensitizer, located at the polymer core, whenever it becomes excited by a photon, i.e., an "encapsulation effect". The difference between the polymers could agree with a larger amount of quencher molecules remote from the core in the higher molecular weight polymer.

Product studies were performed using two different proportions (10% and 20% M) of **PG-BP**, methanol as a solvent, and excitation at wavelengths 400 > λ > 320 nm (Table 1). For comparison, **1** was directly irradiated in methanol at λ > 300 nm in the presence and absence of BP-free hyperbranched

(7) The triplet quantum yield ϕ_T and lifetime τ_T of BP-PG$_{113}$ and BP-PG$_{21}$ are 0.61 and 0.72 ns for the former and 0.55 and 1.42 ns for the latter (see ref 4).

FIGURE 2. Transient absorption spectra of deaerated solutions of **BP-PG$_{21}$** (A) and **BP-PG$_{113}$** (B) in methanol recorded 0.035 μs (−) and 0.62 μs (---) after the laser pulse (355 nm).
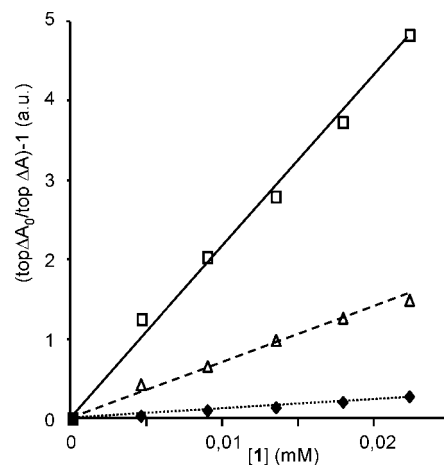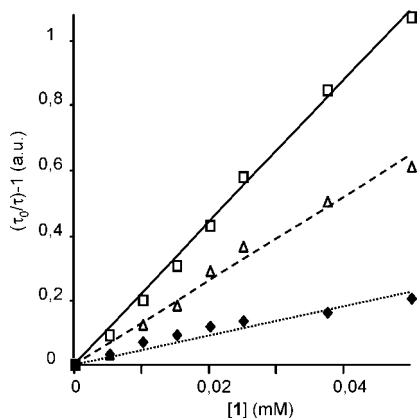

FIGURE 3. Effect of diazo concentration on the absorption of the triplet excited-state of **BP-PG$_{21}$** (□), **BP-PG$_{113}$** (△), and TMBP (◆) in methanol, measured at 500 nm immediately after the laser pulse.

polymer (**PG**) of a molecular weight of 5400 g/mol; the ratio of singlet- to triplet-derived products is similar in both cases (see runs 1 and 2 in Table 1). However, the amount of the solvent O−H insertion product **5** increases in the presence of the polymer. In this case, ^{1}**1*** is generated in the confined and nonconfined media.

The photosensitized irradiation of **1** using 10% of **BP-PG$_{21}$** led to the complete transformation of the diazo compound, affording compound **3** as the major product, but in a slightly smaller quantity than when using TMBP as the photocatalyst (compare runs 3 and 4). This result can be taken as evidence of the occurrence of the reaction predominantly from the triplet excited state. A similar result was obtained when using 10% of **BP-PG$_{21}$Ac$_{21}$** (run 6). No significant differences in yield and product distribution were detected when using a 20% concentration of these photoactive hyperbranched polymers (compare runs 4 and 5). In contrast, the product distribution was significantly

FIGURE 4. Stern−Volmer plot of the quenching of the triplet excited-state of **BP-PG21** (□), **BP-PG113** (△), and TMBP (◆) in methanol by diazo **1**, monitored at 500 nm.

different in the case of **BP-PG113** (run 7); i.e., while the yield of the triplet-derived compound **2** and the solvent O−H insertion product were similar, the fraction of the Wolff product increased at the expense of the cyclopropanation product.[8]

The varying product distribution may reflect a decreased rate constant for the cyclization of the triplet species in the confined space created by the branched shell compared with the fluid medium. In addition, it could reflect the difficulty the reactive species may have in escaping the hyperbranched polymer, which should increase with the molecular weight of the polymer.

In order to test the stability of the macrophotocatalysts, they were separated and recovered from the reaction mixture by dialysis and reused in up to five photocatalytic cycles. The results (see Figure 5 for **BP-PG21** and **BP-PG113**) showed that upon prolonged irradiation, **BP-PG113** afforded a quite similar product distribution, while it changed dramatically in the case of **BP-PG21** (a similar behavior was observed for **BP-PG21Ac21**). Therefore, **BP-PG113** proved to be a remarkably photostable catalyst.

In summary, we have demonstrated the stabilization of a triplet photosensitizer, such as benzophenone, by means of its incorporation at the core of hyperbranched polyethers. The photocatalytic potential of the systems has been evaluated using the triplet photosensitized transformation of a diazo carbonyl compound as the model reaction. These photoactive polymers can be prepared easily, and those with a certain molecular weight can function as efficient, recoverable, and long-lasting photocatalysts.

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(8) A similar product distribution was obtained when using its acetylated derivative **BP-PG113Ac113**.
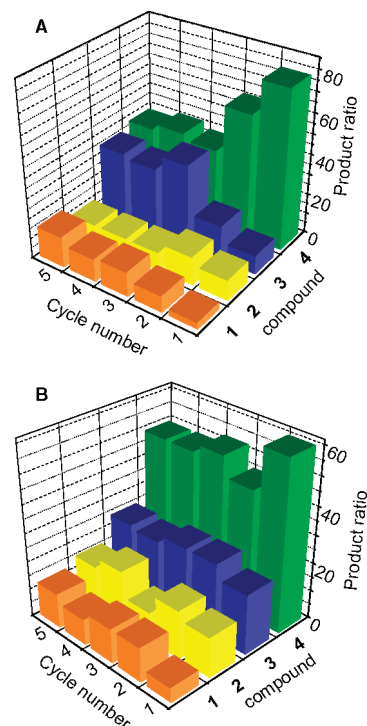
FIGURE 5. Product distribution obtained in the photocatalyzed transformation of diazo compound **1** by **BP-PG21** (A) and **BP-PG113** (B) in up to five cycles. In the case of **BP-PG113**, a 20% of **1** is recovered unchanged in the fifth cycle.

Experimental Section

General Procedure for the Transformation of α-Diazo β-Keto Ester 1 Mediated by BP-PGs. *tert*-Butyl 2-diazo-3-oxo-6-heptenoate (30 mg, 0.134 mmol) was dissolved in 10 mL of distilled MeOH, and a catalytic amount (0.1−0.2 equiv) of the hyperbranched photosensitizer was added under argon atmosphere. The solution was further purged with nitrogen for 15 min and then irradiated for 5 h. At the end of the reaction, the mixture was dialyzed (20 °C, atmospheric pressure) using a cellulose membrane against methanol. The permeate was collected in a flask, the solvent was evaporated, and the reaction crude was analyzed by ¹H NMR. After each dialysis protocol, the retentate was collected; the solvent was evaporated to recover **BP-PG**. The recovered fraction of **BP-PG113** was determined to be around 85%.