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# Recent Advances on Water-Soluble Photoinitiators of Polymerization

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## Abstract

Visible light photopolymerization has extensively been studied during the last decades since alternatives to UV processes have to be found rapidly. Indeed, based on the Minamata Convention, Hg irradiation setups must be suppressed from industrial applications. Even if the use of visible light is beneficial in terms of depth of cure and safety for the manipulator, photopolymerization in water is still far aside to the other polymerization processes. At present, only few visible light photoinitiators are soluble in water, speeding down the development of greener polymerization processes. In this review, an overview of the recent advances on water-soluble photoinitiating systems is provided. Even if water-solubility is a key parameter to polymerize in water, the monomer conversion that can be achieved is also important. For these reasons, comparisons with reference photoinitiating systems soluble in water is provided.

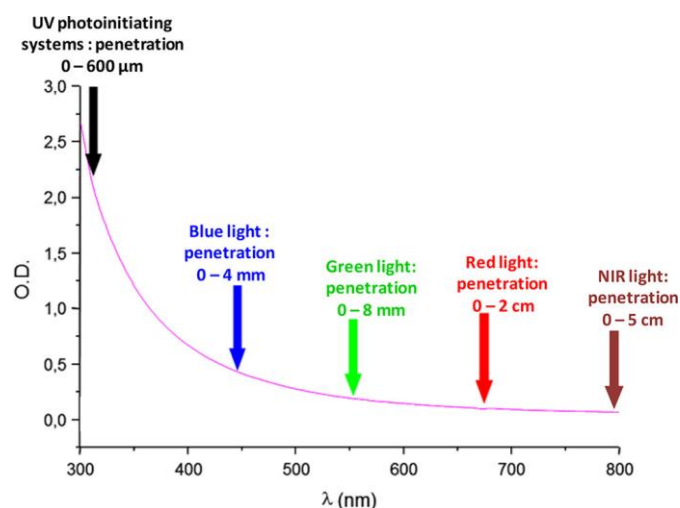
## Keywords

Photoinitiator; water-soluble; photopolymerization; LED; low light intensity; visible light

## 1. Introduction

During the past decades, visible light photopolymerization has become the workhorse of photopolymerists due to the numerous disadvantages UV photopolymerization exhibits. Nowadays, UV light is the focus of numerous safety concerns, UV light being responsible of skins cancers and eye damages.[1–4] Ozone is produced during irradiation, what constitutes another drawbacks.[4] In 2013, the United Nations Environmental Program (UNEP) Minamata Convention on Mercury has resulted in a ban of Hg lamps, which was extensively used in industry to produce UV light. Since 2020, Hg lamps are no longer be allowed to be manufactured, imported and exported. Therefore, new light sources have to be used and, in this field, light-emitting diodes (LEDs) are promising irradiation sources due to their low-costs, compactness, long operating lifetimes and low energy consumptions. Nowadays, photopolymerization is involved in numerous processes ranging from solvent-free paints, dentistry, adhesives, microelectronics, 3D and 4D printing, coatings and varnishes.[5–17] Compared to thermal polymerization, photopolymerization exhibits several specificities such as the possibility to get a spatial and a temporal control of the polymerization process. Photopolymerization can also be carried out without solvents, at room temperature limiting the release of volatile organic compounds (VOCs) but also the polymerization of temperature

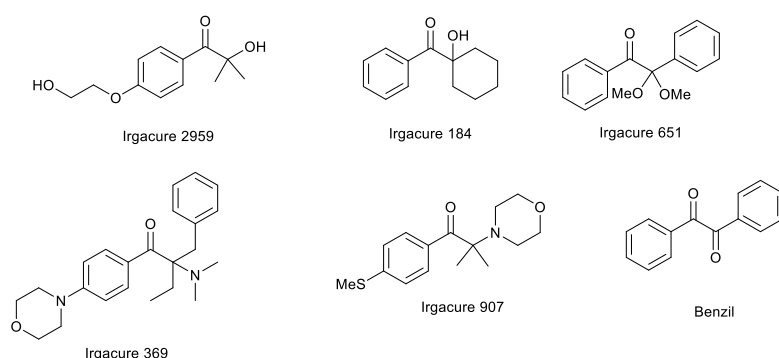
sensitive monomers. In order to improve the depth of cure, longer irradiation wavelengths have to be used. Indeed, as shown in the Figure 1, the depth of cure is dependent of the irradiation wavelengths used for the polymerization process. Thus, if the light penetration is limited to a few hundreds of micrometers at 350 nm, this value can increase up to 5 cm at 800 nm, enabling now to polymerize thick samples and samples containing fillers.[18]



**Figure 1.** Light penetration in a polystyrene latex with an average diameter of 112 nm. Reprinted with permission from Bonardi et al.[18]

If the visible light approach seems to be appealing for photopolymerization, several drawbacks have however to be mentioned. Thus, visible light photoinitiators are coloured compounds often providing an undesired colour to the final coatings. This coloration can constitute a severe limitation for future applications of photopolymers. Visible light photons are also less energetic than UV photons so that more reactive photoinitiating systems have to be used to overcome this lower reactivity. Over the years and in order to improve the reactivity of photoinitiating systems, a wide range of structures has been screened, as exemplified with cyclohexanones,[19–22] phenothiazines,[23–33] carbazoles,[34–47] iridium complexes,[48–55] diketopyrrolopyrroles,[56–58] truxene derivatives,[59] triphenylamines,[60,61] coumarins,[62–74] metal organic framework (MOFs),[75–77] curcumin,[78–81] perovskites,[82,83] cyanines,[84–90] pyridinium salts,[91,92] Schiff bases,[93] silyl glyoximides,[94] chromones and flavones,[95–97] *N*-heterocyclic carbene boranes,[98] thiophene derivatives,[99] squaraines, [100–104] naphthalimides,[105–123] camphorquinones,[124,125] imidazole derivatives,[126] porphyrins,[127,128] viologen derivatives,[129–131] dihydroanthraquinones,[132] anthraquinone,[133] pyrrole derivatives,[134] iodonium salts,[105,135–141] 2,3-diphenylquinoxaline derivatives,[142,143] naphthoquinones,[144] benzylidene ketones,[145–151] Bodipy,[152–157] copper complexes,[158–175] conjugated polymers,[176] polyoxometalates,[177–179] dithienophospholes,[180,181] perylenes,[182–185] iron complexes,[76,186–192] pyrenes,[193–201] zinc complexes,[202] acridine-1,8-diones,[203–205] helicenes,[206,207] benzylidene ketones,[145,146] push-pull dyes,[186,208–221] chalcones,[13,222–234] thioxanthenes,[235–248] benzophenones,[249–256] anthracene,[257] acridones,[258,259] and phenazines,[260]. By

exploring these different structures, high performance photoinitiating systems could be identified. Noticeably, only few water-soluble photoinitiators were proposed in the course of these different investigations. Besides, water-soluble photoinitiators could pave the way towards polymerization done in greener conditions than that currently used.[261,262] In this field, 2-hydroxy-1-[4-(2-hydroxyethoxy) phenyl]-2-methyl-1-propanone (Irgacure 2959) is among the most popular water-soluble photoinitiator (See Figure 2).[263–265] Besides, its absorption maximum located in the UV range ( $\lambda_{\max} = 276$  nm) and its water-solubility lower than 2 wt% are restrictive for numerous applications. To end, Irgacure 2959 is unable to initiate any polymerization in the visible range, this photoinitiator not absorbing after 360 nm. In industry, numerous other water-soluble UV Type I photoinitiators were used, as exemplified by 1-hydroxy-cyclohexylphenylketone (Irgacure 184), 2,2-dimethoxy-2-phenylacetophenone (DMPA, Irgacure 651) and 2-methyl-4'-(methylthio)-2-morpholinopropiophenone (Irgacure 907). But their solubilities in water can be extremely limited as exemplified with Irgacure 907 (17.9 mg/L at 20°C) or Irgacure 184 (1108 mg/L at 25°C). Camphorquinone is another popular photoinitiator. Besides, its low water solubility has incited researchers to investigate its chemical modification.[266,267] By introducing a carboxylate group on camphorquinone, this issue could be addressed.[124] A high degree of double bond conversion could be obtained while using an amine co-initiator. Polymeric benzil macrophotoinitiators were also designed and synthesized as water-soluble photoinitiators, benzil being less prone than the other photoinitiators to quenching reactions by radical termination.[268,269] However, absorption of benzil is strongly UV-centered and cannot be used for visible light polymerization. Extensive efforts were also done to design water-soluble photoinitiating systems with historical photoinitiators such as xanthene dyes.[270] Latex nanoparticles comprising Eosin-Y,[271] inclusion complex of xanthene dyes with methylated- $\beta$ -cyclodextrin,[272] or the formation of charge transfer complexes with the water-soluble triethanolamine[273] were envisioned as possible strategies for water solubility. However, due to the complex structures of xanthene dyes, their chemical modification is a hard work.



**Figure 2.** Chemical structures of water-soluble Type I photoinitiators.

Considering that these water-soluble photoinitiators are difficult to modify in order to redshift their absorptions towards the visible range, photoinitiators of innovative structures have thus to be found. This observation is true for Type I but also for Type II

photoinitiators.[274] Several strategies were thus examined to convert organo-soluble dyes as water-soluble structures using complex approaches. Thus, water-dispersible diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) nanoparticles obtained by oil-in-water microemulsions were reported in the literature.[275] However, drying of volatile microemulsions by spray drying is not easy to handle. Generation of nanoparticles of poly(9,9-dioctylfluorene-*alt*-benzothiadiazole) and poly(9,9-di-*n*-octylfluorenyl-2,7-diyl) by aggregation of polymers in water was also proposed, hydrophobicity of the conjugated polymers facilitating the aggregation process in water.[276] However, these last approaches required nanoparticles preparation prior to polymerization processes.

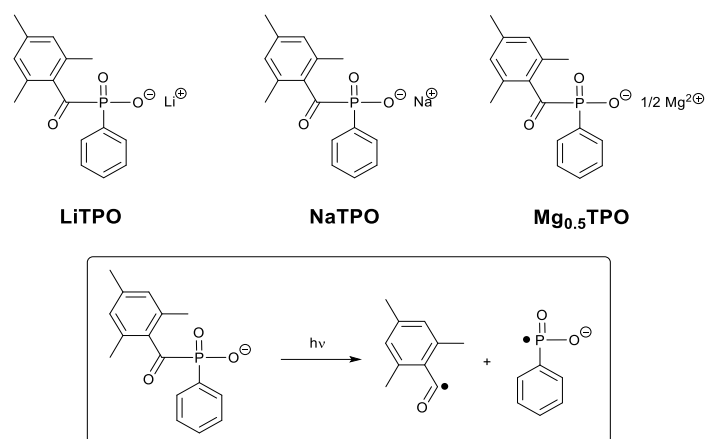
In this review, an overview of the water-soluble photoinitiating systems developed during the last decade is provided. Over the years, several strategies were examined, consisting in introducing water-solubilizing chains such as poly(ethylene glycol) chains, to form charge-transfer complexes with water-soluble amines such as triethanolamine, to form salts or to introduce water water-soluble groups. Water-soluble Type I and Type II photoinitiators were also investigated, expanding the scope of applications. Comparison with reference photoinitiating systems is also provided to evidence the interest of these newly developed structures.

## 2. Water-soluble photoinitiators

### 2.1. *Mono*-acylophosphine oxides and *bis*-acylophosphine oxides derivatives

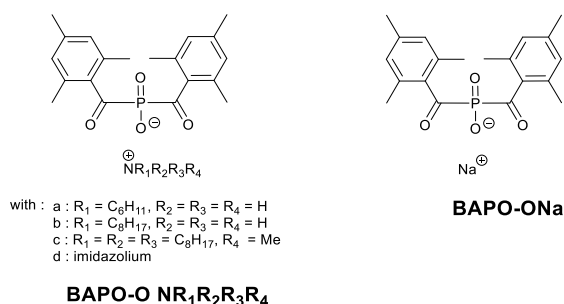
*Mono*-acylophosphine oxides and *bis*-acylophosphine oxides were extensively studied starting from the 90's as visible light photoinitiators of polymerization, the absorptions of these two families of dyes extending up to 450 nm.[277,278] In these two families, diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) and phenyl *bis*(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO) were undoubtedly the most widely studied. However, BAPO and TPO are insoluble in water. Notably, water solubility of TPO is only of 3.13 mg/L.[279] In 1991, Schnabel and coworkers prepared two water-soluble derivatives of TPO, namely LiTPO and MgTPO (See Figure 3).[280] LiTPO and Mg<sub>0.5</sub>TPO exhibited a good solubility in water since solubilities of 85 g/L and 13 g/L were respectively determined for the two photoinitiators. From the mechanistic viewpoint, LiTPO and Mg<sub>0.5</sub>TPO can undergo an  $\alpha$ -scission at the carbonyl-phosphorus bond, producing a benzoyloxy radical and a radical anion which is highly reactive towards olefins such as acrylamide, methacrylamide, methyl methacrylate, acrylonitrile, styrene,[280] or poly(ethylene glycol)diacrylate (PEGDA) (See Figure 3).[281,282] But other monomers such as gelatin methacrylate,[283] norbornene-functionalized PEG macromers or pentaerythritol triacrylate (PETA)[284] were also polymerized with LiTPO.[285] In 2009, the synthesis of TPO salts was greatly improved by Huang and coworkers, and reduced to a simple and straightforward one-pot procedure, enabling to get LiTPO, NaTPO and Mg<sub>0.5</sub>TPO in 66, 77 and 53% yields respectively.[279] 3D Printed structures containing up to 80% water could be produced with a high spatial resolution. Noticeably, a water solubility lower than that previously reported in the literature was determined for LiTPO, being only of 40.5 g/L (vs.

85 g/L for Schnabel and coworkers).[280] Besides, this value is closed to that reported by Liska and coworkers (47 g/L).[286] Solubilities of 49.5 and 15.5 g/L were also found for NaTPO and Mg<sub>0.5</sub>TPO. Here again, the solubility in water of NaTPO is different to that reported by Liska and coworkers (29 g/L).[286] In the case of LiTPO, biocompatible hydrogels using a mixture of acrylamide and PEGDA could be obtained, paving the way towards nontoxic 3D-printed hydrogels.



**Figure 3.** Chemical structures of LiTPO, NaTPO and Mg<sub>0.5</sub>TPO and mechanism of photocleavage.

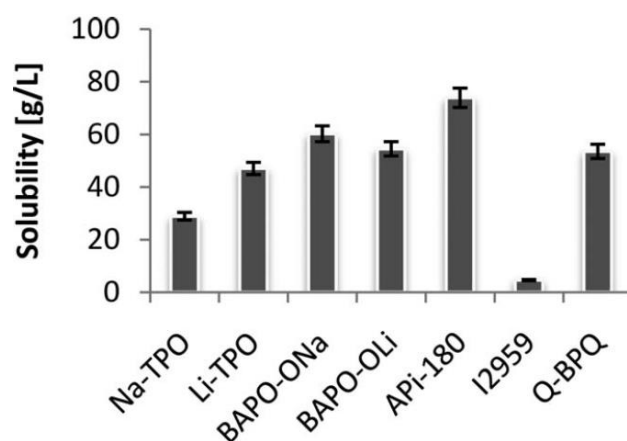
The development of simple synthetic procedures was not limited to TPO derivatives and a one-pot two-step synthesis of sodium *bis*(mesityl)phosphinate was proposed in 2015 by Grützmacher and coworkers.[287] By the versatility of the synthetic approach, a series of ammonium salts and a sodium salt could be prepared in good yields (See Figure 4). In the case of BAPO-ONa, a solubility of 45 g/L could be determined, therefore comparable to that of LiTPO. However, this value is lower than that later reported by the same authors (60 g/L).[286] BAPO-ONa could initiate the surfactant-free emulsion polymerization of styrene, enabling to get monodisperse and spherical nanoparticles.



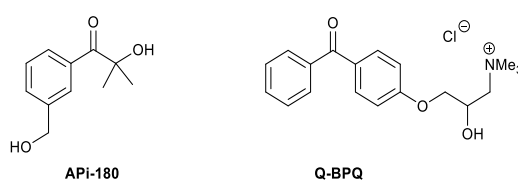
**Figure 4.** Chemical structures of water-soluble BAPO derivatives.

A comparative study carried out on NaTPO, LiTPO, BAPO-ONa and BAPO-OLi revealed the BAPO derivatives to exhibit a higher solubility in water than the TPO salts (See Figure 5). However, these water solubilities are comparable to that of 2-hydroxy-1-[3-(hydroxymethyl)phenyl]-2-methyl-1-propanone (API-180) (74 g/L) or 3-(4-benzoylphenoxy)-2-hydroxy-*N,N,N*-trimethyl-1-propanaminium chloride (Q-BPQ) (54 g/L), but greatly higher

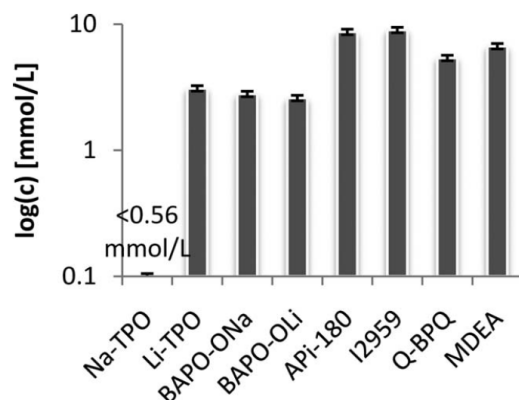
than that of Irgacure 2959 (5 g/L) (See structures in Figure 6). A remarkable stability in deionized water was also evidenced for the TPO and the BAPO salts since no decomposition was detected after one month of storage in the dark. Besides, a lower stability was determined in basic conditions (pH = 11) for all photoinitiators. Examination of their biocompatibilities with mouse fibroblast cells L929 revealed the cytotoxicity of BAPO and TPO salts to be in a similar range than the state-of-the-art photoinitiators (API-180, Q-BPQ or 2-hydroxy-1-[4-(2-hydroxyethoxy) phenyl]-2-methyl-1-propanone (Irgacure 2959) (See Figure 7). More precisely, cytotoxicities of  $LC_{50} = 2.8$  mmol/L for BAPO-ONa and  $LC_{50} = 2.8$  mmol/L for BAPO-OLi were determined. Polymerization tests done on *N*-acryloylmorpholine upon irradiation in the 320-500 nm range and 400-500 nm range revealed the TPO salts to outperform the BAPO salts, irrespective of the irradiation conditions. Noticeably, if significant differences of monomer conversions were determined in the 320-500 nm range, almost similar monomer conversions were obtained with the four salts upon irradiation in the 400-500 nm range (See Figure 8).



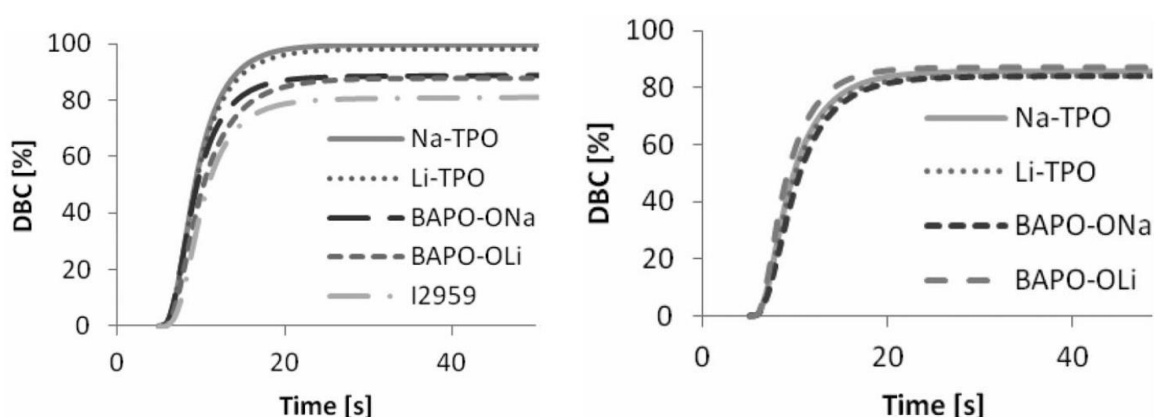
**Figure 5.** Comparison of the water solubility of BAPO and TPO salts with benchmark photoinitiators (API-180, Irgacure 2959 and Q-BPQ). Reproduced with permission of Ref.[286]



**Figure 6.** Chemicals structures of reference compounds tested with BAPO and TPO salts (sodium and lithium salts).

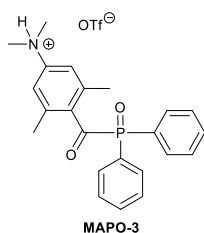


**Figure 7.** Cytotoxicity tests done on mouse fibroblast cells L929 for BAPO and TPO salts and reference compounds. Reproduced with permission of Ref.[286]



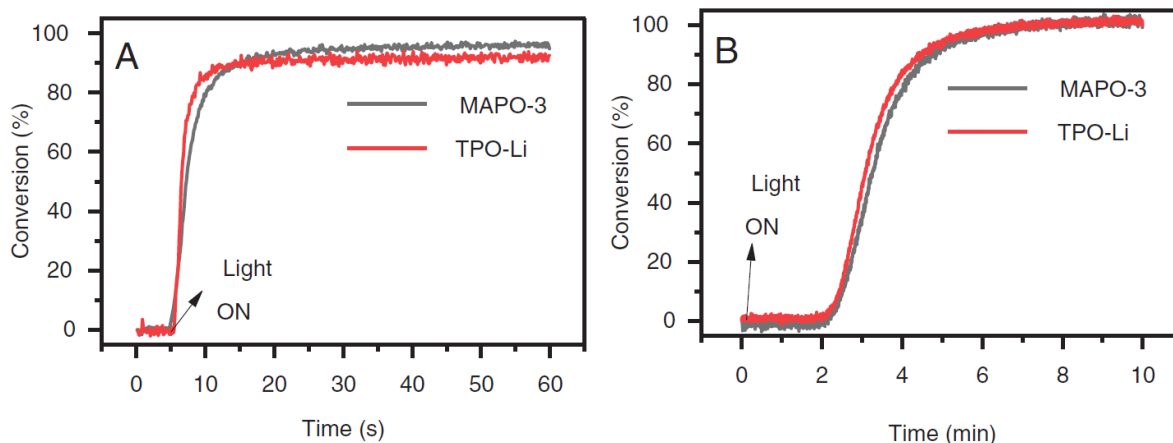
**Figure 8.** Monomer conversions obtained upon irradiation in the 320-500 nm (left) and 400-500 nm (right) range during the FRP of *N*-acryloylmorpholine ( $1\text{ W/cm}^2$ ). Reproduced with permission of Ref.[286]

In 2021, Chemtob and coworkers used a different strategy to provide water-solubility by quaternization of a dimethylamino group on BAPO (See Figure 9).[288] Examination of the absorption properties of MAPO-3 revealed the dye to absorb in the same range than LiTPO. Besides, a higher absorption at 385 nm (wavelength used for the polymerization tests) could be determined for MAPO-3 than LiTPO ( $476\text{ M}^{-1}\cdot\text{cm}^{-1}$  for MAPO-3 vs  $188\text{ M}^{-1}\cdot\text{cm}^{-1}$  for LiTPO respectively). Despite these differences of absorption, LiTPO and MAPO-3 could produce identical polymerization profiles during the FRP of PEGDA at 385 nm and 420 nm (See Figure 10).



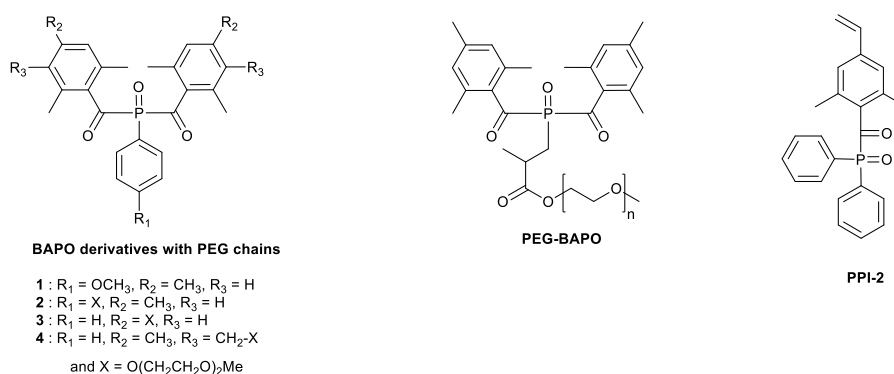
**Figure 9.** Chemical structures of MAPO-3.





**Figure 10.** Monomer conversions determined during the FRP of PEGDA upon irradiation at 385 nm (left) and 420 nm (right). Reproduced with permission of Ref[288].

Several groups also investigated the introduction of poly(ethylene glycol) chains as a tool to provide water-solubility to BAPO derivatives. In 2005, Liska and coworkers developed a series of BAPO derivatives with PEG chains introduced at different positions of the BAPO scaffold. Besides, all structures exhibited a low solubility in water (See Figure 11).[289,290] Indeed, solubilities of 0.2, 1.03, 2.11 and 1.50 mg/L were only determined for compounds 1-4. An opposite situation was found for PEG-BAPO since an exceptional water solubility of 428 g/L was determined for this compound.[291] Improved solubility of PEG-BAPO compared to that of 1-4 can be assigned to the long PEG chains used in PEG-BAPO ( $M_n = 950$ ) whereas an oligomeric 2-(2-methoxyethoxy)ethoxy chain was only used in 1-4, insufficient to provide water solubility. A good storage stability, a high photoreactivity during the FRP of hydrogels (50 wt% water of poly(ethylene glycol)diacrylate (PEGDA)) under visible-light irradiation (460 nm) was evidenced for PEG-BAPO. Especially, comparisons done during the FRP of PEGDA at 460 nm revealed PEG-BAPO to outperform BAPO-ONa and BAPO-OLi in terms of monomer conversions but also of polymerization rates. Notably, a severe reduction of the inhibition time was determined by using PEG-BAPO.



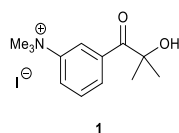
**Figure 11.** BAPO derivatives bearing PEG chains.

Stability of the formulations is often not evoked by the authors in their respective works. In 2001, Norrby and coworkers developed a dimethylacrylamide polymer copolymerized by a TPO-based monomer (PPI-2) (See Figure 11).[292] This polymer proved

to be soluble in water but also extremely stable in solution. Indeed, after 22 months of storage, the polymerization of 2-hydroxyethyl methacrylate (HEMA) remained as efficient as for the freshly prepared solution of polymeric photoinitiator, in terms of polymerization exotherm and polymerization rate.

## 2.2. Alpha-hydroxyalkylphenone

Quaternization of amine has been extensively used in the past for the design of water-soluble alpha-hydroxyalkylphenone.[293] However, most of these photoinitiators could only be activated in the UV range.[263,294–300] Still based on this strategy, a water-soluble derivative of 2-hydroxy-2-methyl propiophenone (Irgacure 1173) was recently proposed in the literature (See Figure 12).[301] This photoinitiator could notably initiate the polymerization of a benchmark organosoluble methacrylate resin (bisphenol A-glycidyl methacrylate (BisGMA)/triethylene glycol dimethacrylate (TEGDMA) (70/30 w/w) upon irradiation at 385 nm and under air in the presence of *N*-heterocyclic carbene borane as an additive. Especially, a polymerization profile identical to that obtained with Irgacure 2959 could be obtained using 1 as the photoinitiator.

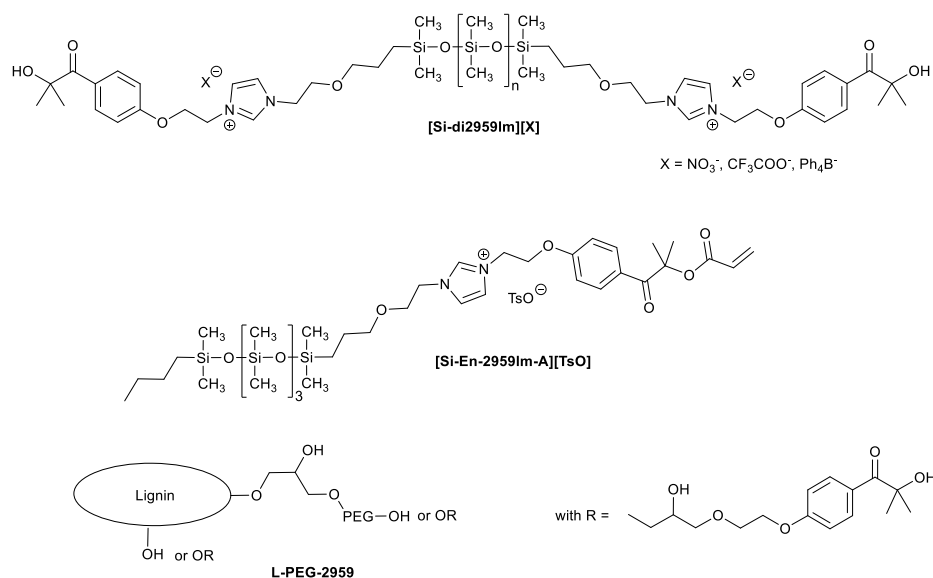


**Figure 12.** Chemical structures of 1.

While examining the polymerization of a water-soluble mixture of monomers i.e. the ethoxylated trimethylolpropane triacrylate (ETPT)/PEGDA (1/2 w/w) blend, a different situation was found at 405 nm and the two-component system based on 1 could furnish a high monomer conversion contrarily to the two-component system based on Irgacure 2959 for which no polymerization could be detected in water. The superiority of 1 compared to Irgacure 2959 in combination with *N*-carbene borane was thus demonstrated. To the best of our knowledge, 1 is the only alpha-hydroxyalkylphenone ever reported in the literature capable to initiate a polymerization process at 405 nm.

Attempts to provide water solubility to 2-hydroxy-1-[4-(2-hydroxy-ethoxy)phenyl]-2-methylpropan-1-one (Irgacure 2959) is not new since pioneering works have been reported as soon as 1995 by Gruber and coworkers with the bonding of Irgacure 2959 to carbohydrates residues such as sucrose, glucose, maltose, 1-amino-D-sorbitol.[302] In 2018, Sun and coworkers developed polysiloxane macrophotoinitiators comprising imidazolium units in their scaffolds (See Figure 13).[265] As interesting features, photoinitiating ability of macrophotoinitiators [Si-di2959Im][X] could be finely tune by the careful selection of the anion ( $X = \text{Br}^-, \text{Ph}_4\text{B}^-, \text{TsO}^-, \text{NO}_3^-, \text{CF}_3\text{COO}^-$ ). Thus, shorter induction time than that obtained with Irgacure 2959 could be determined for macrophotoinitiators comprising  $\text{Ph}_4\text{B}^-$ ,  $\text{CF}_3\text{COO}^-$  and  $\text{NO}_3^-$  as the anions during the FRP of TPGDA. Anions also drastically influenced the water solubility and the following order of water solubility was determined for [Si-di2959Im][X] :

$\text{Ph}_4\text{B}^- < \text{Br}^- < \text{TsO}^- < \text{NO}_3^- < \text{CF}_3\text{COO}^-$ . In the case of  $[\text{Si-di2959Im}][\text{CF}_3\text{COO}^-]$ , a three-fold improvement of the water solubility was measured compared to that of Irgacure 2959 (3.8 wt% vs. 1.2 wt% for Irgacure 2959). By elongating the poly(ethylene glycol) chain in the monofunctional macrophotoinitiator ( $[\text{Si-En-2959Im-A}][\text{TsO}^-]$ ), a significant improvement of the water solubility could be determined for the three macrophotoinitiators. Thus, the solubility increased from 2 wt% to 7 wt% and 12 wt% for  $[\text{Si-En-2959Im-A}][\text{TsO}^-]$  ( $n = 1, 3, 5$ ) respectively.[303] Interestingly, due to the presence of imidazolium groups in the polymer backbone, polymer films prepared with  $[\text{Si-E}_1\text{-2959Im-A}][\text{TsO}^-]$  exhibited an antibacterial activity higher than that of  $[\text{Si-E}_3\text{-2959Im-A}][\text{TsO}^-]$  and  $[\text{Si-E}_5\text{-2959Im-A}][\text{TsO}^-]$ . Conversely, no antibacterial activity was detected for coatings prepared with Irgacure 2959, evidencing the interest of introducing imidazolium groups on photoinitiators. Finally, in 2019, Zhao and coworkers reported for the first time a biosourced water-soluble photoinitiator based on lignin i.e. L-PEG-2959.[296] Advantages of lignin are numerous : abundance in nature, intrinsic biosafety, presence of multiple reactive sites.[304] Additionally, the hyperbranched structure of lignin also enables lignin to act as reinforcing fillers in composites or hydrogels.[305–307] Hydrogels prepared with L-PEG-2959 showed excellent swelling properties and a water-retention ability of 78% could be determined. Due to the hyperbranched structure of lignin, extractability of photoinitiators was considerably reduced compared to the parent Irgacure 2959.



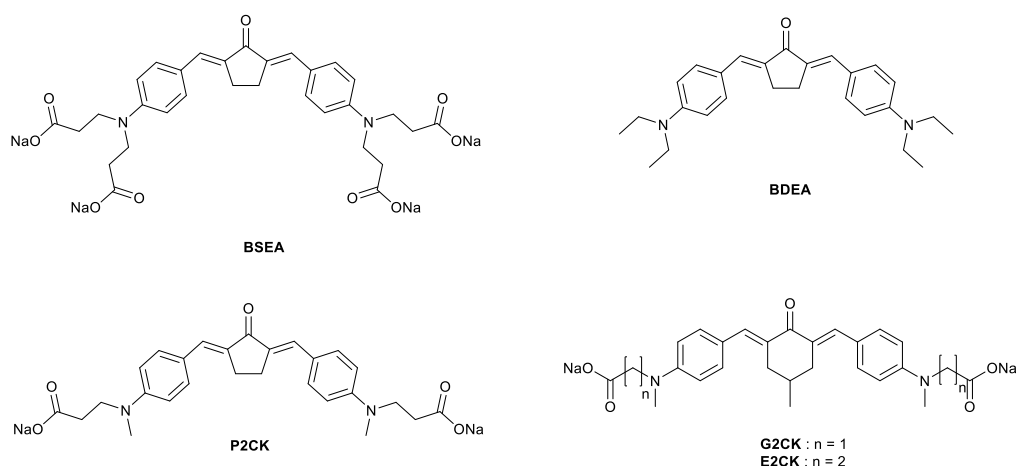
**Figure 13.** Chemical structures of  $[\text{Si-di2959Im}][\text{X}]$ ,  $[\text{Si-En-2959Im-A}][\text{TsO}^-]$  and L-PEG-2959.

### 2.3. Chalcones, benzylidene ketones and cyclanones

The design of water-soluble dyes can constitute a hard work, especially if numerous synthetic steps are necessary to convert a water-insoluble dye as a water-soluble dye. Recently, an interesting approach was developed, consisting in the formation of a charge transfer complex with a water-soluble amine such as triethanolamine (TEOA). As a result of this

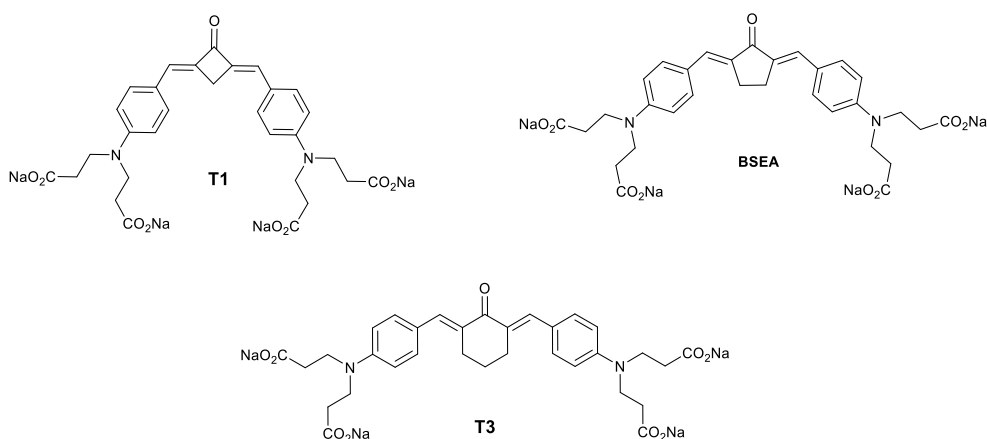


groups constitutes another strategy to provide water solubility to benzylidene ketones. This strategy was applied as soon as 2009 for the synthesis of two-photon photoinitiators.[309] A Two-Photon Absorption (TPA) cross-section of 287 GM at 800 nm was notably determined for BSEA in water. This TPA cross-section is larger than that reported for water-soluble xanthene dyes such as Rose Bengal, Eosin and Erythrosine (< 10 GM at 800 nm) (See Figure 15).[310] However, compared to its water insoluble BDEA analogue, a decrease by ca 50% of the TPA cross-section was determined for BSEA in water, consistent with the trend previously observed by Bazan and coworkers.[311,312] A maximum absorption located at 513 nm was found for BSEA in water.[313] A low threshold energy of 0.51 mW was determined during the FRP of SR610 (80% in water).



**Figure 15.** Chemical structure of BSEA and reference compound BDEA, P2CK, G2CK and E2CK.

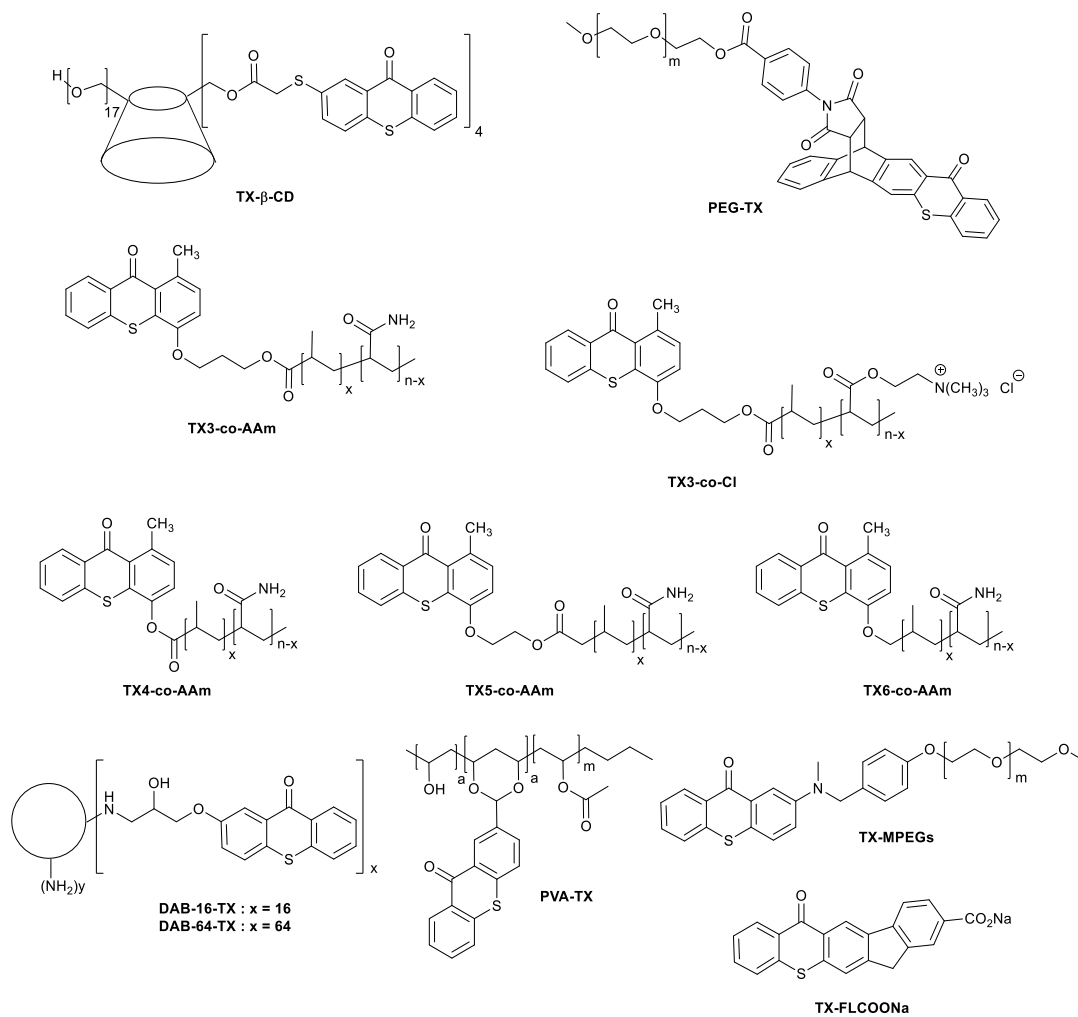
In the same spirit, Liska and coworkers investigated a series of benzylidene cyclanones varying by the size of the central ring but also by the length of the chains used to connect the carboxylate groups.[314] Notably, size of the central ring drastically impacted the TPA cross section of photoinitiators and replacement of cyclopentanone in P2CK by cyclohexanone in E2CK increased the TPA cross-section from 176 GM at 800 nm up to 201 GM for E2CK.[315] Here again, a reduction of the TPA cross-section of water soluble dyes compared to their water insoluble analogues was detected, consistent with the results of Bazan and coworkers. Noticeably, reduction of the length of the alkyl chain in G2CK slightly reduced the TPA cross-section compared to E2CK (163 GM for G2CK compared to 201 GM at 800 nm for E2CK). Influence of the central ring size was also demonstrated for the T1, BSEA, T3 series (See Figure 16).[316] Indeed, TPA cross-sections of 567 GM, 808 GM and 231 GM were respectively determined for the T1, BSEA and T3. The lowest TPA cross-section was measured for the most flexible structure, namely T3 comprising a central cyclohexanone. BSEA proved to be the most promising candidate for one photon and two-photon polymerizations. A low cytotoxicity was also determined for BSEA, 60% of HepG2 cells being still alive after 24 hours of incubation and for the same concentrations than used during the photopolymerization experiments.



**Figure 16.** Chemical structures of T1, BSEA and T3.

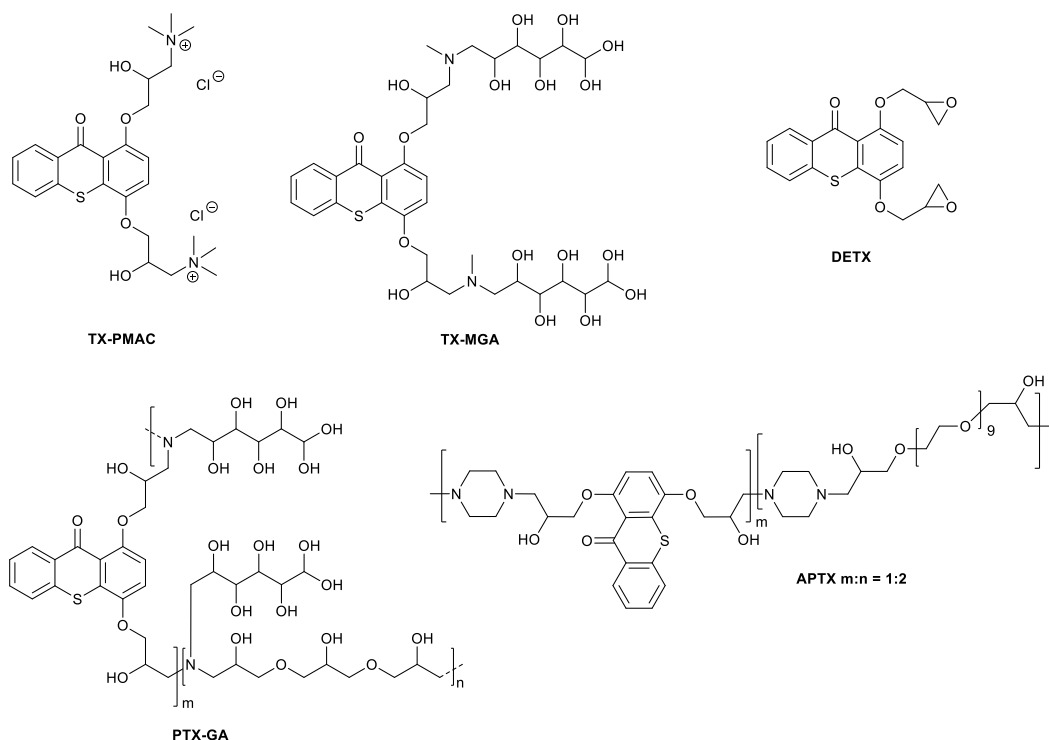
## 2.4. Thioxanthenes

Thioxanthone is a benchmark photoinitiator that was extensively studied in the past due to its low cost, easy availability and its high polymerization efficiency.[235,237–239,242–244,247] Rapidly, derivatization of this high-performance structure was examined and by chemical engineering, water-soluble structures could be obtained at the beginning of the 2000s (See Figure 17). For instance, inclusion of thioxanthenes in cyclodextrin (TX- $\beta$ -CD) enabled to elaborate photoinitiators exhibiting similar spectral characteristics and photoactivity to that of the parent thioxanthone.[317] However, polymerization in water was possible with this structure. By a Diels–Alder [4 + 2] click chemistry strategy, a poly(ethylene glycol) chain could be introduced, enabling to design a one-component polymeric photoinitiator PEG-TX.[318] Copolymerization of a thioxanthone-based monomer with two water-soluble co-monomers, namely acrylamide (AAm) and 2-acryloxyethyl trimethylammonium iodide (MI) enabled to generate water-soluble copolymers (TX3-co-AAm, TX3-co-Cl, TX4-co-AAm, TX5-co-AAm and TX6-co-AAm) that could be advantageously used for the polymerization of acrylamide in water.[319] The dendritic strategy was also examined to design water-soluble thioxanthenes, as exemplified with DAB-16-TX and DAB-64-TX.[320] By a simple acetalization process of polyvinyl alcohol, PVA-TX could be obtained. [321] Interestingly, photopolymerization could proceed even in absence of co-initiators. Indeed, PVA-TX possesses both the light sensitive thioxanthone and the hydrogen donating sites in its structure. By nucleophilic substitution, polyethylene glycol monomethyl ether chains of different lengths could be introduced as peripheral groups in TX-MPEGs.[322] However, photopolymerization of acrylamide in water could only be carried out in the presence of a hydrogen donor, namely *N*-methyldiethanolamine (MDEA). In order to increase the molar extinction coefficient in the visible range, the design of thioxanthone-fluorene conjugates was examined by Yagci and coworkers.[323] By introducing a carboxylate group on TX-FLCOONa, a water-soluble dye could be obtained. Conversely, under its neutral form i.e. TX-FLCOOH, this dye was only soluble in organic solvents and monomers. Noticeably, no polymerization was detected with TX-FLCOONa when used as a monocomponent photoinitiator. However, TX-FLCOONa could act as an efficient initiator in the presence of hydrogen donors in water.



**Figure 17.** Various chemical structures of water-soluble thioxanthone derivatives.

In 2008, Yin and coworkers developed a polymeric photoinitiator containing thioxanthone and glucamine i.e. PTX-GA and its photoinitiating ability was compared to that of low-molecular-weight reference compounds namely TX-MGA and TX-PMAC[324] (See Figure 18).[325]

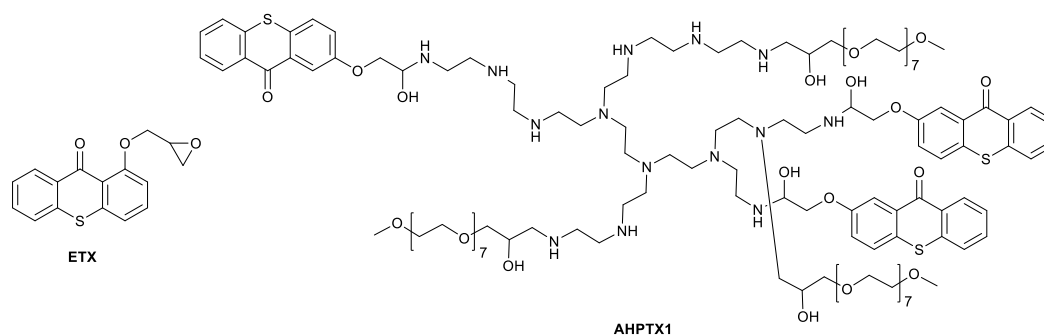


**Figure 18.** Chemical structures of TX-PMAC, TX-MGA, PTX-GA and APTX.

Considering that the three compounds comprise the same chromophore i.e. thioxanthone, similar absorption spectra were found in water. Besides, photoreactivity was different. First, use of *N*-methyl-diethanolamine (MDEA) as a co-initiator was required for TX-PMAC contrarily to TX-MGA and PTX-GA which comprise glucamine. In this case, glucamine could act doubly, first as a co-initiator and as a water-solubilizing agent. Photoluminescence experiments revealed PTX-GA to exhibit a weaker emission than TX-PMAC and TX-MGA, evidencing a more effective quenching of the excited state of thioxanthone by the amino groups of the polymer chains, attributable to a higher concentration of amino groups in the microenvironment of thioxanthone.[326] Polymerization tests done on acrylamide and *N,N'*-methylenebisacrylamide (MBAM) confirmed the trend determined during the photolysis experiments. Thus, PTX-GA furnished the highest monomer conversions upon irradiation with a UV light, consistent with the strong intramolecular interaction existing between the thioxanthone units and glucamine. Conversely, due to the less efficient intermolecular interactions between TX-PMAC and MDEA, less radicals could be produced, resulting in the lowest acrylamide conversion with this two-component system. A similar trend of reactivity was determined for another amphipathic polymeric thioxanthone photoinitiator i.e. APTX (See Figure 18).[324] APTX proved to be very efficient for photoinitiation of acrylate monomers such as 2,2-bis[4-(acryloxypolyethoxy)phenyl] propane (ABPE-10), trimethylolpropane triacrylate (TMPTA) and acrylamide (AM) in water. In comparison to the low-molecular weight photoinitiators DETX and TX-PMAC, a higher monomer conversion could be obtained with APTX, irrespective of the monomers. In the same spirit, hyperbranched structures AHPTXs based on hyperbranched poly(ethylene imine) (HPEI) were reported in the literature (See Figure 19).[327] Here again, compared to the photoinitiating systems based on low-

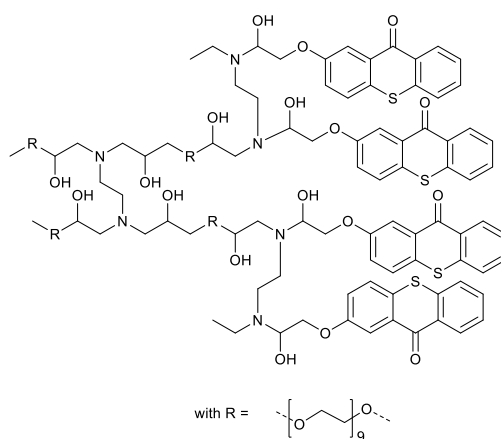


molecular weight structures such as ETX or TX-MGA, AHPTX1 could outperform the two-component systems 2-(2,3-epoxypropyloxy)thioxanthone/triethylamine (ETX/TEA) and TX-MGA/TEA systems, during the FRP of A-BPE-10 and acrylamide in aqueous solutions. The remarkable photoinitiating ability of AHPTX1 was ascribed to an efficient intramolecular hydrogen abstraction between the thioxanthone units and the amino groups of co-initiator, facilitating radical generation. On the opposite, intermolecular interactions between ETX, TX-MGA and triethylamine is less favorable, the viscosity of the resins and the distance between the two partners adversely affecting intermolecular interactions.



**Figure 19.** Chemical structures of ETX and AHPTX1.

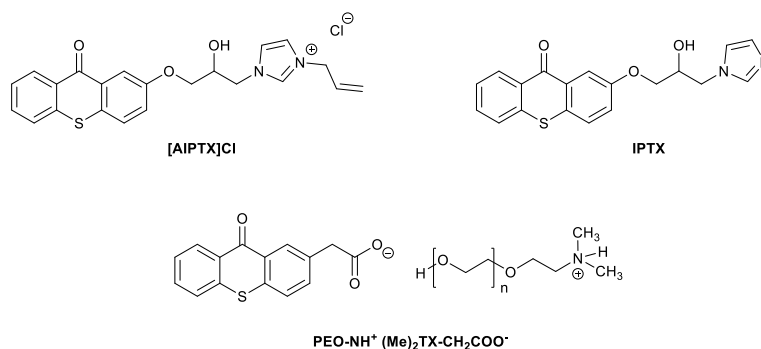
A few years later, the same authors developed a water-soluble thioxanthone (hPEA-TX) and a water-soluble benzophenone (hPEA-BP) based on hyperbranched poly(ether amine) chains (See Figure 20).[328] This strategy is not new since multistimuli responsive polymer nanoparticles based on azobenzene were prepared as soon as 2010 with poly(ether amine) chains.[329,330] Water solubility and photoinitiating abilities were compared to that of small molecules comprising glucamine side-chains (i.e. MGA-TX and MGA-BP). Interest of the hPEA-TX and hPEA-BP structures was the concomitant presence of a poly(ethylene glycol) chain for water solubility and a tertiary amine acting as a co-initiator. Noticeably, hPEA-TX and hPEA-BP showed a good solubility in organic solvents but also in water. A water solubility of 10 wt% was determined for the two dyes.



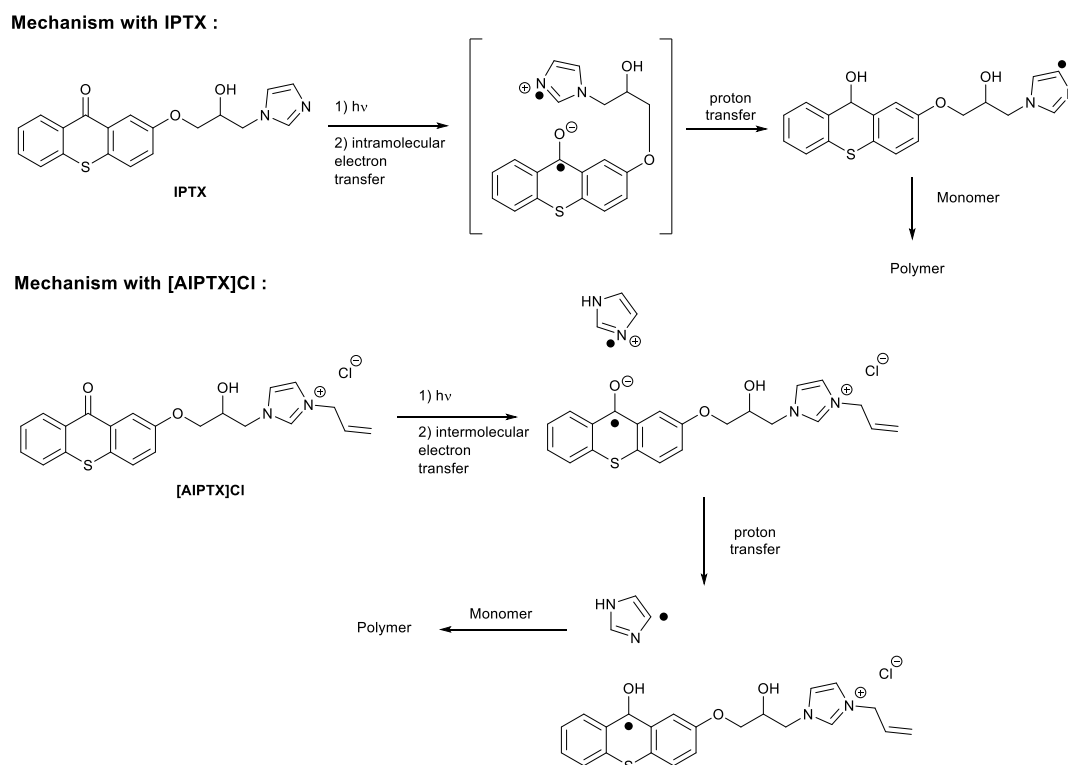
**Figure 20.** Water-soluble thioxanthone based on hyperbranched poly(ether amine) chains.

Photolysis experiments done upon irradiation at 365 nm revealed the photolysis rate to be fast (around 240 s) for hPEA-TX and hPEA-BP whereas almost no photolysis could be detected for MGA-TX and MGA-BP in the same conditions. A different situation was found for the two-component MGA-TX/TEOA and MGA-BP/TEOA systems, consistent with a mechanism including the formation of a radical formed by the carbonyl compound (ketyl-type radical) and another one on the amine. During the FRP of acrylamide in water, hPEA-TXs and hPEA-BPs exhibited higher heat flows and faster polymerization rates than the reference Irgacure 2959 at early stage. Noticeably, hPEA-TXs slightly outperformed hPEA-BPs in terms of final monomer conversion, attributable to the higher molar extinction coefficient of hPEA-TXs at 365 nm. Excellent conversions could also be obtained during the FRP of organosoluble hexanediol diacrylate (HDDA), trimethylolpropane triacrylate (TMPTA) and pentaerythritol tetraacrylate (PETTA), photopolymerization of these multifunctional monomers providing monomer conversions as high as 99, 80 and 60% respectively. In this case, monomer conversions obtained with hPEA-TXs and hPEA-BPs were greatly higher than that obtained with the low-molecular weight photoinitiators MGA-TX and MGA-BP. Overall, during the past decades, a significant effort has been devoted to develop water-soluble thioxanthenes. By developing polymeric structures, a better solubility of thioxanthone in resins could be obtained. A reduction of the extractability of thioxanthone can also be achieved, polymer-based thioxanthenes being intimately mixed with the polymer chains. This property is highly researched, especially for biological and food packaging applications.[331,332]

Over the years, numerous strategies were developed to render thioxanthone a water-soluble photoinitiator. For instance, introduction of an imidazolium group on [AIPTX]Cl enabled to reduce the extractability of the photoinitiator while introducing a water-solubilizing imidazolium group (See Figure 21).[333] Interestingly, in these systems, the imidazole ring was used as a water-soluble hydrogen donor, thus acting as a co-initiator during photopolymerization. Indeed, thioxanthone is well-known to mostly participate to hydrogen atom abstraction events.[334] By mean of a photoreduction reaction, ketyl radicals and imidazolyl free radicals could be produced, the latter being able to initiate a polymerization process. In the case of IPTX, the electron and proton transfer resulted from an intramolecular electron transfer whereas for [AIPTX]Cl, imidazole had to be introduced as an additive, enabling first to induce an intermolecular electron transfer followed by an intramolecular proton transfer (See Scheme 2).

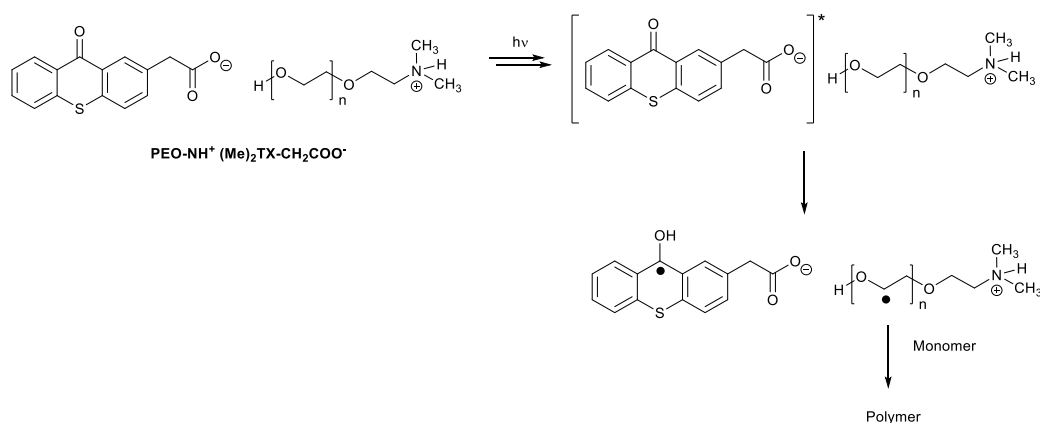


**Figure 21.** Chemical structures of IPTX, [AIPTX]Cl and PEO-NH<sup>+</sup>(Me)<sub>2</sub> TX-CH<sub>2</sub>COO<sup>-</sup>



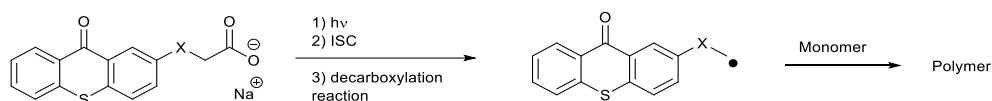
**Scheme 2.** Photochemical mechanism involved in the production of imidazolyl radicals in the case of IPTX and [AIPTX]Cl/imidazole.

In 2012, Yagci and coworkers proposed a thioxanthone salt PEO-NH<sup>+</sup>(Me)<sub>2</sub> TX-CH<sub>2</sub>COO<sup>-</sup> possessing a poly(ethylene oxide) dimethylammonium counter-anion that could act as a hydrogen donating group (See Figure 21 and Scheme 3).[335] Interestingly, this polymeric photoinitiator could be prepared in one step, by a simple acid/base reaction between the dimethylamino-functionalized poly(ethylene oxide) and the acid-substituted thioxanthone, enabling to produce the salt in 94% yield. Introduction of carboxylic groups on the thioxanthone scaffold is not a novel approach since the first reports in this field were published by Fouassier and coworkers in 1988,[336,337] but other research groups later examined this approach.[326,338]



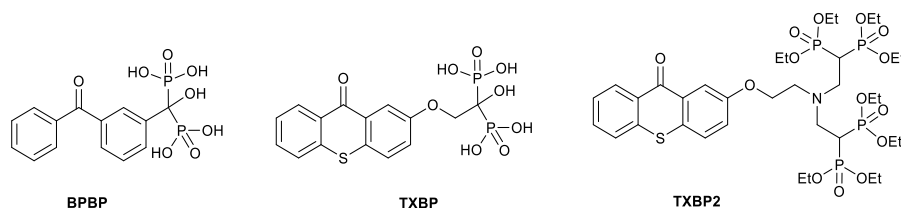
**Scheme 3.** Mechanism involved with PEO-NH<sup>+</sup>(Me)<sub>2</sub>TX-CH<sub>2</sub>COO<sup>-</sup>

By introducing a thioacetic acid group or a carboxymethoxy group on thioxanthone, initiating radicals could be directly generated on photoinitiators (1A and 2A), as shown in the Scheme 4.[339] Due to the decarboxylation reaction occurring on 1A and 2A, the two photoinitiators could be used as monocomponent photoinitiators. Additionally, using this approach, thioxanthone could be connected to the polymer chains, drastically limiting its extractability.



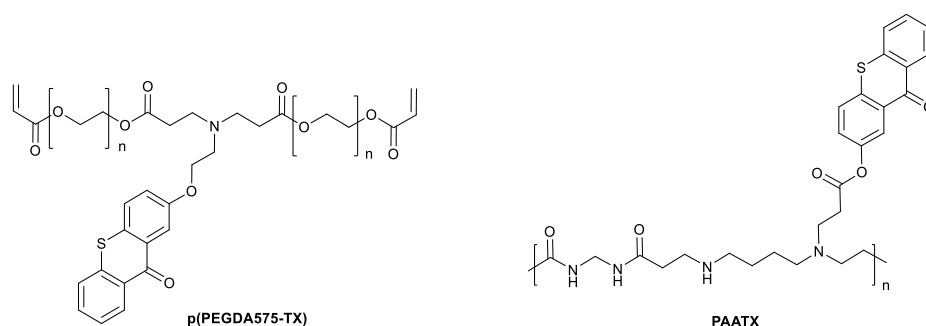
**Scheme 4.** X = O, S 1A : X = O, 2A : X = S

On her side, Avci and coworkers examined the introduction of bisphosphonic acid-groups as water-solubilizing agents for thioxanthone. This strategy was notably applied to TXBP [340] and TXBP2 [341] both exhibiting an absorption maximum located at ca 400 nm. If the bisphosphonic acid-groups do not influence the absorption properties of the dyes, major differences in terms of water solubility could be evidenced. Thus, a remarkable water solubility could be determined for TXBP2, peaking at 86 g/L, far from that reported for Irgacure 2959 (5 g/L) and obtained for TXBP (0.05 g/L). Presence of multiple bisphosphonic acid-groups on TXBP2 was thus beneficial for greatly improving the water-solubility. For comparison, a benzophenone-based analogue BPBP was prepared and exhibited a water-solubility of 28 g/L (See Figure 22). Compared to the previous carboxylic acid derivatives for which a decarboxylation reaction could produce radicals, BPBP, TXBP and TXBP2 could not behave as monocomponent systems and these structures were used in combination with an iodonium salt or an amine (ethyl dimethylaminobenzoate (EDB)).



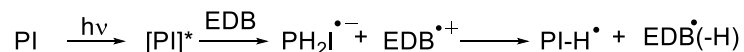
**Figure 22.** Chemical structures of BPBP, TXBP and TXBP2.

As drawback of this approach, lower monomer conversions were obtained when combined with EDB than with the iodonium salt, attributable to an acid/base reaction occurring between the phosphonic acid groups and the amine. The development of water-soluble polymers containing thioxanthone was also examined, as exemplified with p(PEGDA575-TX) that could decompose without additives (See Figure 23).[248]. Indeed, as shown in the Scheme 5, p(PEGDA575-TX) can undergo an intramolecular or an intermolecular photoreduction by the tertiary amines or the ether groups in its structure. A low extractability from the resulting polymers was determined, around 13%, greatly lower than that of thioxanthone (66%). A similar mechanism was proposed for another thioxanthone-based polymer i.e. PAATX.[342] A low extractability was also evidenced for this photoinitiator, being three-times lower than that of thioxanthone.

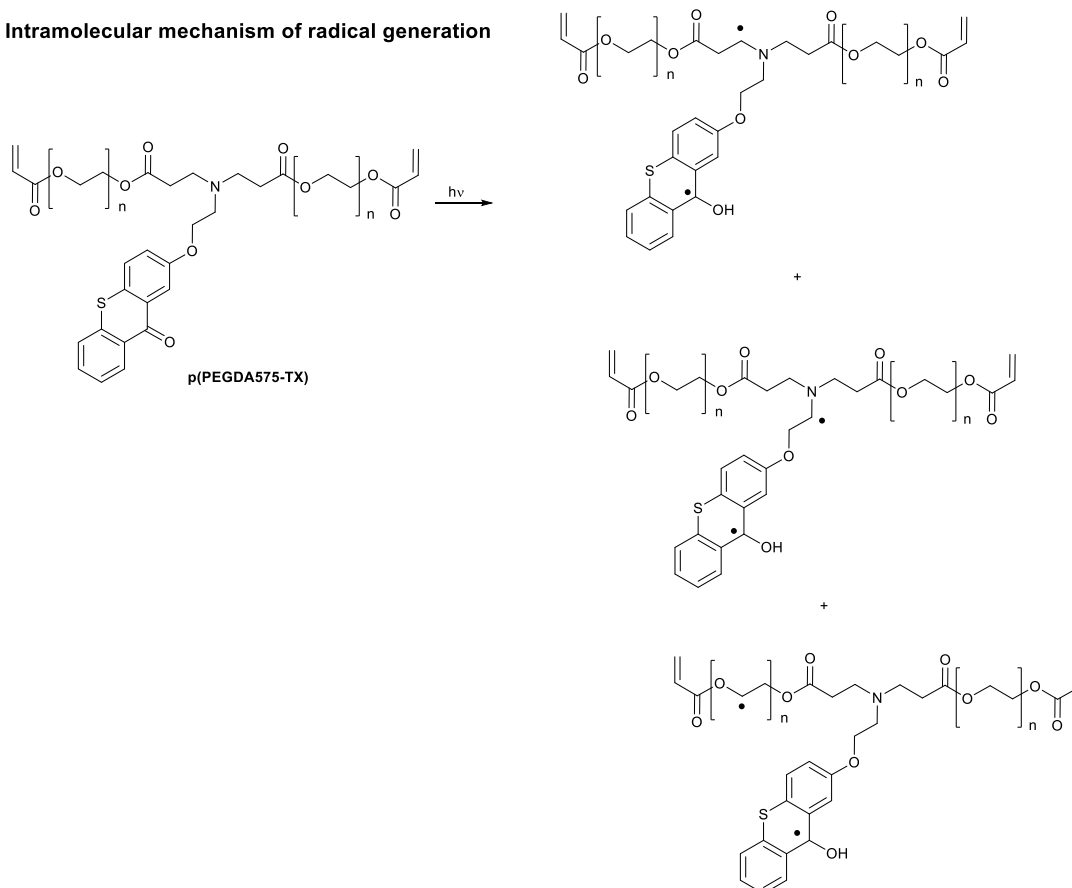


**Figure 23.** Chemical structures of PAATX and p(PEGDA575-TX).

### Intermolecular mechanism of radical generation

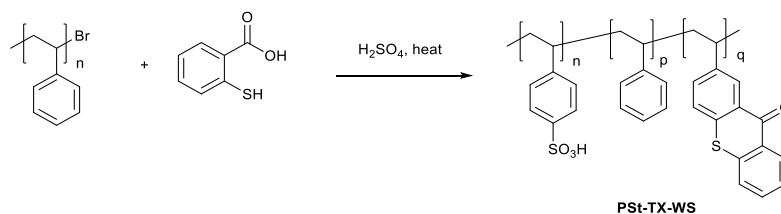


### Intramolecular mechanism of radical generation



**Scheme 5.** Mechanism enabling to generate radicals with p(PEGDA575-TX).

Finally, the same authors developed an original strategy to prepare a water-soluble macrophotoinitiator starting from poly(styrene).[343] By mean of a simultaneous thioxanthonation and sulfonation reaction, PSt-TX-WS could be prepared in one step according to the mechanism depicted in **the Scheme 6.**

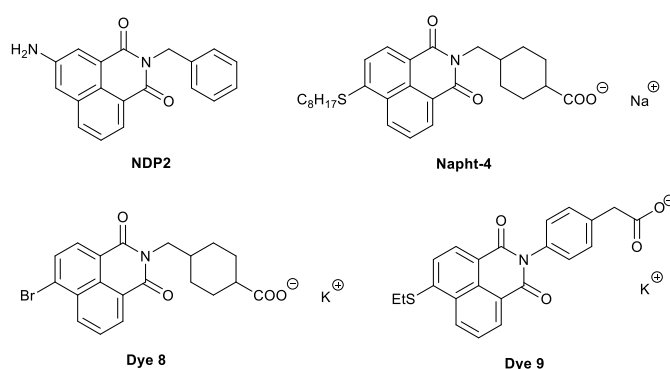


**Scheme 6.** One-pot synthesis of PSt-TX-WS.

## 2.5. Naphthalimides

Naphthalimides were extensively used as visible light photoinitiators due to their high photoluminescence quantum yields, the facile modification of the naphthalimide scaffold in order to provide the desired properties. In 2015, Lalevée and coworkers introduced an amino

group onto NDP2 so that this dye could be encapsulated in 2,6-di-O-Me- $\beta$ -cyclodextrin (See Figure 24).[112] A slight blueshift of the absorption maximum was found after inclusion of NDP2 in cyclodextrin, peaking at 407 nm in water contrarily to 417 nm in acetonitrile. As drawback of this approach, a reduction of the polymerization efficiency during the cationic polymerization of EPOX at 405 nm was found for the two-component NDP2-CD/Iod system compared to its NDP2/Iod analogue, assigned to a confinement of the NDP2<sup>••</sup> radicals inside the cyclodextrin, therefore lowering its reactivity. This issue was addressed with Napht-4 using 4-((6-bromo-1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl)methyl)cyclohexane-1-carboxylic acid as a water solubilizing agent. Precisely, the water-solubility could be obtained while converting Napht-4 as a sodium salt, the neutral form exhibiting only a weak water-solubility.[117] Photopolymerization of a polyethylene glycol diacrylate/water blend could be carried out at 405 nm using the two-component Napht-4/triethanolamine (0.1%/1% w/w) system. Noticeably, by UV-visible absorption spectroscopy, a hyperchromic effect was detected in water for Napht-4 compared to acetonitrile ( $\epsilon = 7000 \text{ M}^{-1}\cdot\text{cm}^{-1}$  in water vs.  $\epsilon = 2570 \text{ M}^{-1}\cdot\text{cm}^{-1}$  in acetonitrile) and this trend is rarely observed between organo-soluble and water-soluble dyes.



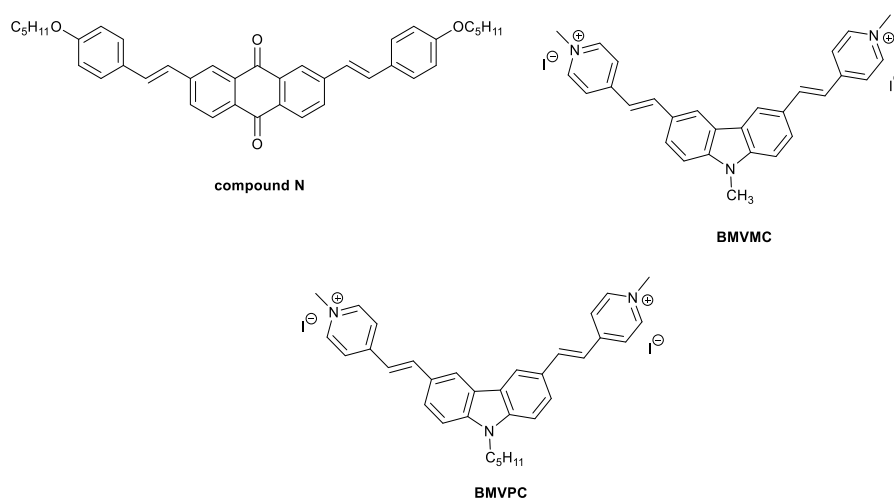
**Figure 24.** Chemical structures of NDP2, Napht-4, Dye 8 and Dye 9.

By varying the substituent onto the naphthalimide core and by introducing a silver salt inside the photocurable resins, antibacterial hydrogels could be prepared with dye 8 and dye 9, by generating in situ silver nanoparticles.[122] Indeed, part of the radicals generated by the three-component dye/iodonium salt/amine system could be used to reduce the silver salt during photopolymerization, enabling to get a homogenous distribution of silver nanoparticles inside the polymer. However, a high polydispersity was also found between nanoparticles, ranging from small particles to aggregates. Noticeably, an optimal antibacterial activity was found for all resins initially containing a concentration of 4 wt% of silver nitrate.

## 2.6. Other structures

Naphthalimides were not the only hydrophobic dyes to be included by mean of a host-guest strategy into water-soluble cavities in order to produce water soluble initiators. Thus, the hydrophobic 2,7-bis(2-(4-pentanoxyphenyl)vinyl)anthraquinone (N) could be immobilized into 2-hydroxypropyl- $\beta$ -cyclodextrin, and furnished a two-photon

polymerization initiator exhibiting a two-photon absorption cross-section of 200 GM at 780 nm.[344] A drastic increase of the two-photon absorption cross-section could be obtained with *bis*[2-(1-methylpyridinium)vinyl]-9-methylcarbazole diiodide (BMVMC) upon complexation with cucurbit[7]uril (CB7).[345] Thus, the two-photon absorption cross section of the complex increased up to 2500 GM whereas a value of only 750 GM was determined for the uncomplexed BMVMC at 830 nm. During the FRP of PEGDA in water, a resolution of 180 nm and a laser threshold of only 3.7 mW was determined. A slightly higher laser threshold of 4.5 mW was found for the BMVPC-CB7 inclusion complex differing from BMVMC-CB7 by the length of the alkyl chain introduced onto the carbazole moiety (See Figure 25).[346]



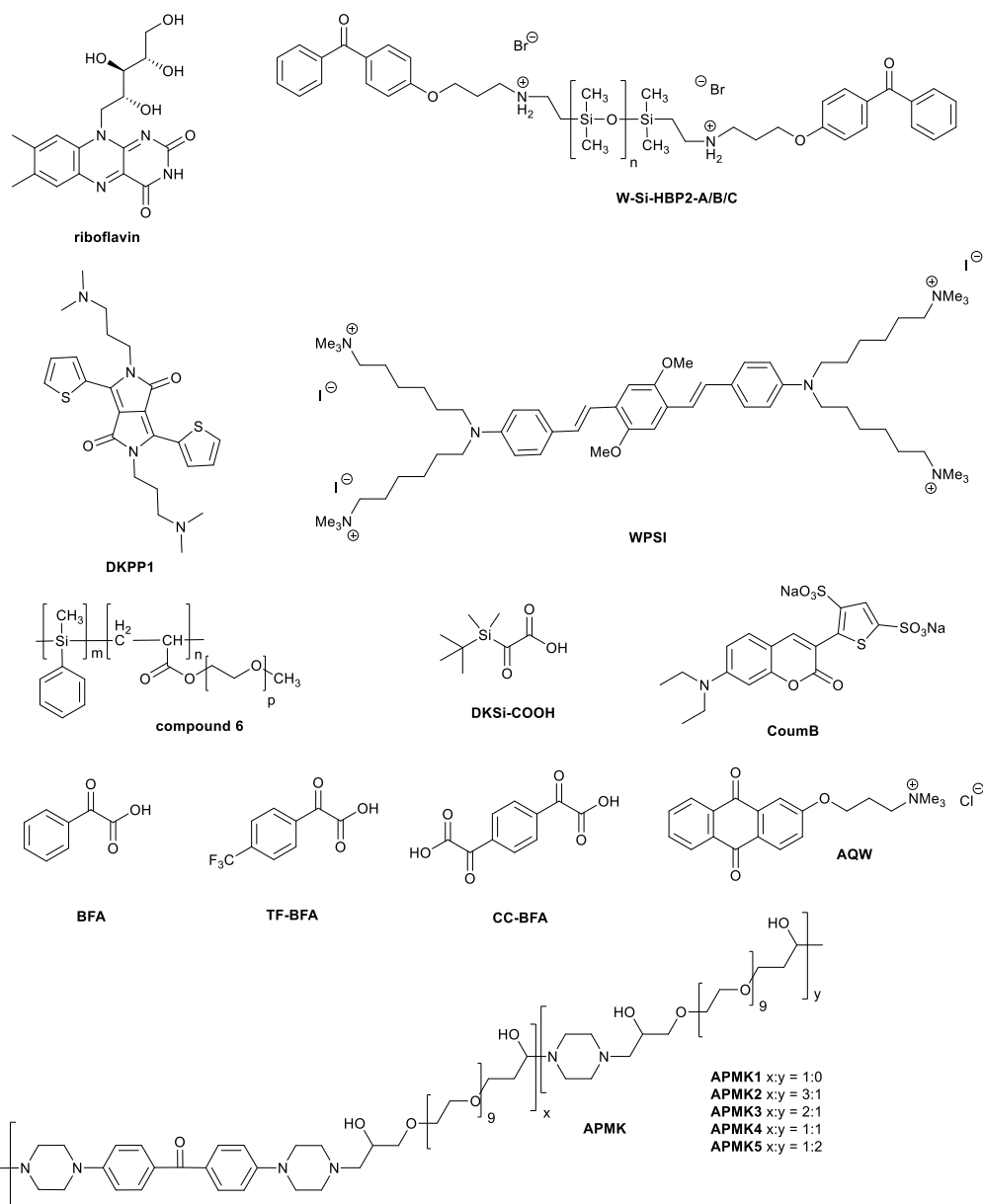
**Figure 25.** Chemical structures of N, BMVMC and BMVPC.

A more common strategy to design water-soluble dyes consisted in introducing polyethylene glycol chains, poly(hydroxy) or polysiloxane chains. Some dyes are naturally substituted with water-soluble chains such as Riboflavin (vitamin B2) (See Figure 26).[347] In combination with triethanolamine, biocompatible polymers could be prepared. In 2013, Sun and coworkers modified a benzophenone with polysiloxane chains.[348,349] However, it has to be noticed that introduction of ammonium substituents on benzophenone is not new since this strategy was used as soon as 1988 by Green and coworkers.[350] Various silicon contents were used in W-Si-HBP2 -A/B/C and a decrease of the water solubility upon elongation of the silicone chain length was detected, assigned to the hydrophobicity of polysiloxane. In water, longer triplet excited state lifetimes were found for all polysiloxane benzophenone photoinitiators compared to the parent 4-hydroxybenzophenone. Similarly, increase of the silicone chain length obviously influenced the triplet lifetimes of polymeric photoinitiators, resulting in a decrease of the excited state lifetimes upon elongation of the chain. It has to be noticed that water-soluble UV photoinitiators were previously reported in the literature, as exemplified with polymethylphenylsilane-co-poly(polyethyleneglycol acrylate) (compound 6).[351] Benzophenone derivatives were the focus of numerous studies for improving their water solubilities. Thus, a series of amphiphilic polymeric Michler's ketone photoinitiators (APMKs) were prepared by incorporating PEO short chains, the Michler's ketone units and the coinitiator amine (piperazine) within a unique polymeric chain.[352] Investigation of the



composition of APMKs revealed the Michler's ketone/PEO/piperazine 2:3:1 ratio was required to generate water-soluble photoinitiators. By increasing the POE content, an improvement of the monomer conversion was obtained. An absorption maximum at 357 nm could be determined for all photoinitiators in water, irrespective of the composition. Results showed that APMKs could efficiently initiate the polymerization of hydrophilic and hydrophobic monomers. Notably, the polymerization of the water-soluble polyethylene glycol diacrylate (PEGDA), and the oil-soluble phenoxy ethyl acrylate (AMP-10G) and 2,2-bis[4-(acryloxypolyethoxy)phenyl]propane (A-BPE-10) monomers were examined in this work. By increasing the POE content in APMKs, an improvement of the PEGDA conversion was detected, assigned to an enhanced flexibility of the APMKs backbone and a higher content of coinitiator amino groups, facilitating radicals generation. Conversion higher than 90% could be determined by photoDSC. A good water solubility could also be provided by introducing ammonium groups onto dyes, as exemplified with 1,4-bis(4-(*N,N*-bis(6-(*N,N,N*-trimethylammonium)hexyl)amino)-styryl)-2,5-dimethoxybenzene tetraiodide (WSPI).[353] Besides, the two-photon absorption cross-section determined at 800 nm was only of 120 GM for WSPI, far from that reported for inclusion complexes prepared with 2,7-bis(2-(4-pentaneoxyphenyl)vinyl)anthraquinone (N), BMVMC and BMVPC. However, this value is comparable to that previously reported for the parent 4,4'-dialkylamino-bis(styryl)benzene derivatives.[312,354] Quaternization of dimethylamino groups is not new since Allen and coworkers reported in 2001 the synthesis of a water-soluble anthraquinone, namely 2-(*N,N,N*-trimethylammoniumpropoxy)anthraquinone chloride (AQW).[268] Hydrogels containing up to 80% water could be obtained at the fast scanning speed of 10 mm/s and for a laser power of 140 mW. The conversion of dialkylamino group as ammonium salt is not still necessary. Indeed, a diketopyrrolopyrrole group bearing dimethylamino groups exhibiting an excellent water solubility.[355] The two-component DKPP1/*N*-methyldiethanolamine (MDEA) 0.15%/8% w/w system could led to an efficient polymerization of 2-hydroxyethyl acrylate (HEA) in water. A hydrogel containing 74% water while starting from a formulation of HEA only containing 40% water could be obtained upon irradiation at 470 nm. In 2020, Lalevée and coworkers reported a small molecule i.e. 2-oxo-2(*tert*-butyldimethylsilyl)acetic acid (DKSI-COOH) that showed an excellent water-solubility.[356] Interestingly, a good absorption in the visible range was found for this phenyl-free photoinitiator, and the design of phenyl-free photoinitiators remains scarce in the literature.[223] Besides, a broad absorption band extending between 400 and 500 nm and an absorption maximum at 442 nm could be determined for DKSI-COOH in acetonitrile. In fact, theoretical calculations revealed the Si-d orbitals to participate to the frontier orbitals of DKSI-COOH, enabling to lower the HOMO-LUMO gap and providing an absorption band in the visible range. A moderate solubility was however determined for DKSI-COOH in water since a solubility as low as 10<sup>-2</sup> M was measured. A good stability in acidic conditions was also determined since after 12 weeks in a methacrylic acid/water blend, no modification of the absorption spectrum was detected. As interesting feature, DKSI could be used as a monocomponent system and excellent photobleaching properties could also be observed during the polymerization of a

BisGMA/TEGDMA blend. This ability is actively researched for numerous applications requiring colorless coatings.[357]



**Figure 26.** Chemical structures of various water-soluble photoinitiators.

Another group which seems to be promising for elaborating water-soluble dyes is the sulfonate group. An example of coumarin-disulfonate (CoumB) was recently reported in the literature.[62] As drawback of this approach, sulfonation using the  $\text{SO}_3\cdot\text{DMF}$  complex is only applicable to dyes comprising a thiophene unit in their scaffolds, therefore drastically limiting the scope of application of this reaction. A more versatile approach was developed by Nie and coworkers that introduced a keto-acid group on a series of photoinitiators (BFA, TF-BFA and CC-BFA).[358] In this case, an oxidation of acetyl group using selenium oxide as the oxidizing agent in pyridine at reflux was used, enabling to get the different photoinitiators with reaction yields ranging between 62 and 80%. If this approach is appealing, it was only investigated for

the design of UV-photoinitiators, the absorption of BFA, TF-BFA and CC-BFA not exceeding 350 nm.

### **Conclusion**

The design of water-soluble dyes is an active research field since almost 30 years. Despite the intense research efforts, the design of water-soluble photoinitiators has mainly been successful for UV photoinitiators. Concerning water-soluble visible light photoinitiating systems, their properties and applications in aqueous media have not been fully explored yet. If numerous groups such as poly(ethylene glycol) chains, ammonium groups or carboxylate groups were extensively used, innovative strategies have been developed during the last few years. Thus, sulfonation of thiophene-based dyes, introduction of benzoylformic groups have recently been successfully used for designing visible light photoinitiating systems. In these different cases, if the water-solubility was obtained, this latter remained however limited when using benzoylformic groups.

### **Future research outlook**

With aim at designing highly soluble dyes in water, the most promising strategy seems to consist in introducing multiple bisphosphonic acid-groups. Several groups also succeeded to introduced water-solubilizing chains also acting as co-initiators so that the resulting photoinitiators could be used as monocomponent photoinitiating systems. If water-solubility was examined for visible dyes, the combination of water-solubility and photobleaching has not been extensively investigated. Future works will consist in combining water-solubility and photobleaching ability in order to design photoinitiators perfectly fitting the industrial requirements. Recent works have notably evidenced that photobleaching could be efficiently obtained with chalcones or push-pull dyes, suppression of the  $\pi$ -conjugation between the donor and the acceptor in push-pull dyes enabling to suppress the color.[357] Similarly, in chalcones, suppression of the electron acceptor proved to be an efficient strategy to get an efficient photobleaching. Introduction of water-soluble substituents on these structures could enable to combine water solubility and photobleaching.

### **Acknowledgments**

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### **Conflicts of Interest**

The authors declare no conflict of interest.

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