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ACTIVE-BAPO – A Versatile Transfer Agent for Photoactive Bis(acyl)phosphane Oxide Units

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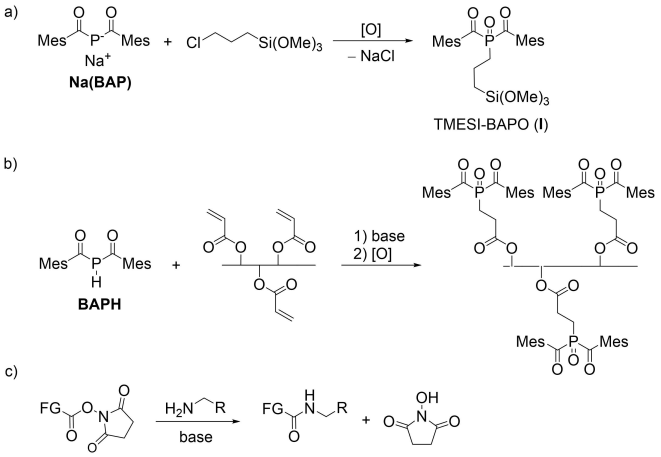
Abstract: A N-hydroxy succinimide (NHS) ester substituted bis(acyl)phosphane oxide (ACTIVE-BAPO) was prepared by phospha-Michael addition and used for an easy one-step BAPO ligation with substrates containing primary amino groups, such as amino acids, proteins, and poly(amidoamine) (PAMAM) dendrimers. Thereby, a range of new molecular and polymeric photoinitators was obtained. Real-time photorheology experiments demonstrated the outstanding efficiency of the PAMAM BAPOs as photoinitiators for free radical polymerization. Remarkably, it is found that PAMAM BAPOs also act as crosslinking agents to convert monofunctional methacrylate monomers into thermosetting networks without any further additives. Depending on the number of the attached BAPOs, thermosets with a different degree of crosslinking and swelling capability in water were obtained.

Introduction

Photoinitiators (PIs) play a key role in photopolymerizations, generating free radicals upon light irradiation that rapidly react with C=C double bonds. Among all known PIs to date, bis(acyl)phosphane oxides (BAPOs, R^1-$PO(COR^2)_2$) are especially useful because they can be activated with visible light of wavelengths from 360 to 420 nm. Under these conditions they are highly reactive Norrish type I initiators, which decompose according to $R^1\text{-}PO(COR^2)_2 + h\nu \rightarrow R^1\text{-}P^{\bullet}O(COR^2) + {}^{\bullet}COR^2$. BAPOs are widely used in various industrial processes for coatings, adhesives, inks, and dental materials.[1–4] Recently, Möckl et al. showed, that BAPOs are also photo-latent cytotoxic agents and potential photo-latent anticancer drugs.[5] Despite these applications, there are relatively few methods available to functionalize BAPO compounds. Because the σ^4,λ^5-phosphoryl radical $R^1\text{-}P^{\bullet}O(COR^2)$ is significantly more reactive, a modification of the R^1 group is especially important and has a deep impact on the physical properties of the polymeric material. A commonly used strategy is the reaction of sodium bis(mesitoyl)phosphide, $Na[P(COMes)_2]$ **[Na(BAP)]** (Scheme 1a), with primary alkyl halides, RCH_2-X, giving P-functionalized BAPOs. These can subsequently be used for the decoration of surfaces with photoactive groups. For example, the trimethoxysilyl-functionalized BAPO compound (TMESI-BAPO, Scheme 1a) can be used for covalent linkage of BAPO units to a cotton textile.[2,6] Subsequent light-induced polymerization from these surface-grafted BAPO units allowed to render these cotton fabrics water- and oil repellent in a durable way. Another method to prepare P-



Scheme 1. Synthetic methods for molecule functionalization with BAPO; Mes = 1,3,5-trimethylphenyl. a) Synthesis of TMESI-BAPO (I) by nucleophilic substitution; b) Synthesis of polymeric multiple BAPOs by phospha-Michael addition (PMA); c) Reaction scheme for the functionalization of a primary amine with an NHS ester, FG = functional group.

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functionalized BAPOs is the phospha-Michael addition (PMA) of **BAPH** as Michael donor to a substrate functionalized with an activated C=C double bond as Michael acceptor. This highly atom-efficient method leads to P-functionalized bis(acyl)phosphanes, BAPs, which are subsequently oxidized to the corresponding BAPO.[7] As an example, the synthesis of γ-cyclodextrin substituted BAPOs is schematically shown in Scheme 1b, which served as multiple photoinitiators and cross-linking agent.[8,9]

However, the synthetic methods mentioned above require either reactive halide functions or activated C=C double bonds in the substrate molecules, which are not always easily introduced in a substrate. Furthermore, the oxidation of the BAP compounds in the second step of the syntheses shown in Scheme 1 exclude functional groups in the substrates, which are sensitive to oxidizing agents (peroxides, oxygen, or oxygen transfer agents such as DMSO or iodosobenzene). We therefore wanted to develop a BAPO reagent, which allows the easy and simple transfer of a complete BAPO unit to a substrate entity. Many bioactive molecules or macromolecules carry a defined number of primary amino groups. It deemed us especially interesting to functionalize these compounds with BAPO units and thereby open new possibilities for the use of BAPOs in bio- and medical devices and allow the synthesis of macromolecular compounds which carry a defined number of BAPO units. One of the most versatile techniques for functionalizing biomolecules such as amino acids and peptides involves the use of chemical groups that react selectively with primary amines. For this purpose, NHS esters have proven the most popular amine-specific functional groups, employed not only for ligations to peptides and proteins but also to dendrimers with terminal NH_2, such as poly(propylenimine) dendrimers (DAB-dendrimer) and poly(amidoamine) dendrimers (PAMAM).[11–22] The reactions are usually performed in aqueous media under mild conditions upon formation of the ligate with an amide bond and giving *N*-hydroxy succinimide, NHS, as the only by-product (Scheme 1c). This preparative method is very convenient for water-soluble substrates and several ligation kits with activated esters are commercially available.[23]

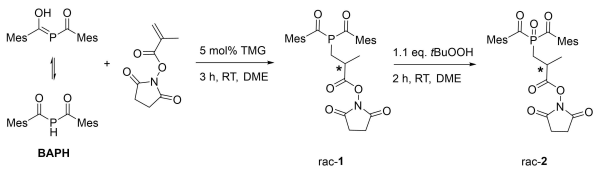
Here, we report the synthesis of an NHS ester substituted BAPO, which we name ACTIVE-BAPO, and which is suitable for an easy one-step ligation of BAPO units to substrates with primary amino functions. The reactions can be performed in water as solvent and a wide range of compounds carrying primary amino groups such as amino acids, peptides, and macromolecular polyamines such as PAMAM dendrimers and gelatin can be used. The latter is a bioderived substrate from porcine skin that has been widely investigated for the preparation of hydrogels.[24–29] As result, multiple BAPOs acting as two-in-one highly efficient photoinitiators for free-radical polymerization and cross-linking agents were obtained. Remarkably, these multiple photoinitiators convert monofunctional methacrylate oligomers into a 3D thermosetting network without any further additives.

Results and Discussion

ACTIVE-BAPO (rac-**2**) was synthesized as racemic mixture of the R- and S-stereoisomer via a tetramethylguanidine (TMG) catalyzed phospha-Michael addition (PMA) between **BAPH** and *N*-succinimidyl methacrylate followed by an oxidation (Scheme 2). The bis(acyl)phosphane rac-**1** [$\delta(^{31}P\{^1H\}) = 47.5$ ppm (s)] is an intermediate in this reaction sequence and was converted without further purification with *t*-BuOOH to give the corresponding BAPO rac-**2** as a yellow, air-stable crystalline solid in 80% yield [$\delta(^{31}P\{^1H\}) = 22.9$ ppm (s)].

Yellow single crystals suitable for X-ray diffraction experiments were grown from a saturated DME solution of rac-**1** or a toluene solution of rac-**2** layered with *n*-hexane. Both compounds crystallize as racemic mixtures and plots of the structures of one stereoisomer of S-**1** and R-**2** are shown in Figure 1.

The P-C_{acyl} bond lengths in the phosphine S-**1** (1.876 and 1.892 Å) do not change much upon oxidation to the phosphane oxide R-**2** (1.888 and 1.895 Å), and remain unusually long, which is a specific feature of BAPO molecules including the commercially available *Omnirad® 819* (previously *Irgacure® 819)*. Notably, the distances between the phosphorus atom and the mesitoyl groups are significantly longer than the P–C21 bond to the phenyl substituent (1.809 Å) although all these P–C bonds involve carbon centers with a sp^2-valence electron configuration.[30,31] With respect to the central P=O group, both mesitoyl substituents in R-**2** show an almost anti-planar



Scheme 2. Synthesis of ACTIVE-BAPO (**2**) from **BAPH** and *N*-succinimidyl methacrylate. The stereocenter is marked with *.

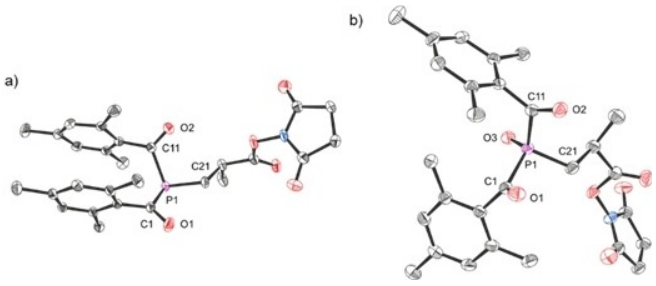
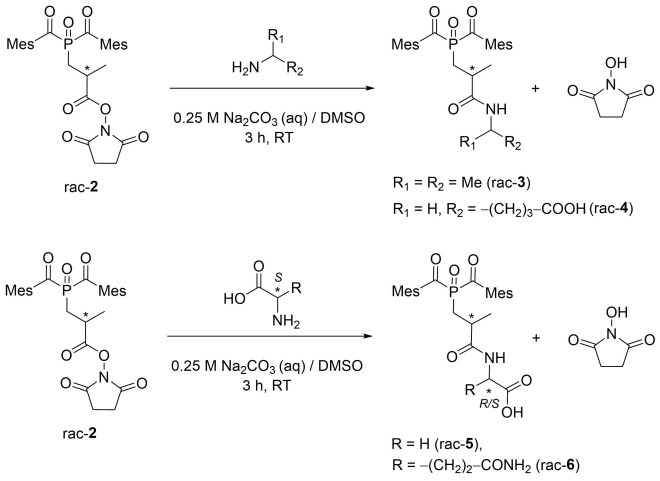


Figure 1. a) ORTEP plot of rac-**1**. Displacement ellipsoids are depicted at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-C1 1.875(1), P1-C11 1.892(2), P1-C21 1.848(1), C1-O1 1.213(2), C11-O2 1.216(2), C1-P1-C11 99.67(6), C11-P1-C21 99.78(6), C1-P1-C21 98.08(6), O1-C1-C11-O2 −23.6(2). b) ORTEP plot of rac-**2**. Displacement ellipsoids are depicted at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-C1 1.895(2), P1-C11 1.888(1), P1-C21 1.809(2), P1-O3 1.480(1), C1-O1 1.210(2), C11-O2 1.209(2), C1-P1-C11 101.20(6), C11-P1-C21 108.21(7), C1-P1-C21 99.38(7), O1-C1-P1-O3 −164.8(1), O2-C11-P1-O3 −150.3(1).

arrangement of the C=O units (O1–C1–P1–O3 −164.8° and O2–C11–P1–O3 −150.3°). The O–C–C–O torsion angle does not significantly change upon oxidation, from 23.7° in S-**1** to 31.8° in R-**2**. A similar anti,anti-conformation of the C=O and P=O units was also observed in other BAPO structures.[10,32]

To test the reactivity of rac-**2**, it was treated with two amines and three amino acids as examples in aqueous solution. Isopropyl amine, diisopropyl amine, γ-aminobutyric acid (GABA), glycine, or L-glutamine, were dissolved in 0.25 M carbonate buffer and ACTIVE-BAPO rac-**2** was added as DMSO solution (Scheme 3). The ligation with isopropyl amine, a secondary amine, was not successful and only a hydrolysis of the active ester moiety in rac-**2** was observed, which gives HOOC-CH(Me)-CH_2-PO(COMes)$_2$ as product.[33] All other reactions proceed smoothly as indicated in Scheme 3 and the new products, **3**–**6**, were obtained as yellow solids in 71% (rac-**3**), 78% (rac-**4**), 72% (rac-**5**) and 57% (rac-**6**) isolated yields. All compounds are light sensitive but air-stable and slightly soluble in water.



Scheme 3. Synthesis of ligated BAPOs. Top: BAPO isopropyl amine (**3**) and BAPO GABA (**4**) and bottom: BAPO glycine (**5**) and BAPO glutamine (**6**). Stereocenter is marked with *.

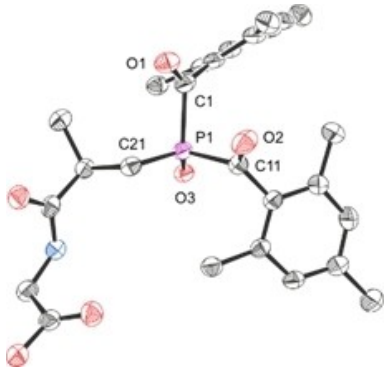


Figure 2. ORTEP plot of S-**4**. Displacement ellipsoids are depicted at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-C1 1.882(4), P1-C11 1.874(3), P1-C21 1.795(3), P1-O3 1.467(3), C1-O1 1.197(4), C11-O2 1.201(4), C1-P1-C11 99.1(2), C11-P1-C21 106.3(2), C1-P1-C21 104.7(2), O1-C1-P1-O3 154.5(3), O2-C11-P1-O3 171.6(3), O1-C1-C11-O2 −27.6(3).

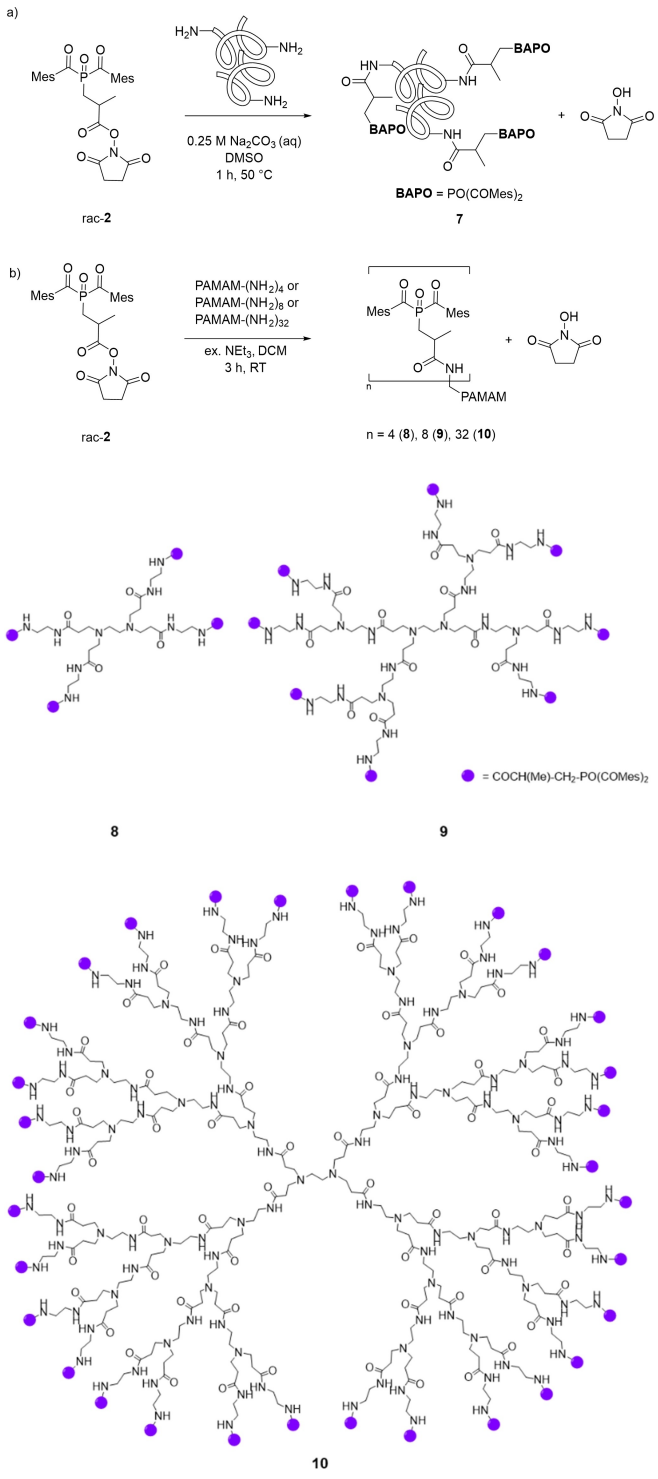
The $^{31}P\{^1H\}$ NMR spectra of rac-**3**, rac-**4** and rac-**5** show one singlet at $\delta(^{31}P\{^1H\}) = 25.3$ ppm (**3** and **5**) and $\delta(^{31}P\{^1H\}) = 24.6$ ppm (**4**) that are slightly shifted to higher frequencies in comparison to the starting material ($\delta(^{31}P\{^1H\}) = 22.9$ ppm). As expected, the $^{31}P\{^1H\}$ NMR of rac-**6** shows two equally intense signals at $\delta(^{31}P\{^1H\}) = 25.5$ and 24.1 ppm, which are assigned to the two diastereomers R,S-**6** and S,S-**6**. Yellow single crystals of BAPO glycine, rac-**4**, suitable for X-ray diffraction experiments, were obtained from a $CHCl_3$ solution layered with Et_2O and a plot of the structure is shown in Figure 2. All bond lengths and angles are very similar to the ones seen in R-**2** and again the anti,anti-arragement of the two C=O units with respect to the central P=O group is observed. After the desired reactivity of rac-**2** as BAPO-transfer reagent was verified using small target molecules containing primary amino functions, it was reacted with macromolecular polyamines (Scheme 4).

Firstly, gelatin from porcine skin, a lysine-rich protein mixture, was tested in a 0.25 M carbonate buffer/DMSO mixture at 50 °C.[26] After purification by lyophilization, the product (**7**) was isolated as a water-soluble pale-yellow powder in about 59% yield (Scheme 4a). The ^{31}P NMR of **7** in DMSO-d_6 shows a broad signal at $\delta(^{31}P) =$ 25.1 ppm, in a similar chemical shift region as the ones of the BAPOs **3**–**6**.

To synthesize multiple photoinitiators with a defined number of attached BAPO units, rac-**2** was reacted with three generations of PAMAM dendrimers, namely G0, G1 and G3 with 4, 8 and 32 NH_2 groups, respectively. The ligations were performed in a DCM/MeOH mixture in presence of an excess of triethylamine. The products, BAPO-PAMAM–G0 (**8**), BAPO-PAMAM–G1 (**9**) and BAPO-PAMAM–G3 (**10**) were recovered as bright yellow powders in 88% (**8**), 51% (**9**) and 66% (**10**) yield, respectively (Scheme 4 b). In the ^{31}P NMR spectra broad signals at $\delta(^{31}P) = 25.1$ ppm (**8**), 25.2 ppm (**9**) and 25.3 ppm (**10**) are recorded. The line broadening is caused by a multitude of possible orientations of the BAPO units and the presence of a chiral carbon atom in the lateral chain, which leads to mixture of stereoisomers. The complete functionalization of all NH_2 groups in PAMAM–G0 and PAMAM–G1 to give **8** and **9** was confirmed by high-resolution mass spectrometry (see Supporting Information) and although no proof could be obtained in case of **10**, we assume that here likewise complete substitution was reached.

Given that **7**–**10** are multiple-PIs, their capacity as "two-in-one" photoinitiators was investigated, which do not only initiate a radical polymerization of a mono-functional monomer but also serve as crosslinking agents mainly via radical combination of growing polymer chains from each multiple-PI molecule. It has been demonstrated in the past that multifunctional photoinitiators can be used to convert monofunctional monomers into thermosetting networks, acting as crosslinking points.[8,34] Real-time photo-rheology was used to monitor the photopolymerization kinetics of poly(ethylene glycol) methyl ether methacrylate (PEGMEMA), which was chosen as reference monofunctional oligomer.

First, the performance of **7** was compared with that of a monofunctional molecular BAPO, namely BAPO-PEG-950, which is water-soluble and contains an oligomeric poly(ethyleneglycol) (PEG) chain bound to the phosphorus center.[35] For both photoinitiators, the polymerization of PEGMEMA started immediately after the beginning of the irradiation. However, no gel point (crossover point



Scheme 4. Ligation of ACTIVE-BAPO rac-**2** with macromolecular polyamines; a) gelatin and b) PAMAM G0, G1 and G3 dendrimers.

between G′ and G″ curves, see Figure S27) was observed when using BAPO-PEG-950. This confirmed that no chemical cross-linking occurred, which is typical when a monofunctional monomer in the presence of a monofunctional BAPO is used, since only the growing of a linear polymer chain is expected.[34] In contrast, the use of **7** resulted in a crosslinked thermosetting polymer (gel point after 411 s), having a 100-times higher storage modulus than the polymer obtained with BAPO-PEG-950 (see Supporting Information for details).

Subsequently, **8**–**10** with a defined number of BAPO units (8, 16 and 32, respectively) were tested for the photopolymerization of thermosets from PEGMEMA as monomer. Three photocurable formulations were prepared by dissolving the BAPO dendrimers in PEGMEMA, and the concentration of each formulation was adapted such that the same molecular number of photoactive BAPO units is obtained in all solutions. Figure 3a shows the evolution of the viscoelastic moduli G′ and G″ during UV-light irradiation of all formulations. The results clearly reveal that the gel points correlate with the amount of BAPO units grafted on PAMAM, that is the higher number of BAPOs, the shorter the irradiation time to reach gelation of the formulation (Figure 3b and Table 1). This confirms that the crosslinking efficiency of the multifunctional photoinitiators **8**–**10** increases with an increasing amount of BAPO units on the PAMAM dendrimer, due to the higher number of PAMAM-$(PO^{\bullet})_n$ radicals generated upon photolysis that can serve both as initiating centers for polymerization and as crosslinking net-points of the growing thermosetting network. Also, higher G′ values are reached at the plateau with an increasing number of BAPOs grafted on PAMAM. This was further demonstrated by the results of frequency sweep measurements performed on freshly cured samples, which

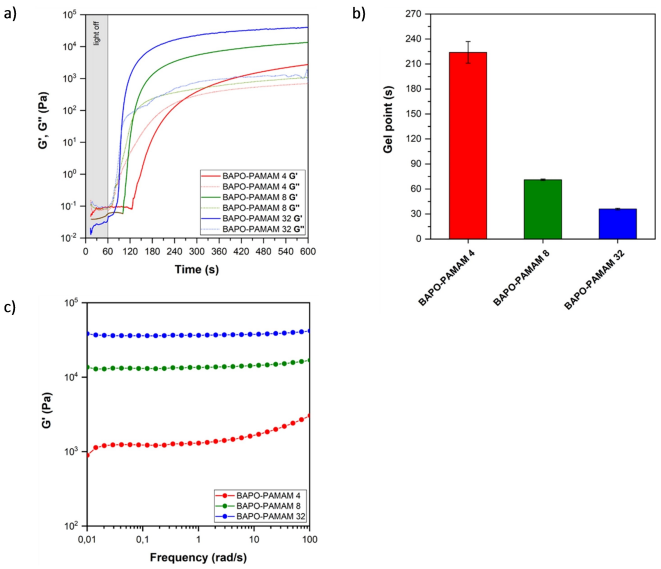


Figure 3. a) Photo-rheology curves corresponding to the photopolymerization kinetics of the three photocurable formulations prepared by dissolving **8**–**10** in PEGMEMA; b) gel points of the formulations and c) G′ of the cured thermosets as a function of the number of BAPO units grafted on PAMAM.

Table 1. Gel point, G′, swelling degree (SD) and water content (WC) values obtained for the BAPO dendrimers **8**–**10**.

PI	Gel point [s]	G′ [kPa]	SD [%]	WC [%]
BAPO PAMAM G0 (**8**)	224 ± 13	1.8 ± 0.4	588.4 ± 8.2	85.5 ± 0.2
BAPO PAMAM G1 (**9**)	71 ± 1	15.1 ± 2.9	456.9 ± 5.7	82.0 ± 0.2
BAPO PAMAM G3 (**10**)	36 ± 1	38.8 ± 2.4	342.1 ± 6.4	77.4 ± 0.3

confirmed that the G′ of the photo-cured thermosets correlates with the amount of BAPO units grafted on PAMAM (see Figure 3c, Table 1).

The increasing crosslinking efficiency of **8**–**10** was further confirmed by swelling measurements performed in water. The results reveal that all completely cured samples extensively absorb water due to the high mobility of flexible chains, which are expectedly obtained when a monofunctional monomer is used. These can undergo large expansions, but both, the swelling degree (SD) and the water content (WC), gradually decrease as the number of BAPO units on the PAMAM carrier molecules is increased (Figure 4, Table 1).

This finding proves that the amount of BAPOs grafted on PAMAM correlates with the density of crosslinking of the thermosetting polymers obtained upon UV irradiation of the monofunctional PEGMEMA. Indeed, the higher the amount of BAPO units on PAMAM, the higher the crosslinking density of the thermoset obtained by UV curing and thus the lower will be its swelling capability.

Conclusion

The functionalization of macromolecules with photoactive BAPO units is challenging. It requires advanced synthetic skills, multiple steps and it is often limited by the compatibility of the substrate with the oxidation conditions. The ester functionalized photoinitiator ACTIVE-BAPO, overcomes these limitations and readily reacts with primary amines in a simple one-step ligation under mild conditions and in aqueous solution. Gelatin, a bioderived, biodegradable macromolecule which would be very difficult to functionalize using the common BAPO grafting methods of polyacrylation followed by a phospha-Michael addition, was easily functionalized with ACTIVE-BAPO giving a multifunctional photoinitiator. Full functionalization of three PAMAM dendrimers was achieved and gives macromolecular multiple photoinitiators in good yields. These multiple BAPOs serve as "two-in-one" components, namely as crosslinkers and photoinitiators. Although it remains presently unclear how many BAPO units are actually activated by light per time unit, it is clearly demonstrated that such PIs can be used for the convenient photogeneration of thermosets with a tunable degree of crosslinking. Therefore, the results encourage the use of ACTIVE-BAPO as component in customizable kits for grafting BAPO units to complementary functionalized molecules, surfaces, and materials, which in turn will allow to explore multifunctional BAPOs in material science and for biomedical applications.

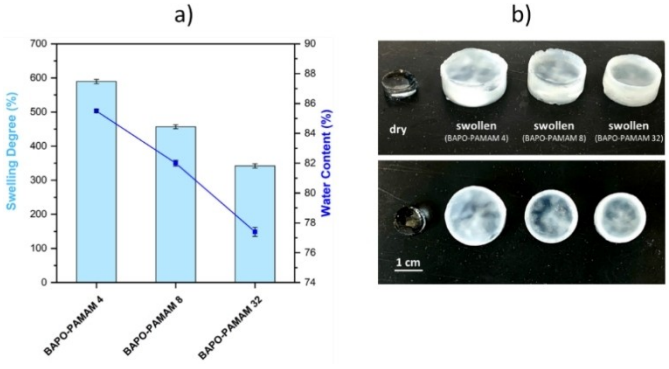


Figure 4. a) SD and WC of the three thermosets obtained from the photocurable formulations prepared by dissolving **8**–**10** in PEGMEMA and b) dry samples obtained upon the UV curing and swollen samples after 24 h immersion in water.

Experimental Section

Synthesis of 2,5-dioxopyrrolidin-1-yl 3-(bis(2,4,6-trimethylbenzoyl)phosphoryl)-2-methylpropanoate (2): BAPH[7] (18.00 g, 0.55 mol, 1 equiv) is loaded in a 250 ml Schlenk flask under argon followed by 120 ml of dry DME. TMG (0.31 g, 0.35 ml, 0.03 mol, 0.05 equiv) is added to the stirred bright yellow solution, followed by *N*-succinimidyl methacrylate (10.10 g, 0.55 mol, 1 equiv). The reaction mixture is stirred at room temperature for three hours. A ^{31}P NMR spectrum is recorded to verify the completion of the reaction (product signal of **1** at $\delta = 47.4$ ppm). The solvent is evaporated, and the product dissolved in 120 ml of dry toluene. A solution of 2 M HCl in diethyl ether (1.38 ml, 3 mmol, 0.05 equiv) is added dropwise under vigorous stirring, then the reaction is protected from light and a solution of 5.5 M *tert*-butyl hydroperoxide in decane (11.03 ml, 0.61 mmol, 1.1 equiv) is added dropwise. After two hours, a ^{31}P NMR spectrum is recorded to verify the completion of the reaction (product signal at $\delta = 23.1$ ppm), the solvent is evaporated, the product dissolved in ethyl acetate (100 ml) and filtered through a silica plug. The silica plug is washed with ethyl acetate to completely recover the product. The solvent is evaporated, and a bright yellow solid is isolated and characterized as the desired product **2** (23.29 g, 80 % yield). A single crystal suitable for X-ray diffraction is grown from a toluene solution of **2** layered with *n*-hexane. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 6.84 (s, 4H, H_{arom} Mes), 3.25 (m, 1H, C*H*), 2.85 (m, 1H, CH_2), 2.80 (s, 4H, NHS-CH_2), 2.38 (m, 1H, CH_2), 2.28 and 2.27 (s, 6H, *p*-CH_3), 2.25 and 2.24 (s, 12H, *o*-CH_3), 1.48 (d, $^{3}J_{HH} = 7.1$ Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ (ppm): 215.0 (d, $^{1}J_{CP} = 52.7$ Hz, P-*C*=O), 214.9 (d, $^{1}J_{CP} = 54.2$ Hz, P-*C*=O), 170.5 (d, $^{3}J_{CP} = 13.0$ Hz, NHS–O–*C*=O), 168.7 (s, N-*C*=O), 141.7 (s, C^4 Mes), 135.9 (s, $C^{2,6}$ Mes), 135.7 (d, $^{2}J_{CP} = 13.1$ Hz, C^1 Mes), 129.4 (s, $C^{3,5}$ Mes), 31.6 (d, $^{3}J_{CP} = 2.2$ Hz, *C*H), 28.6 (d, $^{1}J_{CP} = 53.2$ Hz, –CH_2-P), 25.6 (s, NHS-CH_2), 21.3 (s, *p*-CH_3), 19.8 (d, $^{4}J_{CP} = 14.1$ Hz, *o*-CH_3), 18.5 (d, $^{3}J_{CP} = 3.0$ Hz, CH-CH_3). ^{31}P NMR (203 MHz, $CDCl_3$): δ (ppm): 22.9 (m, O=*P*R_3). ^{31}P{^{1}H} NMR (203 MHz, $CDCl_3$): δ (ppm): 22.9 (s, O=*P*R_3). ESI-TOF (m/z) (+): 548.1810 $(M+Na)^+$. Elemental analysis for $C_{28}H_{32}NPO_7$: calculated: C 63.99 %, H 6.14 %, N 2.67 %, found: C 63.82 %, H 6.34 %, N 2.84 %.

General ligation procedure in water/DMSO: The target substrate (0.75 mmol, 1.3 equiv) is dissolved in 6 ml of 0.25 M sodium carbonate buffer (corresponding to 1.43 mmol, 2.5 equiv of base) in a 25 ml round bottomed flask. **2** (300 mg, 0.57 mmol, 1 equiv) is dissolved in 2 ml of DMSO in a vial protected from light. The solution of **2** is added dropwise to the aqueous solution under vigorous stirring. The mixture is stirred vigorously for 3 h at room temperature under exclusion of light, filtered, transferred to a separating funnel, and 15 ml of DCM are added followed by 15 ml of 2 M HCl. After the separation, the organic phase is washed 2 times with 15 ml of brine. The collected brine phases are washed with 15 ml of DCM. The collected organic phases are dried using Na_2CO_3. After filtering off the drying agent, the solvent is evaporated, and the product isolated.

Deposition Number(s) 2222284 (**5**), 2222285 (**2**), and 2222286 contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge

Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of Interest

There are no conflicts to declare.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: bis(acyl)phosphane oxide · dendrimers · ligation · multiple photoinitiators · polymerization

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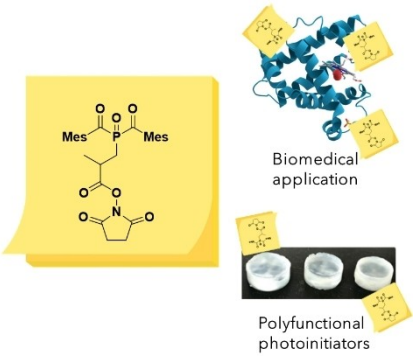
RESEARCH ARTICLE

Active BAPO - An NHS ester substituted bis(acyl)phosphane oxide (BAPO) is synthesized by phospha-Michael addition and used as the first versatile transfer agent for the grafting of photoactive BAPO units. Amino acids, porcine skin, and poly(amido)amine (PAMAM) dendrimers were functionalized with the photoactive units and used for the synthesis of thermosets with a different degree of crosslinking.



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1 – 7

ACTIVE-BAPO – A Versatile Transfer Agent for Photoactive Bis(acyl)phosphane Oxide Units