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Recent Advances on Benzylidene Ketones as Photoinitiators of Polymerization

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Abstract

Visible light photopolymerization is facing a revolution with the development of monocomponent photoinitiating systems greatly simplifying the composition of the photocurable resins. Among unimolecular photoinitiators, chalcones and related structures are extensively studied due to the easiness of synthesis, the versatility of the substitution pattern and the good thermal stability. Among chromophores that can be used for the design of photoinitiators, benzylidene ketones have been identified as promising scaffolds due to their facile syntheses reduced to a unique synthetic step, the possibility to access to these structures using environmentally friendly conditions and their good absorptions in the visible range. In this review, an overview of the recent advances on benzylidene ketones used as visible light photoinitiators is provided. Notably, these structures could be used for both one photon and two-photon polymerizations, evidencing the versatility of these structures. To evidence the interest of benzylidene ketones, comparisons with benchmark photoinitiators are provided.

Keywords

Photoinitiator; benzylidene ketone; photopolymerization; LED; low light intensity

1. Introduction

During the past decades, visible light photopolymerization has been the focus of intense research efforts supported by the wide range of applications using this polymerization technique. [1–19] Active research activity on visible light photoinitiating systems is notably supported by the recent safety concerns raised by the use of UV light photoinitiating systems. Notably, the production of ozone during irradiation, the dangerousness of UV light that can cause eye damages and skin cancers can be cited as the main factors causing the abandoning of UV photopolymerization. [20–23] Besides, photopolymerization remains an interesting polymerization technique used in research fields such as microelectronics, 3D and 4D printing, adhesives, dentistry and coatings.[24–33] Compared to thermal polymerization, photopolymerization exhibits several specificities allowing a clear distinction to be made between these two polymerization techniques. Notably, a temporal and a spatial control of the polymerization process can be efficiently obtained. If desired, photopolymerization can also be carried out without solvents, avoiding the release of volatile organic compounds (VOC).[23]

Contrarily to UV photopolymerization for which the light penetration remains limited within the photocurable resins, a higher light penetration can be obtained in the visible range, as shown in the Figure 1.[34] Thus, if a light penetration around 4 mm can be achieved at 450 nm, this latter can reach 5 cm at 800 nm, greatly higher than what can be achieved in the UV range (around 600 μm).

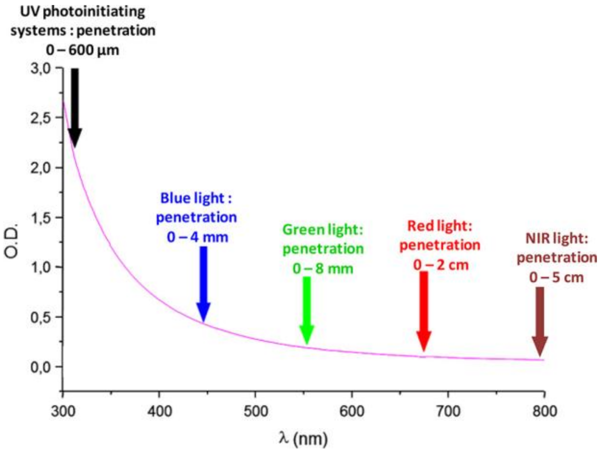


Figure 1. Light penetration in a polystyrene latex with an average diameter of 112 nm. Reprinted with permission from Bonardi et al.[34]

If visible light photopolymerization seems to be an appealing and promising alternative to UV photopolymerization, the fact to use less energetic irradiation wavelengths adversely impact the reactivity of visible light photoinitiators. To address this issue, numerous families of dyes have been investigated during the last 15 years, as exemplified with coumarins,[35–47] chromones and flavones,[48–50] pyrrole derivatives,[51] iodonium salts,[52–59] thioxanthones,[60–73] iridium complexes,[74–81] curcumin,[82–85] thiophene derivatives,[86] anthracene,[87,88] acridones,[89,90] conjugated polymers,[91] 2,3-diphenylquinoxaline derivatives,[92,93] diketopyrrolopyrroles,[94–96] truxene derivatives[97] phenazines,[98] camphorquinones,[99,100] acridine-1,8-diones,[101–103] chalcones,[32,104–117] Schiff bases,[118] dithienophospholes,[119,120] copper complexes,[121–137] dihydro-anthraquinones,[138] perylenes,[139–142] carbazoles,[143–156] metal organic framework (MOFs),[157–159] iron complexes,[158,160–166] pyrenes,[167–175] helicenes,[176,177] phenothiazines,[178–188] zinc complexes,[189,190] Bodipy,[191–196] cyanines,[197–203] benzylidene ketones,[204,205] push-pull dyes,[160,206–220] viologen derivatives,[220–222] naphthoquinones,[223] porphyrins,[224,225] triphenylamines,[226,227] perovskites,[228,229] polyoxometalates,[230–232] glyoximides,[233] naphthalimides,[52,234–250] squaraines,[251–255] benzophenones,[256–264] and cyclohexanones.[265–268] By using these different families, efficient photoinitiating systems activable from the near UV/visible range until the near infrared range could be prepared. Besides, most of the efficient photoinitiating systems are three-component systems comprising a dye used as the photosensitizer for the sensitization of an iodonium salt. In order to render the system catalytic, a sacrificial amine is often used, improving the final monomer conversion. From a practical viewpoint, use of three-component systems remains a complicated approach as it requires the ratio of the three partners to be perfectly adjusted to optimize the monomer conversion. In industry, in addition of a complicated mixture, use of amines is preferably avoided due to potential toxicity issues but also due to yellowing of coatings by amines.[269–272] However, this is the cost to pay to get highly efficient photoinitiating systems. At present, the development of Type II monocomponent photoinitiating systems remains limited due to the necessity to introduce within the same molecule a hydrogen donor used as a co-initiator connected to a hydrogen acceptor. In this field, thioxanthones[273–275] and benzophenones[256,261,276,277] are the most popular hydrogen acceptors reported in the literature even if a few new structures such as bithiophene derivatives[258] or naphthalimides[234,240,241] have recently been examined as possible structures. However, such compounds can only be obtained in multistep synthesis, rendering this approach less appealing for industrial applications due to the high cost of such structures. The access to monocomponent photoinitiating systems which can be obtained in a minimum of synthetic steps are thus highly researched. With aim at developing dyes strongly absorbing in the visible range while enabling to initiate both one photon and two photon polymerization processes, benzylidene ketones are one of those. Especially, a great deal of efforts has been devoted to develop monocomponent photoinitiators with this structure, with aim at reducing the number of synthetic steps. α,α'-*Bis*(substituted benzylidene)ketones have been extensively studied in the literature as these structures (where D and A respectively stand for donor and acceptor) can be used as precursors for the design of biologically active molecules by mean of multicomponent reactions.[278–280] These D-π-A-π-D structures also exhibit a good electronic delocalization due to their π-conjugated scaffolds, the electron-withdrawing ability of the ketone group enabling these dyes to exhibit high molar extinction coefficients combined with a strong absorption located in the visible range. Face to these considerations, benzylidene ketones were thus logically investigated as visible light photoinitiators of polymerization. Over the years, scope of applications of these structures was broaden by enabling one and two-photon polymerization processes to be carried out.

Parallel to the polymerization efficiency, the ability of the photoinitiating system to bleach during the polymerization process is an important issue.[40,84,179,267,281–285] Indeed, photobleaching can allow a better light penetration and thus improve the depth of cure.[286] This point is of crucial importance, notably in dentistry. [287–290] Parallel to this, visible light photopolymerization is greatly slowed down by the colour imposed by the visible light photoinitiator that are dyes strongly absorbing in the visible range. Industrials prefer to choose the colour of their polymers instead of the colour to originate for the photoinitiators. At present, photoinitiators capable to bleach remains scarce in the literature. However, as later detailed in this review, benzylidene ketones exhibited promising properties in this field.

In this review, an overview of the recent advances concerning benzylidene ketone-based photoinitiating systems is reported. To evidence the interest of these structures, comparisons with reference compounds are provided.

2. Benzylidene ketones

2.1. Symmetrically substituted benzylidene ketones for one and two-photon photopolymerization

2.1.1. Two-photon polymerization

Two-photon photopolymerization constitutes an interesting method for the fabrication of complex three-dimensional structures of micrometre-size while achieving a remarkable spatial resolution.[291] When irradiated, some molecules are capable to absorb simultaneously two photons, giving rise to what is named a two-photon absorption (TPA).[292] As specificities, the probability of absorption of the electronic transition is proportional to the square of the incident intensity. As a result of this quadratic dependency, the absorption process is limited to the immediate vicinity of the focal point. In the presence of a monomer, a high spatial resolution of the excited volume can be achieved, enabling to generate 3D structures with a high spatial resolution. In 2003, Baldeck and coworkers reported 1,13-*bis*-[4-(diethylamino)phenyl]-trideca-1,3,5,6,8,10,12-hexaen-7-one (TPP-1) as photoinitiator for two-photon polymerization (TPP) (See Figure 2).[293] Especially, TPP-1 was designed in analogy to Michler's ketone which is a benchmark UV photoinitiator only exhibiting a weak sensitivity to two-photon absorption (TPA).[294,295]

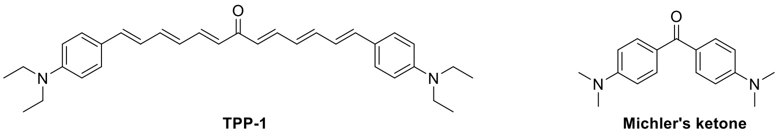


Figure 2. Chemical structure of TPP-1 and the benchmark Michler's ketone.

Noticeably, this molecule could initiate the photopolymerization of acrylates upon irradiation with an inexpensive Nd-YAG microlaser. Indeed, one major drawback of TPP relies in the necessity to use onerous femtosecond Ti:sapphire lasers for three-dimensional (3D) microfabrications.[296,297] This is notably related to the fact that photoinitiators exhibiting very weak sensitivities for TPA are often used, requiring the use of high laser intensities to compensate the low absorption. This issue can be addressed if electron-rich photoinitiators are used, as exemplified with TPP-1. Indeed, TPP-1 showed a broad two-photon absorption band ranging between 800 and 1100 nm with a cross-section of 100 × 10^{-50} $cm^4.s.photon^{-1}$ at 1.06 µm. As shown in the Figure 3, an absorption maximum at 509 nm could be determined, with a molar extinction coefficient of 79 500 $M^{-1}.cm^{-1}$. TPA properties could also be determined between 800 and 1100 nm, with a maximum centered at 950 nm, with a cross-section of 200 × 10^{-50} $cm^4.s.photon^{-1}$ at 950 nm. These values are greatly higher than that determined for benchmark resins such as SCR701, SCR751, HS671 or Nopcocure800.[296] Determination of the minimal energy density required in order the resin (a mixture of monomers composed of 70% (tris(2-hydroxyethyl)isocyanurate triacrylate and 30% poly(styrene-co-acrylonitrile)) to polymerize was determined as being 5 500 J/cm^3. An incident exposure dose (in J/cm^2) required for polymerization of 2 050 J/cm^2 was also determined, six times lower than that required for benchmark UV photoinitiators.[296] Development of this new symmetrical conjugated ketone with terminal dimethylamino groups was thus an efficient strategy for the design of TPA photoinitiators.

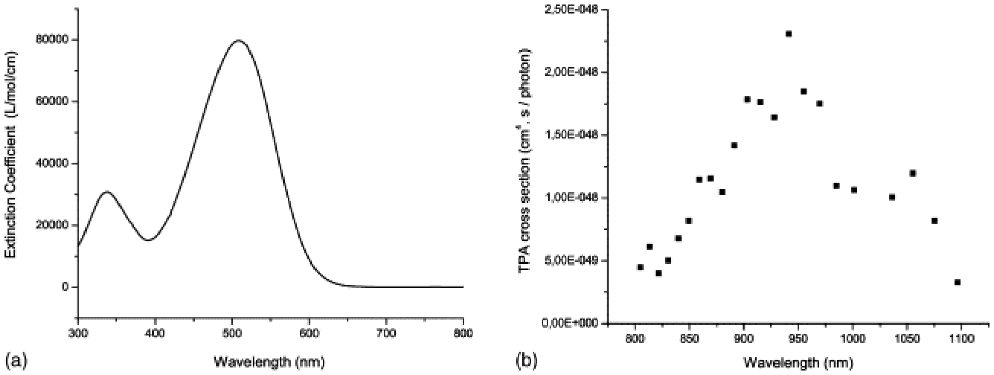


Figure 3. a) UV-visible absorption spectrum and b) TPA spectrum of TPP-1 in chloroform. Reproduced with permission of Ref.[293]

In 2006, the same authors revisited TPP-1 in the context of a more extended study in which seven derivatives i.e. M2K, TPP-1, BK2, BK4-BK7 were simultaneously examined (See Figure 4).[298] By modifying the conjugation length, all dyes exhibited TPA properties ranging between 700 and 1100 nm, with maximum cross sections ranging between 200 to 325 × 10^{-50} $cm^4.s.photon^{-1}$. Noticeably, influence of the π-conjugated spacer used to design the different dyes on TPA polymerization performances was examined and polyenic, stilbenic and diazo-based systems were thus introduced. Examination of their UV-visible absorption spectra in chloroform revealed the absorption to redshift upon elongation of the π-conjugation (See Figure 5). Thus, a bathochromic shift of the absorption maxima from 456 to 486, 509 and 540 nm could be determined, going from M2K to BK2, TPP-1 and BK4 respectively. Noticeably, a saturation effect could be evidenced with the number of double bonds, what could be determined for the longest molecules of the series i.e. compounds TPP-1 and BK4, as shown in the Figure 6.

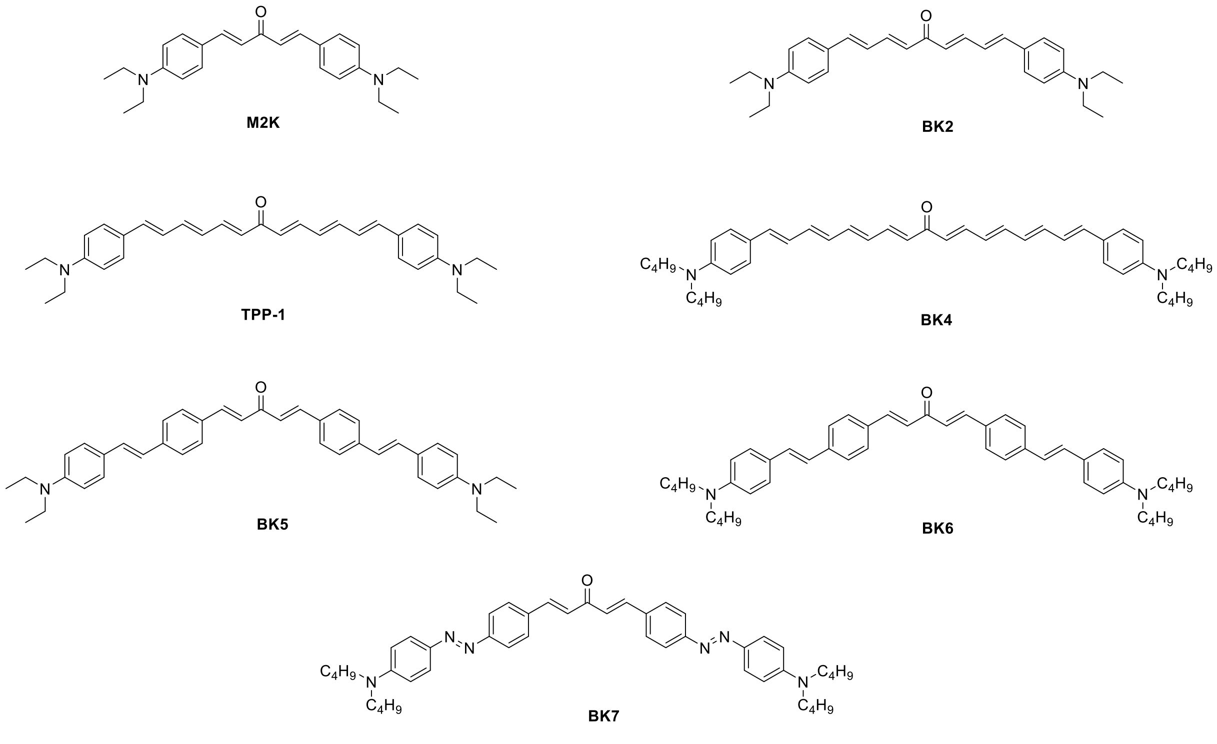


Figure 4. Chemical structures of the different TPA dyes investigated by Andraud and coworkers. Reproduced with permission of Ref.[298]

Introduction of a stilbenic system in BK5 and BK6 furnished dyes with absorption maxima located at 466 nm, standing between that of compounds M2K and BK2. Introduction of a diazo spacer in BK7 drastically redshifted the absorption compared to that of compounds BK5 and BK6. Thus, an absorption maximum located at 503 nm could be determined for BK7, close to the absorption maximum found for TPP-1. Blue-shifted absorptions of BK5 and BK6 compared to that of BK4 exhibiting the same conjugation length were assigned to the lower planarity of the stilbenic structures compared to that of the purely polyenic system in BK4.

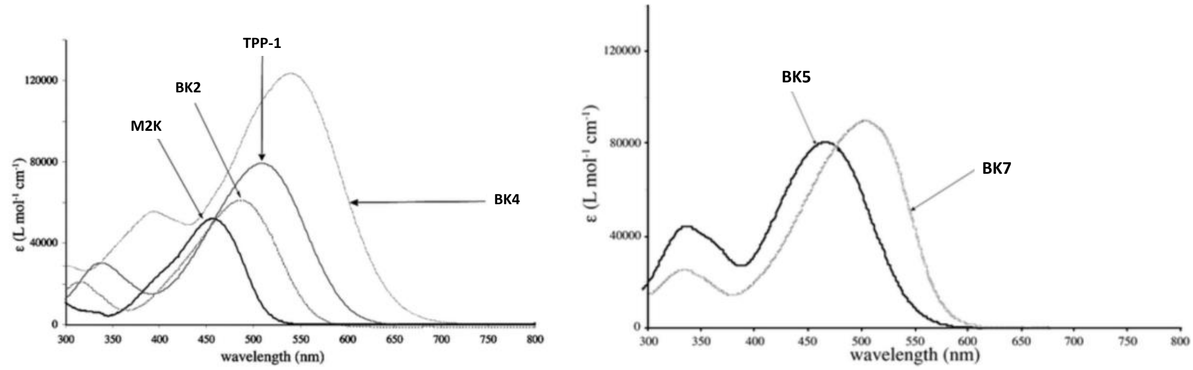


Figure 5. UV-visible absorption spectra of M2K, TPP-1, BK2, BK4-BK7 in chloroform. Reproduced with permission of Ref.[298]

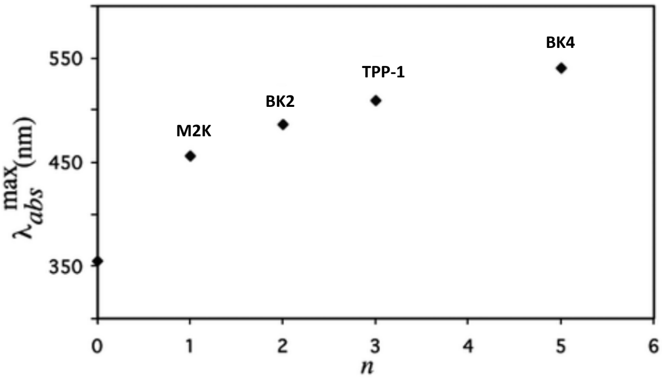


Figure 6. Maximum absorption wavelength as a function of the number of double bonds for M2K, BK2, TPP-1 and BK4. Reproduced with permission of Ref.[298]

Examination of the two-photon excitation spectra of the different dyes in chloroform revealed a similar trend to that observed for linear absorptions. Thus, upon elongation of the π-conjugation, a redshift of the purely allowed two-photon transition from 800 to 900 and 950 nm could be respectively determined for M2K, BK2 and TPP-1. The largest cross section was determined for BK2, peaking at 325 × 10^{-50} $cm^4.s.photon^{-1}$. Noticeably, a similar cross section was found for TPP-1 and BK5, being of 200 × 10^{-50} $cm^4.s.photon^{-1}$. Finally, in this series of dyes, only TPP-1 was tested for TPA photopolymerization, furnishing results comparable to that previously published by the same authors.[293]

Table 1. Optical characteristics of dyes M2K, BK2, TPP-1, BK4, BK5 and BK7 in chloroform.

Molecule	λ_{max} (nm)	ε_{max} (M^{-1}.cm^{-1})	λ_{max} TPA (nm)	σ_{max} TPA (cm^{4}.s.photon^{-1})
M2K	456	52 300	800	250×10^{-50}
BK2	486	61 300	900	325×10^{-50}
TPP-1	509	79 500	950	200×10^{-50}
BK4	540	123 500	-	-
BK5	466	81 000	900	200×10^{-50}
BK7	503	90 100	-	-

In 2009, TPA properties of M2K was compared by Liska and coworkers with that of a series of five dyes in which the vinylene spacer was replaced by triple bonds (See Figure 7). Indeed, even if no clear evidence was given for this undesired phenomenon, the possible cis/trans isomerization of the vinylic bonds during irradiation was postulated as a possible mechanism supporting the reduced TPA activity of the vinylene-based dyes.[299–302] It has to be noticed that, in this series, M3K was previously examined by the same authors for one and two photon polymerization experiments.[303] In this work, influence of the electron donating groups (i.e. methoxy, dimethylamino, diphenylamino or dibutylamino groups) on the TPA cross sections of photoinitiators was also examined, in addition to the influence of the type of spacer used. Noticeably, introduction of electron donating groups in *para*-positions of the phenyl groups contributed to red-shift the absorption in acetonitrile from 322 nm for H3K up to 449 nm for B3K. Comparisons between M3K and B3K differing by the length of the alkyl chain introduced onto the dialkylamino group revealed the absorption of B3K to be redshifted by ca. 15 nm compared to M3K. Conversely, introduction of diphenylamino group slightly blue-shifted the absorption of P3K compared to the other dyes, at 438 nm. Comparison between M3K and M2K differing by the conjugated spacer (triple or double bonds) revealed the two dyes to exhibit similar absorption maxima, at 434 nm.

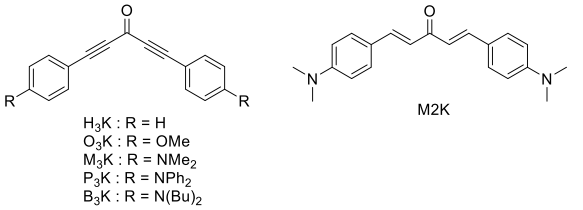


Figure 7. Chemical structures of M2K and TPA dyes H3K, O3K, M3K, P3K and B3K.

Determination of the TPA cross section at 800 nm by Z-scan analyses revealed the values of TPA cross sections to increase while improving the donor strength of the substituents introduced in *para*-position of the aromatic rings. Thus, the TPA cross section increased from 20 GM for O3K up to 256 GM for P3K, close to the values determined for M2K (261 GM).

Significant differences could however be determined between the TPA cross section of M3K and B3K only differing by the length of the alkyl chain, resulting from a shift of the TPA spectra.

Table 2. Photophysical properties of the different PIs in acetonitrile.

PI	Φem	ν_{abs} (eV)	ν_{em} (eV)	λ_{abs} (nm)	λ_{em} (nm)	ε_{max}^{a} ($M^{-1}.cm^{-1}$)	σ^{b} [GM]
H3K	0.00	3.85		322		25000	
O3K	0.02	3.50	2.25	352	526	32000	<10
M3K	0.00	2.84		434		53000	165
B3K	0.00	2.76		449		65000	238
P3K		2.82	1.80	438	650	50000	256
M2K		2.84	2.11	434	569	48000	261

[a] Measured in acetonitrile. [b] 1 GM = 10^{-50} $m^4.s.photon^{-1}$.

Polymerization tests carried out with a 1:1 mixture of ETA/TTA (where ETA and TTA respectively stands for trimethylolpropane triacrylate and ethoxylated (20/3)-trimethylolpropane triacrylate) revealed B3K to be the best initiator of the series with the broadest structuring process window at laser intensities as low as 5 μW. Due to the presence of butyl chains, B3K also exhibited a very good solubility in the resin, contrarily to P3K which was only partially soluble in resins due to its marked polyaromaticity. Very low photoinitiator content could be used, as low as 1.6×10^{-6} mol PI/g of resin. Interestingly, a processing window broader than that of the reference compound, namely 2-benzyl-2-(dimethylamino)-1-[4-(morpholinyl) phenyl)]-1-butanone (Irgacure 369) could be determined.[304–306] Finally, at the lowest concentration (1.6×10^{-7} mol PI/g resin), only H3K could furnish well-defined structures, despites a very small process window at 600 nm.

2.1.2. One-photon polymerization

If historically, symmetrically substituted benzylidene ketones were used for TPA applications, starting from 2019, a wide range of dyes were developed for one-photon polymerization experiments. In 2019, Tao Wang and coworkers reported two benzylidene ketones bearing two peripheral groups extensively used in photopolymerization, namely triphenylamine[226] and carbazole.[149,155] TPAK and CZK were notably used to initiate the free radical polymerization of tripropylene glycol diacrylate (TPGDA) using triethanolamine (TEOA) as co-initiator (See Figure 8).[205] Noticeably, the two dyes exhibited interesting photobleaching properties upon irradiation at 460 and 520 nm and the polymerization of ceramic suspensions could even be realized.

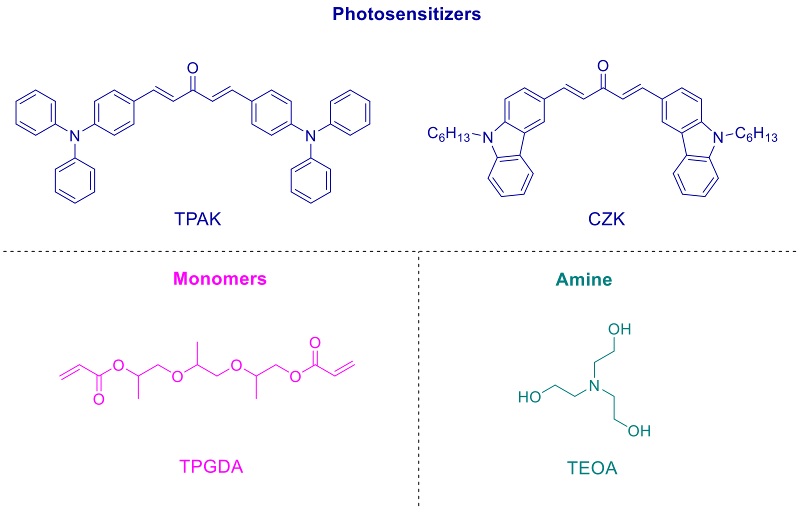


Figure 8. Chemical structures of TPAK and CZK, the monomer TPGDA and the additive (TTA)

It has to be noticed that photocuring of ceramic suspensions is a major concern, especially in the UV range due to a limited light penetration within the photocurable resins in this spectral range.[76,307–312] To overcome this drawback, an efficient strategy consists in developing photoinitiating systems of low absorbance at the irradiation wavelength so that the polymerization of thick samples but also of filled samples become possible. As other alternative, a decrease of the optical density during the polymerization process can allow a deeper light penetration within the resins so that filled or thick samples can be polymerized.[313,314] This goal could be notably achieved with TPAK and CZK, that combined low absorption at the irradiation wavelengths and good photobleaching properties. As shown in the Figure 9 and the Table 3, the two dyes absorb beyond 450 nm so that polymerization tests could be carried out at 460 and 500 nm. Noticeably, if TPAK exhibited a 18-fold enhancement of the molar extinction coefficient at 460 nm compared to CZK, almost similar molar extinction coefficients could be determined at 520 nm. Steady state photolysis experiments carried out in THF upon irradiation at 460 nm with a LED revealed the two-component TPAK/TEOA and CZK/TEOA systems to furnish faster photolyses than TPAK or CZK considered alone (See Figure 10). In the case of the two two-component systems, a faster photolysis was obtained using CZK as the photosensitizer.

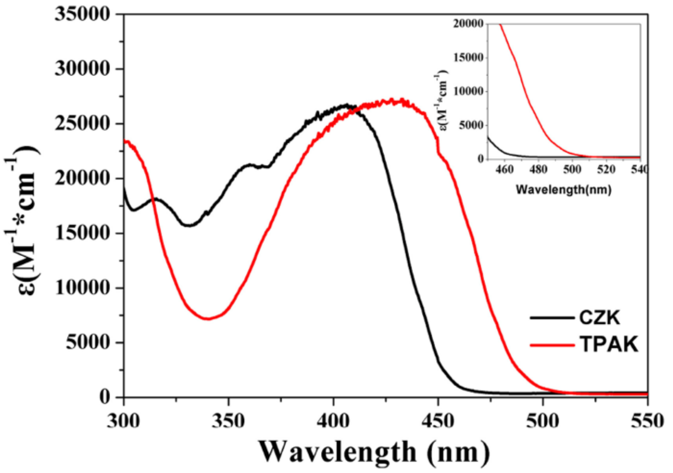


Figure 9. UV-visible absorption spectra of TPAK and CZK in THF. Reproduced with permission of Ref. [205]

Table 3. Photophysical characteristics of TPAK and CZK in THF. Positions of their frontier orbitals and difference between the HOMO and LUMO energy levels.

	ε_{460nm} ($M^{-1}.cm^{-1}$)	ε_{520nm} ($M^{-1}.cm^{-1}$)	HOMO Energy (eV)	LUMO Energy (eV)	Δ Energy (eV)
TPAK	18370	340	3.90 eV	1.44 eV	2.46 eV
CZK	1000	410	4.04 eV	1.29 eV	2.75 eV

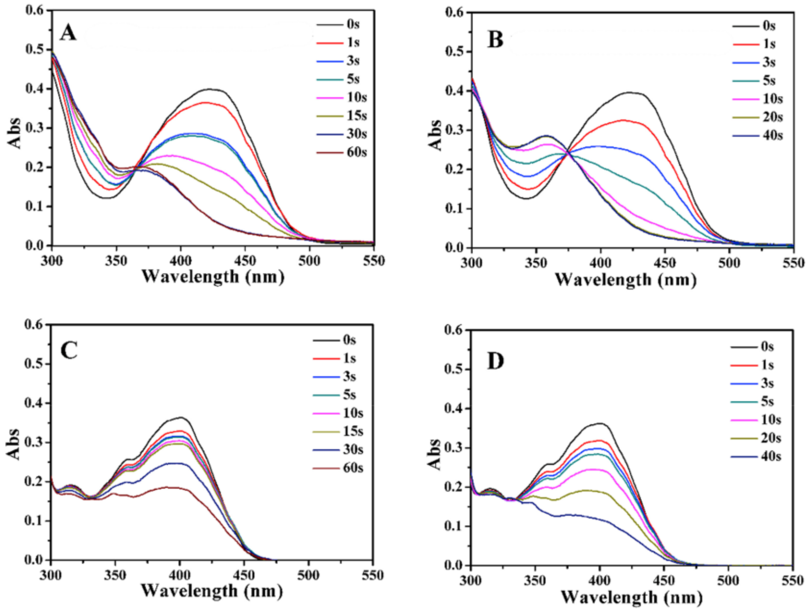


Figure 10. Photolysis experiments done in THF for a) TPAK, b) TPAK/TEOA, c) CZK, d) CZK/TEOA. Reproduced with permission of Ref. [205]

Photopolymerization experiments carried out at 460 and 520 nm revealed the two-component dye/TEOA systems to furnish different monomer conversions, depending on the irradiation wavelength. Thus, higher TPGDA conversions were obtained at 460 nm compared to 520 nm, resulting from higher molar extinction coefficients at 460 nm. Irrespective of the irradiation wavelength, all CZK-based photoinitiating systems outperformed that formed with TPAK (See Figure 11). However, the polymerization rate with the two-component TPAK/TEOA system at 520 nm was faster than that of the CZK/TEOA system, demonstrating that the molar extinction coefficient was not the only parameter governing the reactivity of the benzylidene ketones. This trend was confirmed at 460 nm, where TPAK exhibits a molar extinction coefficient 18 times higher than that of CZK. Noticeably, upon increase of the amine concentration from 0 up to 6 wt%, an enhancement of the monomer conversions could be clearly evidenced, increasing from 5% up to 85% for the two-component CZK/TEOA system, from 5% up to 70% for the two-component TPAK/TEOA system upon irradiation at 460 nm. Noticeably, while using TPAK and CZK as monocomponent systems, monomer conversions ranging between 3 and 5% could be determined at 460 and 520 nm, demonstrating that these two dyes are hydrogen-trapping photoinitiators that must be used in combination with amines (See Table 4) While examining the polymerization kinetics, the highest initial rate of polymerization was obtained with the two-component system based on CZK at 460 nm, directly related to its high molar extinction coefficient at this wavelength.

Table 4. Monomer conversions obtained while using TPAK and CZK as mono or multi-component photoinitiating systems.

Dye/irradiation wavelength	λ = 460 nm	λ = 520 nm
TPAK (0.1 wt%)	5% (18 s)	4% (18 s)
TPAK/TEOA (0.1%/3% w/w)	60% (18 s)	58% (18 s)
CZK (0.1 wt%)	3% (18 s)	4% (18 s)
CZK/TEOA (0.1%/3% w/w)	60% (18 s)	74% (18 s)

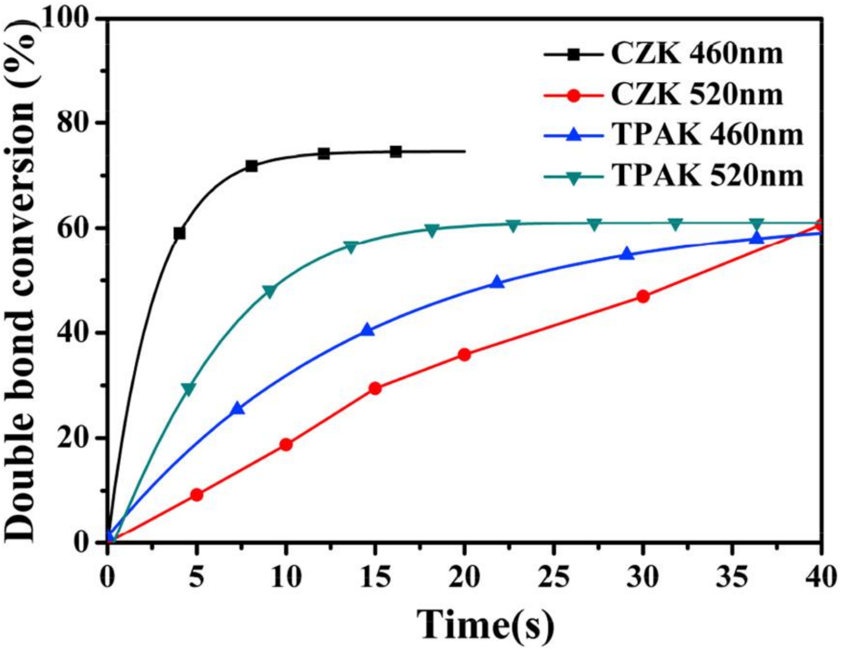


Figure 11. Final monomer conversions obtained during the FRP of TPGDA upon irradiation at 460 and 520 nm with different two-component dye/TEOA systems. Reproduced with permission of Ref. [205]

Interestingly, a good photobleaching could be evidenced with the two dyes (See Figure 12). Thus, a complete bleaching of the resin could be obtained after only 7 s of irradiation at 460 nm for the CZK-based resin whereas 20 s were necessary for the TPAK-based resin. To support the photobleaching process, a mechanism based on an electron transfer between TEOA and the dye in first step followed by a proton transfer in second step could break the π-conjugation, enabling to produce colorless side products (See Scheme 1).

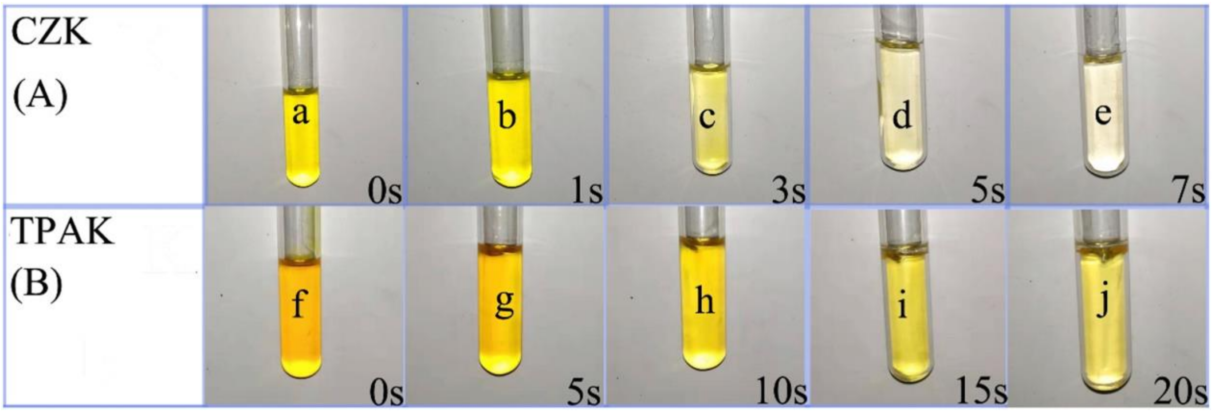
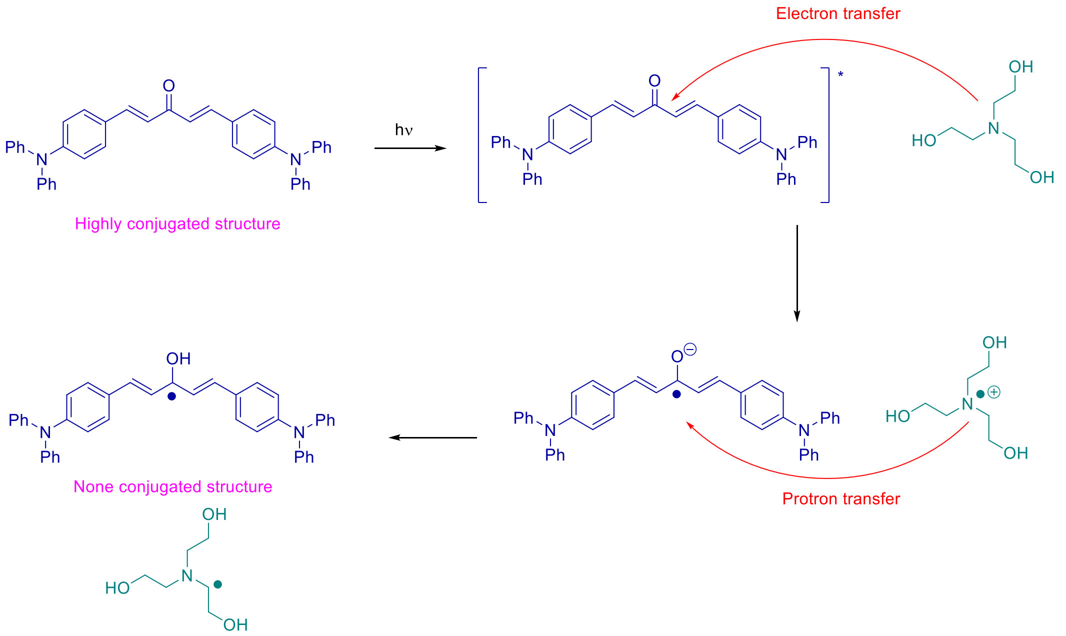


Figure 12. Photobleaching observed for TPGDA-based resins using the two-component dye/TEOA 0.1%/3.0% w/w upon irradiation at 460 nm. Reproduced with permission of Ref. [205]



Scheme 1. Mechanism involved in the photobleaching process during photopolymerization experiments.

Based on these photobleaching properties, the depth of cure was examined with the two two-component dye/TEOA systems upon irradiation at 460 nm and 520 nm for 40 s. Thus, upon irradiation at 460 nm and by reducing the dye content from 1 wt% to 0.031 wt%, the depth of cure increased from 0.3 cm at 1 wt% up to 6.8 cm at 0.016 wt% for the TPAK-based system. Similarly, the depth of cure increased from 1.3 cm at 1 wt% up to 7.9 cm at 0.031 wt%. Conversely, at 520 nm, a reduction of the depth of cure was detected for the two dyes, resulting from a lower molar extinction coefficient at this wavelength. Thus, a depth of cure of 6.1 cm was obtained with the TPAK system at 0.031 wt% whereas this value decreased to 4.2 cm for the CZK-based system at 0.125 wt% (See Figure 13).

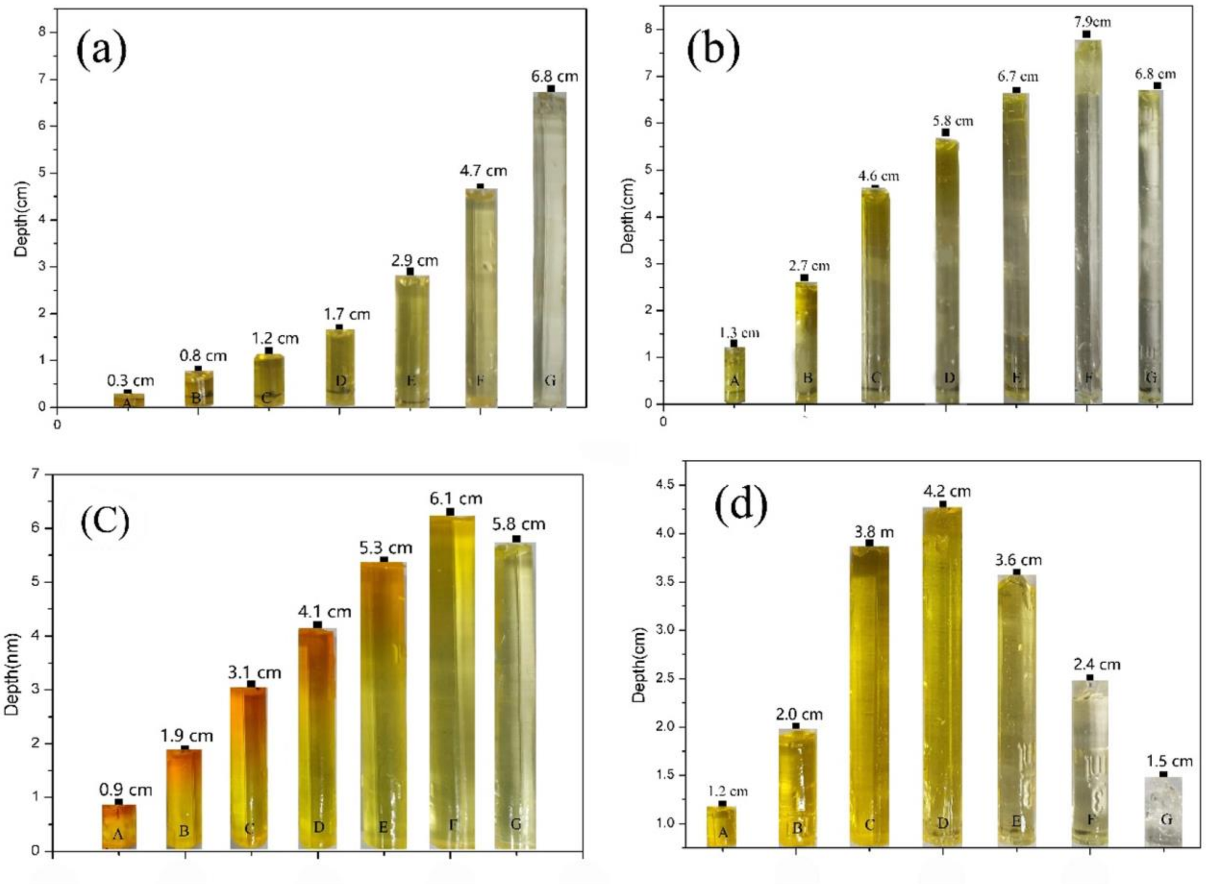


Figure 13. Depth of cure depending on the dye concentration upon irradiation at 460 nm and 520 nm with LEDs. (a): TPAK/TEOA, 460 nm; (b): CZK/TEOA, 460 nm; (c): TPAK/TEOA, 520 nm; (d): CZK/TEOA 520 nm using TPGDA as the monomer and TEOA at constant concentration: 3 wt%. Concentrations of dye: A: 1 wt%; B: 0.5 wt%; C: 0.25 wt%; D: 0.125 wt%; E: 0.063 wt%; F: 0.031 wt%; G: 0.016 wt%. Reproduced with permission of Ref. [205]

Finally, among the most interesting findings, photopolymerization of ceramic suspensions could be carried out at 460 and 520 nm. Noticeably, a severe reduction of the depth of cure was detected at the two wavelengths, resulting from a limited light penetration in these resins. Therefore, if for the pure resins, depths of cure were measured in centimetres, in the case of ceramic suspensions, depth of cure was limited to only millimetres. If an increase of the depth of cure was observed for the two dyes upon increase of the dye concentration upon irradiation at 460 nm, a different situation was found at 520 nm (See Figure 14). In this case, by increasing the dye content, a severe reduction of the depth of cure was detected, resulting from additional inner filter effects, adversely affecting the light penetration, in complement to that caused by the ceramic suspension. Here again, the possibility to elaborate colorless coatings was demonstrated.

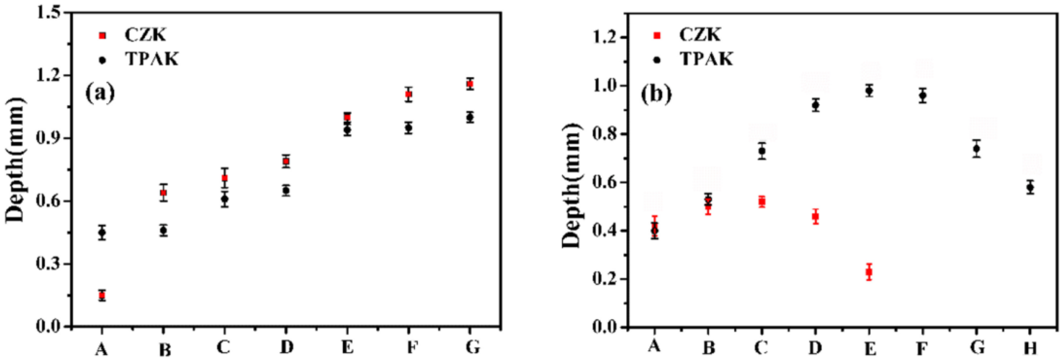


Figure 14. Depth of cure for ceramic suspensions photopolymerized with different concentrations of CZK or TPAK at 460 nm (a) and 520 nm (b). Photoinitiator content: A: 1 wt%; B: 0.5 wt%; C: 0.25 wt%; D: 0.125 wt%; E: 0.063 wt%; F: 0.031 wt%; G: 0.016 wt%; H: 0.008 wt%. Reproduced with permission of Ref. [205]

Good photobleaching properties were also obtained by replacing the carbazole groups of CZK by phenothiazine units in BMPPO (See Figure 15).[179] Noticeably, photoinitiating ability of (1E,4E)-1,5-*bis*(10-methyl-10*H*-phenothiazin-3-yl)-1,4-pentadien-3-one was compared to that of 4-(10-methyl-10*H*-phenothiazin-3-yl)but-3-en-2-one (PBO) only comprising a phenothiazine unit. Due to the simultaneous presence of two phenothiazine moieties in BMPPO, a significant redshift of the absorption spectrum was observed compared to that of PBO, the absorption maximum peaking at 442 nm vs. 400 nm for PBO in DMSO (See Figure 16).

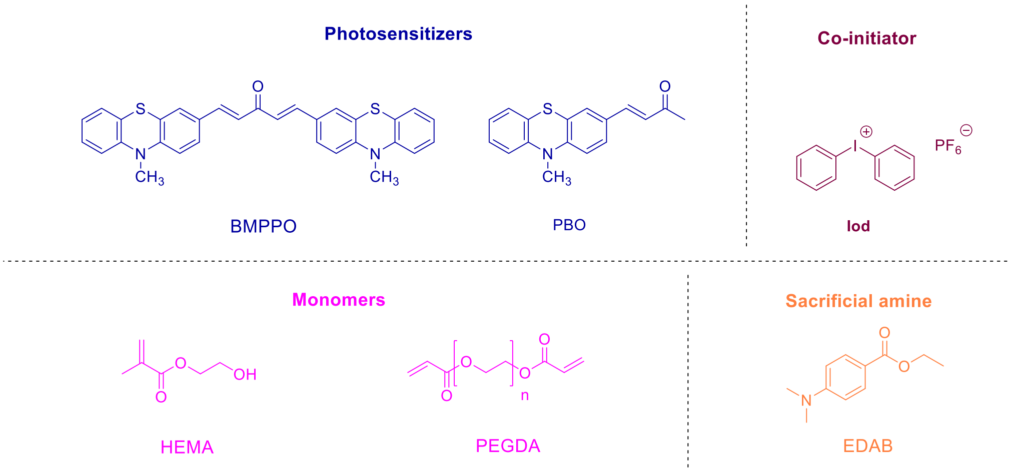


Figure 15. Chemical structures of BMPPO and PBO, different monomers and additives.

This is directly related to the presence of two electron-donating groups in BMPPO. Noticeably, BMPPO exhibited an absorption redshifted compared to that of CZK, attributable to the fact that phenothiazines are better electron-donating groups than carbazoles. Additionally, if carbazole exhibits a UV centered absorption, conversely, phenothiazine already exhibits an absorption in the visible range, supporting the redshifted absorption of BMPPO compared to that of PBO. Based on theoretical calculations, this intense absorption band detected in the visible range was assigned to π–π^* transitions located onto the π-conjugated structure.[267]

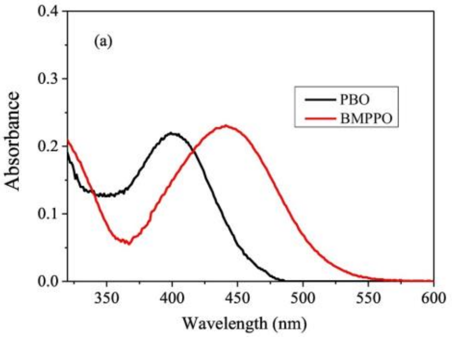


Figure 16. UV-visible absorption spectra of BMPPO and PBO in DMSO. Reproduced with permission of Ref. [179]

Based on the broad absorption of BMPPO, polymerization tests of poly(ethylene glycol) diacrylate (PEGDA) could be carried out at 440 nm and even under sunlight irradiation. As anticipated, addition of diphenyliodonium hexafluorophosphate (Iod) or ethyl 4-(dimethylamino)benzoate (EDAB) improved the monomer conversion of BMPPO compared to BMPPO used as a monocomponent system. Higher conversions were obtained with the two-component BMPPO/Iod (0.1%/1% w/w) system compared to its BMPPO/EDAB (0.1%/1% w/w) analogue what is generally observed by comparing these two two-component systems. In fact, organic dyes can generally be more easily oxidized than reduced. Use of a three-component system in which BMPPO can be regenerated in its initial redox state enabled to drastically improve the monomer conversion. Thus, PEGDA conversions could be increased from 80, 85 up to 98% after 500 s of irradiation for the BMPPO/EDAB (0.1%/1% w/w), BMPPO/Iod (0.1%/1% w/w) and BMPPO/Iod/EDAB (0.1%/1%/1% w/w/w) systems. Proper choice of the monomer is another crucial parameter governing the monomer conversion. Thus, an improvement of the monomer conversion could be obtained from hydroxyethyl methacrylate (HEMA) to trimethylolpropane triacrylate (TMPTA) and PEGDA using the three-component BMPPO/Iod/EDAB (0.1%/1%/1% w/w/w) system upon irradiation at 440 nm (See Figure 17 and Table 5).

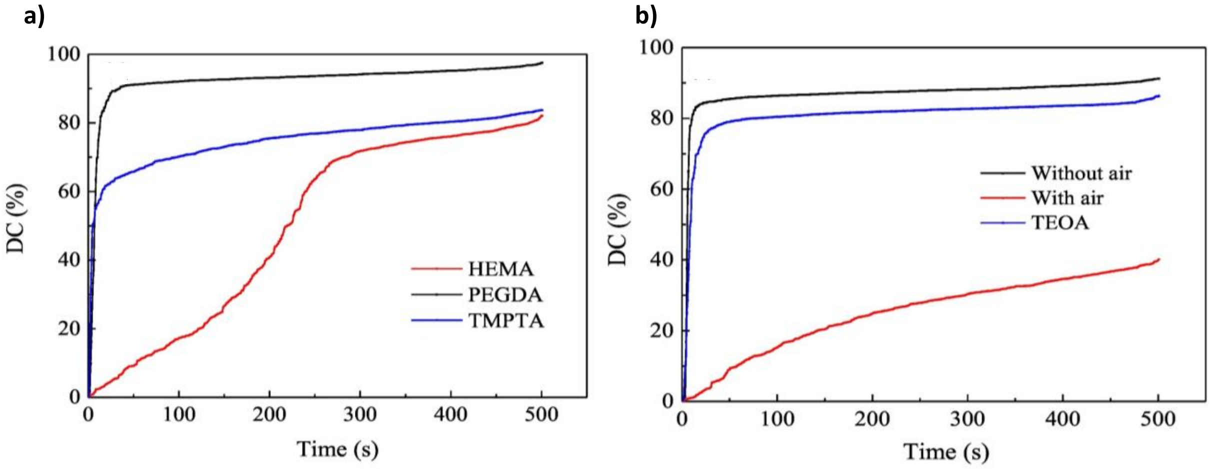


Figure 17. (a) Photopolymerization profiles obtained with the three-component BMPPO/Iod/EDAB (0.1%/1%/1% w/w/w) system upon irradiation at 440 nm. b) Photopolymerization profiles obtained with the two-component BMPPO/Iod (0.1%/1% w/w) system in PEGDA with and without air and the three-component BMPPO/Iod/TEOA

(0.1%/1%/1% w/w/w) under air upon irradiation at 440 nm. Reproduced with permission of Ref. [179]

It has to be noticed that choice of the monomer can also drastically influence the monomer conversion. Indeed, if HEMA is a monofunctional monomer, PEGDA and TMPTA are respectively di and trifunctional monomers. Normally, by increasing the number of reactive groups per monomer, a reduction of the monomer conversion should be observed, resulting from reactive functions remaining unreacted within the polymer network. However, as shown in the Table 5, by increasing the functionality of monomers from HEMA to TMPTA, similar conversions could be obtained (80 and 82% respectively). Other parameter such as the viscosity, the solubility of dyes in monomers have also to be considered. However, as shown in the Figure 17a, major differences of initial polymerization rates could be determined between the three monomers. Thus, the highest polymerization rates were obtained for the polyfunctional monomers, namely PEGDA and TMPTA. Influence of oxygen on the FRP of PEGDA was also demonstrated. Thus, if almost similar monomer conversions were obtained with the two-component BMPPO/Iod (0.1%/1% w/w) and the three-component MPPO/Iod/TEOA (0.1%/1%/1% w/w/w) systems (See Figure 17b), a two-fold reduction of the PEGDA conversion was obtained under air, consistent with a radical process.[315,316]

Table 5. Monomer conversions obtained with different monomers using different mono, two and three-component systems upon irradiation of the resins at 440 nm.

	Photoinitiating systems	440 nm
PEGDA		
	BMPPO (0.1 wt%)	71% (500 s)
	BMPPO/EDAB (0.1 wt%/1 wt%)	80% (500 s)
	BMPPO/EDAB (0.1 wt%/2 wt%)	93% (500 s)
	BMPPO/Iod (0.1 wt%/1 wt%)	85% (500 s)
	BMPPO/Iod (0.1 wt%/2 wt%)	87% (500 s)
	BMPPO/Iod/EDAB (0.1 wt%/1 wt%/1 wt%)	98% (500 s)
HEMA		
	BMPPO/Iod/EDAB (0.1 wt%/1 wt%/1 wt%)	80% (500 s)
TMPTA		
	BMPPO/Iod/EDAB (0.1 wt%/1 wt%/1 wt%)	82% (500 s)

Mitigate results obtained with TMPTA as the monomer was assigned to the trifunctionality of this monomer and its fast gelation, letting numerous unreacted acrylate functions within the polymer network. Oxygen inhibition can also drastically impact the monomer conversion, what was demonstrated during the FRP of PEGDA (See Figure 17d). Thus, while using the two-component BMPPO/Iod (0.1%/1% w/w) system under air, the PEGDA conversion could only peak at 40% after 500 s of irradiation, far from the conversion obtained without air i.e. 90%. Finally, by using the three-component BMPPO/Iod/EDAB (0.1%/1%/% w/w/w) photoinitiating system, monomer conversions close to that obtained without air for the two-component BMPPO/Iod (0.1%/1% w/w) system could be obtained. Interestingly, the high reactivity of the two-component BMPPO/Iod (0.1%/1% w/w) system could be demonstrated by using Sun as the light source. Using sunlight, curing times similar to that required with artificial light sources were necessary to get equivalent TMPTA conversions. Here again, a good photobleaching was observed during photopolymerization, resulting from a reduction of the π-conjugation in BMPPO (See Figure 18) according to a mechanism similar to that depicted in the Scheme 1.

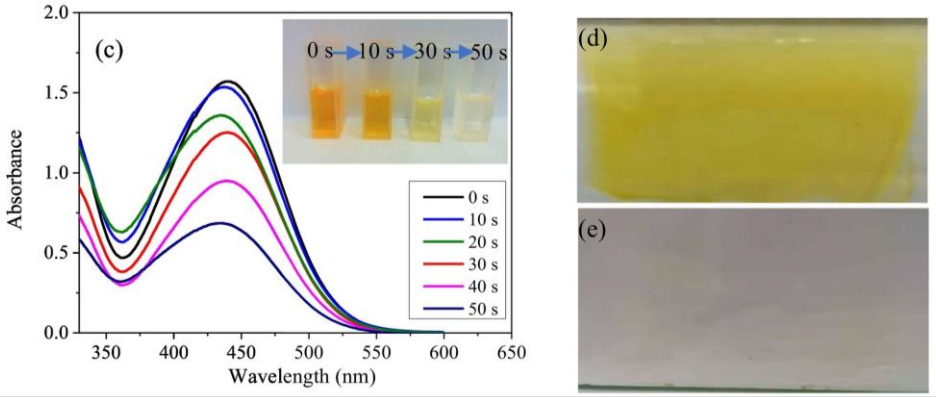


Figure 18. (c) Photobleaching observed during photolysis experiments in DMSO upon irradiation at 440 nm (d) Photobleaching observed in polymer films. Reproduced with permission of Ref. [179]

Recently, influence of the electron-donating groups of benzylidene ketones on the photoinitiating ability was examined with a series of four dyes (C3PH, C3PO, C3PS and C3PN) in which ethoxy, methylthio and dimethylamino groups were used as electron donating groups (See Figure 19).[317]

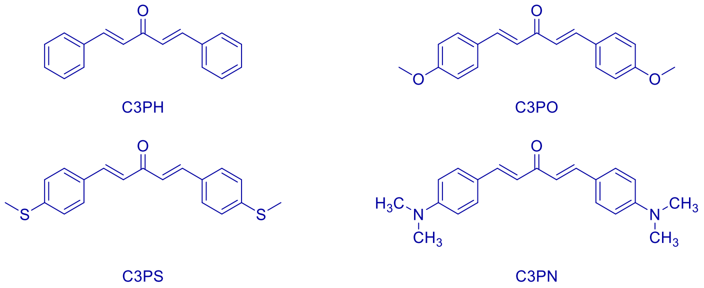


Figure 19. Chemical structures of C3PH, C3PO, C3PS and C3PN.

As anticipated, by improving the electron donating ability of the peripheral groups, a redshift of the absorption maxima could be obtained, shifting from 323 to 356, 372 and 435 nm for C3PH, C3PO, C3PS and C3PN respectively (See Figure 20). Based on their absorptions, polymerization tests could be carried out at 365, 405 and 460 nm.

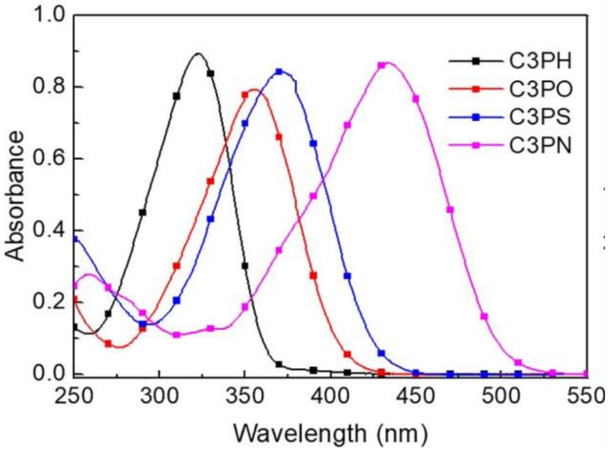


Figure 20. UV-visible absorption spectra of C3PH, C3PO, C2PS and C3PN in acetonitrile. Reproduced with permission of Ref. [317]

Noticeably, irrespective of the irradiation wavelength, only low monomer conversions were obtained with the different dyes when used as monocomponent systems. Conversely, upon addition of TEOA, a significant enhancement of the monomer conversion could be evidenced. If almost similar conversions were obtained both at 365 and 405 nm, a severe decrease of the conversion was obtained at 460 nm, especially for the C3PH and C3PN-based photoinitiating systems (See Figure 21 and Table 6). Surprisingly, C3PN furnished the lowest monomer conversion at 460 nm whereas this dye exhibits the highest molar extinction coefficient. Once again, evidence that parameters other than the molar extinction coefficient can drastically impact the monomer conversion and affect the photochemical reactivity was demonstrated. Irrespective of the irradiation wavelength, C3PO clearly outperformed all the other dyes.

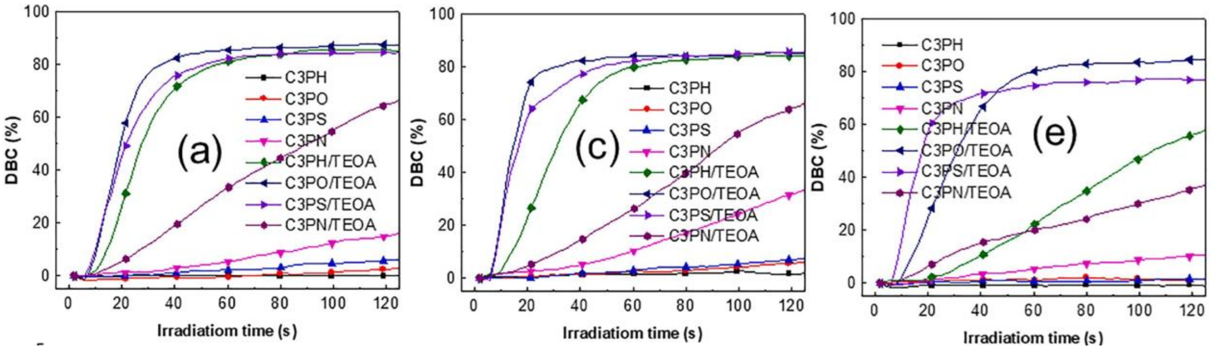


Figure 21. Polymerization profiles obtained with different two and three-component systems upon irradiation at 365, 405 and 460 nm with LEDs (I = 70 mW/cm²) and while using TPGDA as the monomer. Reproduced with permission of Ref. [317]

Table 6. Final monomer conversions obtained with the different benzylidene ketones using mono and two-component photoinitiating systems upon irradiation at different wavelengths.

Dye/irradiation wavelength	365 nm	405 nm	460 nm
C3PH (0.1 wt%)	1% (120 s)	1% (120 s)	1% (120 s)

C3PH/TEOA (0.1%/3% w/w)	82% (120 s)	83% (120 s)	58% (120 s)
C3PO (0.1 wt%)	2% (120 s)	4% (120 s)	3% (120 s)
C3PO/TEOA (0.1%/3% w/w)	83% (120 s)	83% (120 s)	82% (120 s)
C3PS (0.1 wt%)	2% (120 s)	4% (120 s)	3% (120 s)
C3PS/TEOA (0.1%/3% w/w)	84% (120 s)	83% (120 s)	74% (120 s)
C3PN (0.1 wt%)	12% (120 s)	32% (120 s)	9% (120 s)
C3PN/TEOA (0.1%/3% w/w)	84% (120 s)	61% (120 s)	38% (120 s)

Notably, if presence of methoxy and methylthio groups could improve the hydrogen atom transfer efficiency, an opposite situation was found for C3PN bearing dimethylamino groups. Investigations of the influence of co-initiators on the photoinitiating abilities revealed TEOA and *N*-methyldiethanolamine (DEOA) to outperform tertiary amines such as triethylamine (Et$_3$N) or EDAB for the composition of two-component systems. Here again, examination of the polymerization kinetics revealed the benefits of introducing an amine. Indeed, compared to the monocomponent systems, higher initial polymerization rates could be obtained with the two-component systems, irrespective of the dyes used. Determination of the free energy changes between C3PO and the different co-initiators revealed the C3PO/TEOA to exhibit the most negative value i.e. -19.38 kcal/mol and thus the largest photoinduced electron transfer driving force. A direct correlation between oxidation potential of amines and polymerization efficiency could be evidenced. More precisely, TEOA and DEOA both exhibit hydroxy groups, and presence of this group was suspected as playing a key role in the reactivity of these amines with the dyes. By theoretical calculations, structures and geometries of the complex formed between C3PO and the different co-initiators could be determined. As shown in the Figure 22, the two C3PO/DEOA and C3PO/TEOA complexes exhibited the lowest energy barriers for the formation of complex, 2.49 and 1.87 kcal/mol respectively, supporting the facile photoinduced electron transfer.

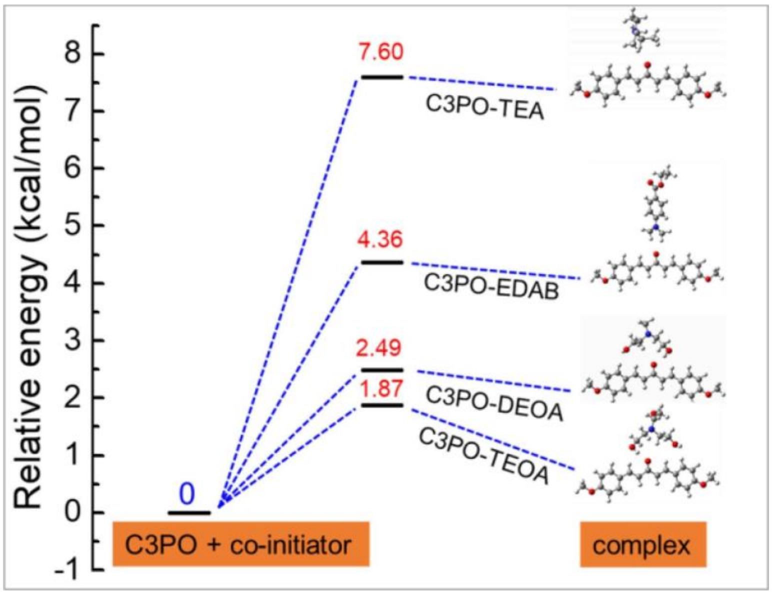


Figure 22. Optimized structures for the different C3OP/co-initiators complex and energy for the complex formation. Reproduced with permission of Ref. [317]

Photobleaching of the photocurable resins is a major concern of visible light photopolymerization. Indeed, due to the fact that dyes absorbing in the visible range are used, the photosensitizer is often responsible of an undesired colour imposed to the final coatings, adversely affecting the development of visible light photopolymerization. Face to these considerations, photoinitiating systems exhibiting photobleaching properties are actively researched. Recently, in 2021, the group of Tao Wang and coworkers developed several benzylidene ketones exhibiting this interesting property. Notably, C3PY can be cited as a relevant example (See Figure 23).[281] Due to the good electron donating ability of pyrrole, an absorption maximum located at 414 nm could be determined in acetonitrile. Therefore, the absorption of C3PY was appropriate for polymerization experiments done at 405 nm but also at 460 nm.

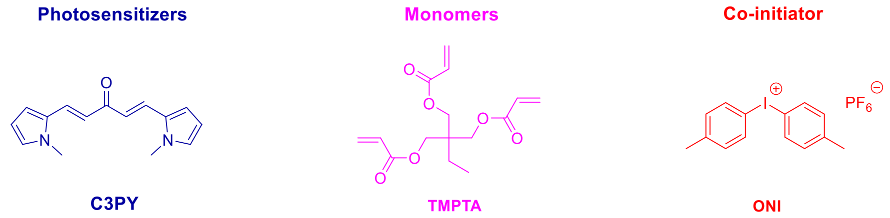


Figure 23. Chemical structure of C3PY, the acrylic monomer and the iodonium salt.

Interestingly, C3PY could initiate alone the free radical polymerization (FRP) of TPGDA due to the dual presence of the ketone and the tertiary amine in C3PY. After 600 s of irradiation at 405 nm, a final monomer conversion of 65% could be determined at 0.1 wt%. When used as a photosensitizer in two-component systems, an improvement of the monomer conversion was both obtained with di-*p*-tolyliodonium hexafluorophosphate (ONI) and TEOA. Thus, after 600 s of irradiation, monomer conversions of 91 and 76% were respectively obtained with the two-component C3PY/ONI (0.1%/2% w/w) and C3PY/TEOA (0.1%/3% w/w) systems. This order of reactivity was confirmed during the FRP of trimethylolpropane triacrylate (TMPTA), with conversions of 30%, 39% and 50% for the C3PY (0.1 wt%), C3PY/ONI (0.1%/2% w/w) and C3PY/TEOA (0.1%/3% w/w) systems. Interestingly, major differences could be found concerning the colour of the final coatings. Thus, if colorless coatings could be obtained with the two-component C3PY/TEOA system, conversely, red-violet and red-blue coatings could be obtained during the FRP of TPGDA and TMPTA. In these two cases, new absorption bands were detected at 513 and 637 nm by UV-visible absorption spectroscopy for the different photopolymers.

Upon irradiation at 460 nm, an enhancement of the monomer conversion was obtained with the two-component C3PY/ONI system, benefiting from a better light penetration at 405 nm than at 460 nm. Conversely, a reduction of the monomer conversion was detected for C3PY and the two-component C3PY/TEOA system, resulting from a low absorbance at this wavelength. Photolysis experiments done in acetonitrile for the two-component C3PY/ONI system furnished results differing from that obtained during photopolymerization. Thus, no formation of coloured photoproducts was detected in solution upon irradiation at 405 nm and a complete bleaching of the solution was obtained after 60 s of irradiation. For the two other systems i.e. C3PY and C3PY/TEOA, a clear bleaching was observed in solution, consistent with that observed during photopolymerization. While drastically increasing the concentration of the two-component C3PY/ONI system in acetonitrile, appearance of a new absorption band that could not detected at low concentration was evidenced (See Figure 23c).

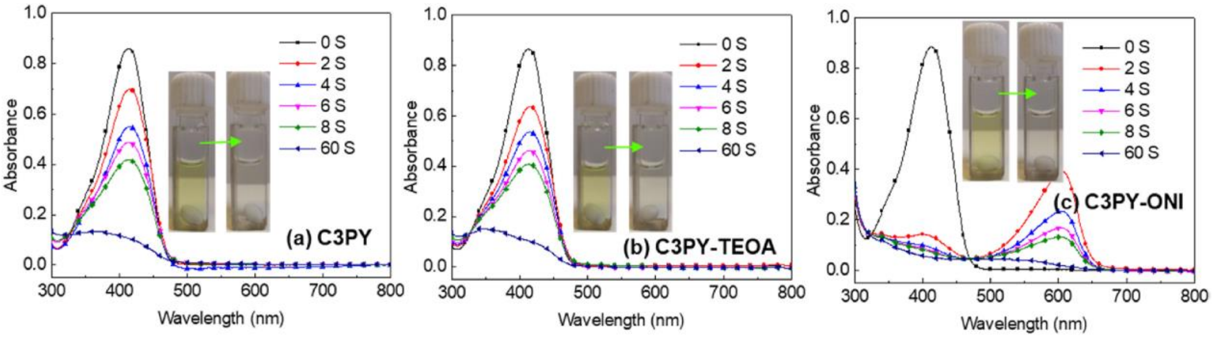


Figure 23. Photolysis experiments carried out in acetonitrile for a) C3PY, b) C3PY/TEOA and c) C3PY/ONI. Reproduced with permission of Ref. [281]

This new absorption band was observed at 600 nm in acetonitrile, close to that observed in the solid state for photopolymers (637 nm). Further investigations on this absorption band revealed this absorption band to appear within a few seconds in solution (See Figure 24). Noticeably, upon elongation of the irradiation time, severe modifications of the solution colour were detected, shifting from yellow to green and finally blue. Parallel to this, a decrease of the intensity of the absorption band was detected, resulting in the formation of a new band centered at 513 nm. Investigation of the origin of this colour revealed the coloured product to be the protonated form of C3PY i.e. $C3PYH^+$. Indeed, the two-component C3PY/ONI system is well-known to release Bronsted acid within the reaction medium.[186] Upon addition of TEOA, a complete bleaching of the solution was observed, consistent with the protonation of C3PY. Considering that C3PY possesses two possible sites that can be protonated, theoretical calculations that were carried out on C3PY revealed C3PY to be protonated on the ketone side. Indeed, a Gibbs free energy of 41 kcal/mol was determined for C3PY when protonated on the pyrrole side. These results were confirmed by ^1H NMR experiments. Notably, formation of a pyrrolium cation would drastically modify the shape of the ^1H NMR spectra, what was not observed. On the opposite, only a shift of all signals was detected, consistent with a protonation of the ketone moiety.

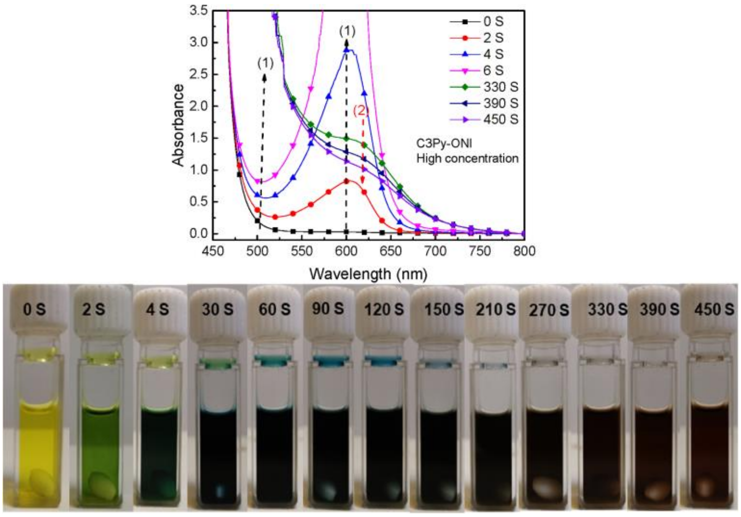
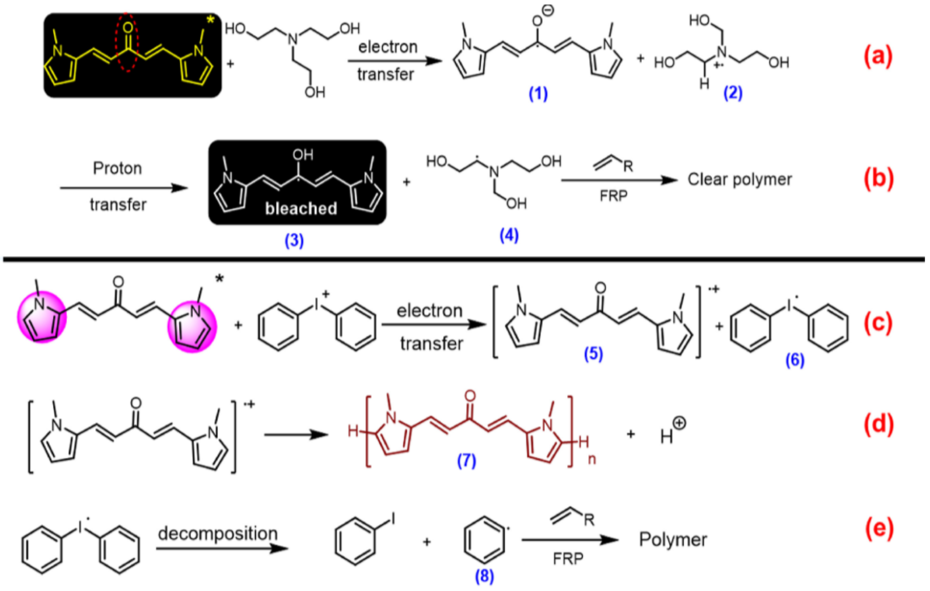


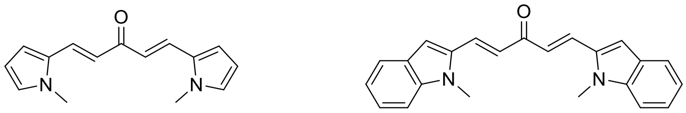
Figure 24. Photolysis of the two-component C3PY/ONI system in acetonitrile upon irradiation at 405 nm with a LED (I = 80 $\mathrm{mW/cm^2}$). Reproduced with permission of Ref. [281]

Finally, formation of the absorption band at 513 nm was assigned to an oligomerization of the radical cations formed by electron transfer from C3PY to ONI (See Scheme 2, equations c and d). Based on the simulated absorption spectra, this absorption band was assigned to the formation of dimers and not from oligomers of higher molecular weight. In the case of the C3PY/TEOA system, photobleaching of C3PY was assigned first to an electron transfer generating C3PY$^{\cdot-}$ which rapidly evolved towards a colorless species by proton transfer (See Scheme 2, equations a and b).



Scheme 2. Mechanism involved in the formation of photoproducts absorbing at 513 nm. Reproduced with permission of Ref. [281]

Following this work, the same group replaced the pyrrole groups of C3PY by indole groups in C3ID (See Figure 25).[318] From the absorption viewpoint, only a slight redshift of the absorption maximum was found for C3ID (λ_{max} = 422 nm) compared to that of C3PY (λ_{max} = 414 nm) (See Table 7). Due to the broad absorption band of C3ID, C3ID could maintain a high molar extinction coefficient at 460 nm reaching 21 000 $M^{-1}.cm^{-1}$. On the opposite, the absorption of the parent structure i.e. C3PY was lower, only reaching 6 400 $M^{-1}.cm^{-1}$. Theoretical calculations revealed the electronic density of the highest occupied molecular orbital (HOMO) to be centered on the indole or pyrrole moieties and the lowest unoccupied molecular orbital (LUMO) to be localized onto the ketone moiety for the two dyes.



C3PY **C3ID**

Figure 25. Chemical structures of C3ID and its parent structure C3PY.

Table 7. Photophysical properties of C3PY and C3ID in acetonitrile.

	Λ_{max} (nm)	ε_{max} ($M^{-1}.cm^{-1}$)	ε_{405nm} ($M^{-1}.cm^{-1}$)	E_{460nm} ($M^{-1}.cm^{-1}$)	λ_{em} (nm)
C3PY	414	43 300	42 200	6 400	499
C3ID	422	39 220	36 500	21 000	544

Overall, it could be determined that the intramolecular charge transfer was corresponding to a π-π* transition. Redshift of the absorption spectra of C3ID compared to that of C3PY was assigned to an enlarged molecular plane for C3ID, favoring the electronic delocalization (See Figure 26).

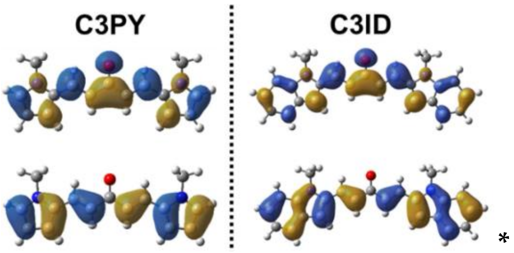


Figure 26. Contour plots of the HOMO and LUMO energy levels of C3PY and C3ID. Reproduced with permission of Ref. [318]

Investigation of their photoinitiating abilities during the FRP of TPGDA revealed C3PY and C3ID to be capable to initiate a polymerization process, even when used as monocomponent systems. Thus, final monomer conversions of 60 and 80% could respectively be determined for C3PY and C3ID upon irradiation at 405 nm. In two-component dye/TEOA systems, CI3D clearly outperformed C3PY. After 100 s of irradiation, conversions of 84 and 77% could be measured for C3ID and C3PY. Overall, only a slight improvement of the monomer conversions was observed for the bimolecular systems compared to the monocomponent systems. At 460 nm, due to its remarkable molar extinction coefficient, C3ID could furnish a conversion of 67%, higher than that of C3PY only reaching 20% (See Table 8). Steady state photolysis experiments carried out in acetonitrile revealed the photolysis kinetics of C3PY and C3ID to be only slightly affected by the addition of TEOA, consistent with the polymerization results. Due to the simultaneous presence of a tertiary amine and a ketone moiety, an intramolecular hydrogen atom transfer could be efficiently promoted, even in the absence of TEOA. In order to promote an intramolecular hydrogen transfer, an important parameter concerns the distance between the ketone and the tertiary amine. Theoretical calculations revealed the distance to be minimalized for the *E,Z*-isomers (See Figure 27). Considering this point, a hydrogen atom transfer occurring after a photoinduced isomerization was suggested as a plausible mechanism.

Table 8. Final monomer conversions determined during the FRP of TPGDA while using mono and two-component photoinitiating systems upon irradiation at 405 and 460 nm.

Dye/irradiation wavelength	405 nm	460 nm
C3PY (0.1 wt%)	60% (600 s)	4% (600 s)
C3PY/TEOA (0.1%/3% w/w)	77% (600 s)	58% (600 s)
C3ID (0.1 wt%)	80% (600 s)	67% (600 s)
C3ID/TEOA (0.1%/3% w/w)	84% (600 s)	78% (600 s)
C3CZ (0.1 wt%)	70% (600 s)	20% (600 s)
C3CZ/TEOA (0.1%/3% w/w)	88% (600 s)	80% (600 s)

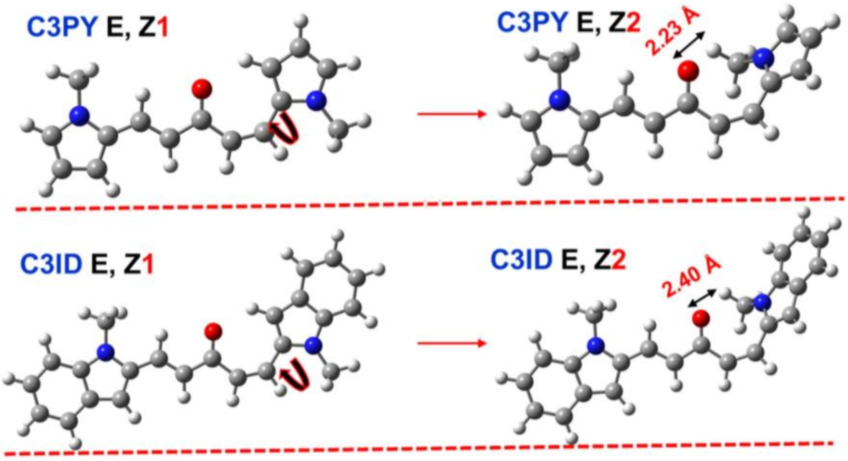


Figure 27. Optimized geometries of C3PY and C3ID for different conformations. Reproduced from Ref. [318] with permission from Elsevier.

Finally, the mechanism depicted in the Figure 28 was proposed. In first step, an isomerization reaction occurs upon irradiation, enabling to convert the *E,E*-isomer as the E,Z and even the Z,Z-isomers(See Figure 28a). As a result of this isomerization, a hydrogen atom transfer can occur, producing an unstable biradical that can undergo a radical recombination. Considering that the hydrogen atom transfer is going faster for C3PY than for C3ID, it therefore explains why C3ID exhibit higher photoinitiating abilities than C3PY. As shown from the polymerization results, an intermolecular hydrogen atom transfer can also occur with TEOA, facilitated by the large excess of amine used (See Figure 28b). As a result of this, an improvement of the monomer conversion upon addition of TEOA was logically observed. To end, a hydrogen atom transfer can occur between the excited dye and the ground state dye, producing initiating radicals (See Figure 28d).

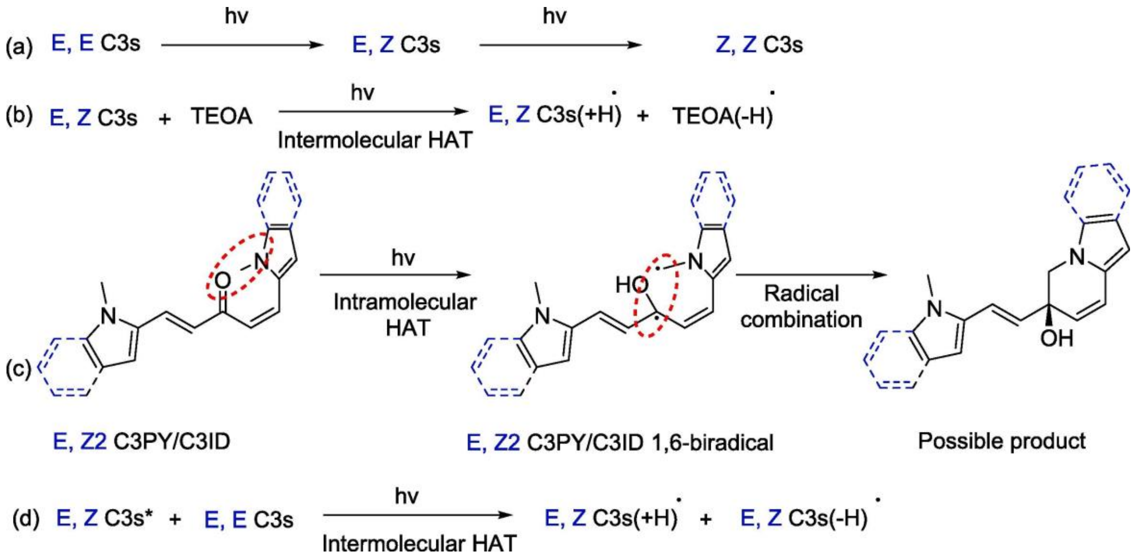


Figure 28. Photochemical transformations occurring for C3PY and C3ID with/without TEOA. Reproduced from Ref. [318] with permission from Elsevier.

Considering the remarkable performance of the pyrrole-based benzylidene ketones, investigations of their furane analogues were logically conduced. In this work, photoinitiating ability of 1,5-di(furan-2-yl)penta-1,4-dien-3-one (DFP) was compared to that of a chalcone also possessing two furane moieties, namely 1,3-di(furan-2-yl)prop-2-en-1-one (DFP-e) but differing by the conjugation length (See Figure 29).[319]

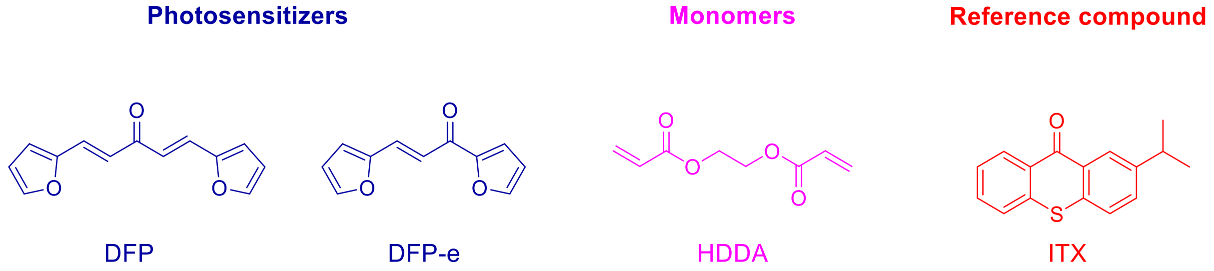


Figure 29. Chemical structures of DFP, DFP-e, HDDA and ITX.

From the absorption viewpoint, major differences could be found between DFP and DFP-e. Thus, by elongation of the π-conjugation in DFP and by introducing an additional double bond in DFP, a redshift of 17 nm could be determined between DFP and DFP-e, from 343 nm to 360 nm. This intense absorption band corresponds to π–π* transitions located on the conjugated structure. Molar extinction coefficients of 48250 and 42950 $M^{-1}.cm^{-1}$ were respectively determined at the absorption maxima for DFP and DFP-e, benefiting from the electronic delocalization existing between the electron-donating furane and the electron-accepting ketone (See Figure 30). As anticipated, a localization of the HOMO energy level on the π-conjugated system excepted the ketone moiety was evidenced. Conversely, a high electronic density could be determined on the ketone group, consistent with its electron-withdrawing ability.

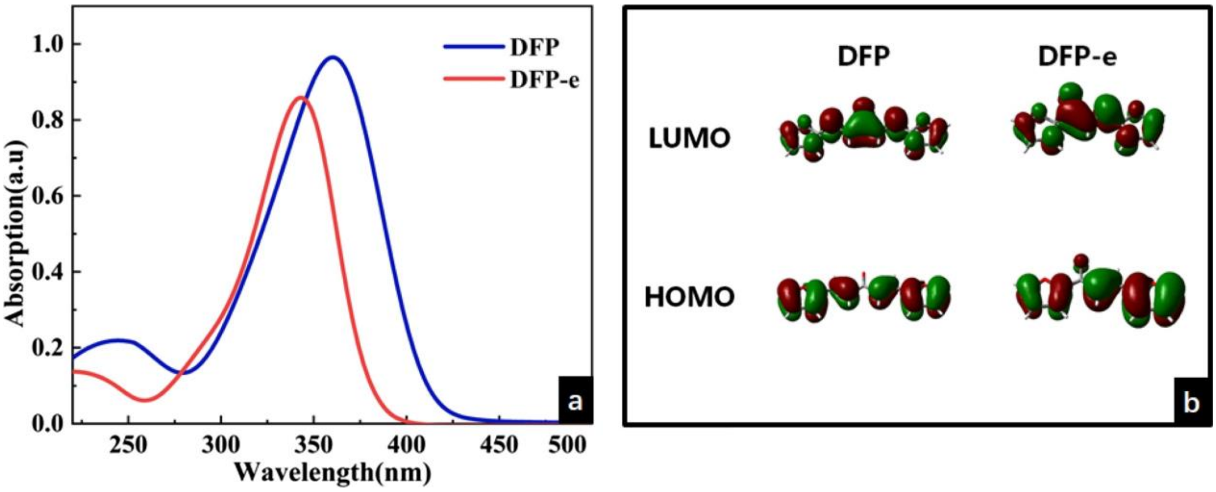


Figure 30. UV-visible absorption spectra of DFP and DFP-e in acetonitrile (left). Contour plots of the frontier orbitals determined by theoretical calculations (right). Reproduced with permission of Ref. [319]

When used in two-component dye/EDAB (0.0625%/1%, w/w) systems, DFP and DFP-e could furnish high monomer conversions during the FRP of hexamethylene diacrylate (HDDA) upon irradiation at 365 nm with a LED (I = 70 mW/cm²) (See Figure 31a). Thus, conversions of 68 and 48% were respectively determined for DFP-e and DPF, greatly higher than that obtained with the reference compound 2-isopropylthioxanthone (ITX), only reaching 34% after 600s of irradiation. However, it has to be noticed that the highest initial polymerization rate and the shortest inhibition time was obtained with ITX, demonstrating the interest of this thioxanthone in photopolymerization. Due to the hydrogen donor ability of PEGDA possessing ether groups, the different compounds can thus be used without addition of hydrogen donors. Using this approach, conversions of 87, 77 and 28% could be obtained for DFP-e, DFP and ITX (See Figure 31b). Noticeably, from the polymerization results, it could be concluded that the chalcone could furnish higher monomer conversions than its benzylidene ketone analogue, irrespective of the monomers or the photoinitiating systems used. By electron spin-resonance spin trapping (ESR-ST) experiments, formation of aminoalkyl radicals could be clearly detected, constituting the initiating species. Noticeably, very low photoinitiator content could be used, as low as 0.0625 wt%, greatly lower than that commonly used for the benchmark ITX (1-2 wt%).[320]

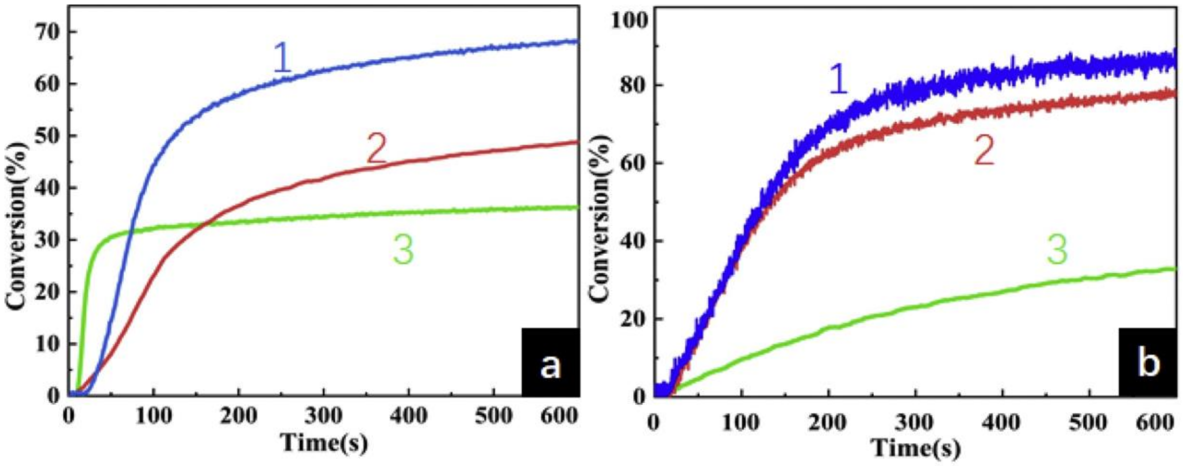


Figure 31. a) Polymerization profiles obtained during the FRP of HDDA at 365 nm using the two-component (1) DFP-e/EDAB (0.0625%/1%, w/w); (2) DFP/EDAB (0.0625%/1%, w/w); (3) ITX/EDAB (0.0625%/1%, w/w) systems; b) Photopolymerization profiles of PEGDA using (1) DFP-e; (2) DFP and (3) ITX as photoinitiators. Reproduced with permission of Ref. [319]

Finally, investigation of the photobleaching properties in acetonitrile solution revealed DFP and DFP-e to bleach rapidly, within 30 s. In the case of DFP-e, appearance of a new absorption band around 300 nm was clearly evidenced, corresponding to the absorption of photodegradation products. In the case of DFP, a blueshift of the absorption maximum by ca. 40 nm was determined, assigned to the formation of photoproducts and not to photodegradation, based on previous experiments.[105,265]

This year, four double benzylidene ketones were proposed by Wang and coworkers as visible light photoinitiators of polymerization, namely TPA-H, CZ-H, TPA-C and CZ-C (See Figure 32).[204] Compared to TPAK and CZK that respectively absorb at 440 and 410 nm, synthesis of double benzylidene ketones did not significantly modify their absorptions compared to their mono-benzylidene ketone counterparts since absorption maxima peaking at 448 and 400 nm could be respectively determined for TPA-C and CZ-C (See Table 9). Conversely, due to the presence of stronger electron-donating groups in TPA-C and CZ-C, absorptions of TPA-C and CZ-C are redshifted of 38 and 20 nm compared to that of TPA-H and CZ-H. Jointly, an enhancement of the molar extinction coefficients was observed for TPA-C and CZ-C, consistent with an elongation of the π-conjugated system compared to TPA-H and CZ-H. Based on their absorptions, all dyes are suitable for irradiation done at 460 and 532 nm.

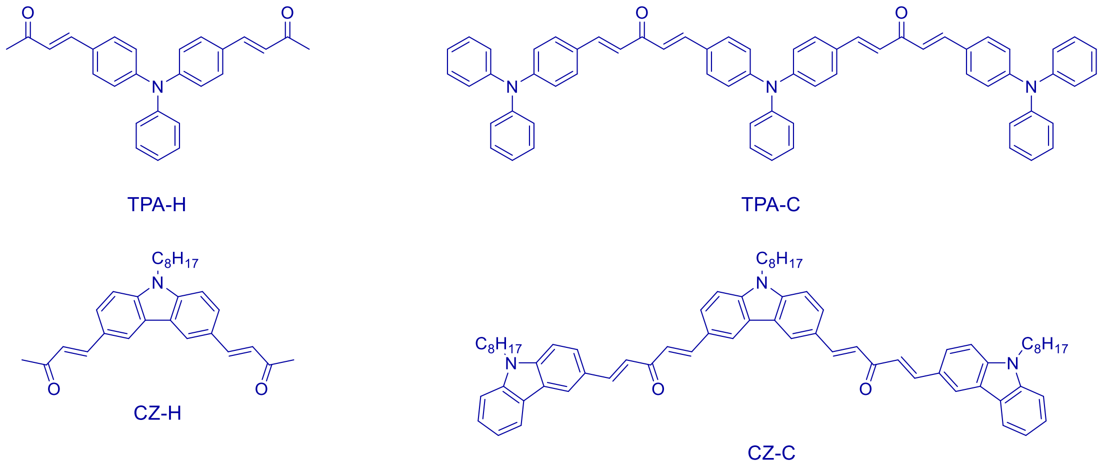


Figure 32. Chemical structures of double benzylidene ketones.

Table 9. Photophysical characteristics of TPAK and CZK in THF, TPA-H, TPA-C, CZ-H and CZ-C in dichloromethane.

	λ_{max} (nm)	ε_{max} ($M^{-1}.cm^{-1}$)	ε_{460nm} ($M^{-1}.cm^{-1}$)	ε_{520nm} ($M^{-1}.cm^{-1}$)	ε_{532nm} ($M^{-1}.cm^{-1}$)
TPAK	410	27500	18370	340	-
CZK	440	27000	1000	410	-
TPA-H	411	41962	9051	-	202
TPA-C	448	84322	81444	-	6065
CZ-H	380	41442	146	-	-
CZ-C	400	55935	19358	-	264

Photopolymerization of TPGDA with the different double benzylidene ketones revealed TPA-C and CZ-C to outperform TPAK and CZK upon irradiation at 460 nm but also at 520/532 nm. Thus, if monomer conversions of 73 and 80% at 460 nm, 75 and 86% could be determined with the two-component TPA-C/TEOA (0.1%/3% w/w) and CZ-C/TEOA (0.1%/3% w/w) systems, higher than that obtained with TPAK and CZK in the same conditions (See Figure 33). Comparisons with TPA-H and CZ-H revealed these dyes to furnish lower monomer conversions than TPA-C and CZ-C due to reduced molar extinction coefficients at the two irradiation wavelengths (460 and 532 nm). To support the improvement of the polymerization efficiency with the double benzylidene ketones, the double presence of ketone functions was suggested as being beneficial for monomer conversion by guarantying an increase of the charge transfer rate between the excited dyes and TEOA.

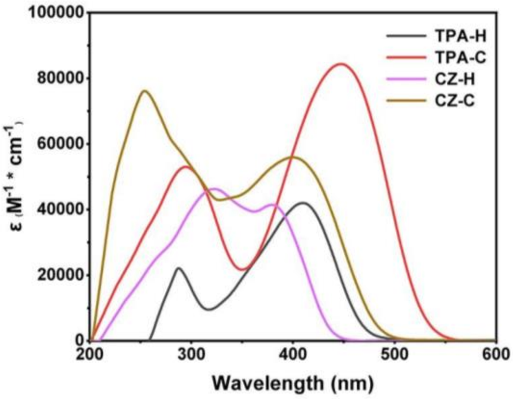


Figure 33. UV-visible absorption spectra of the four double benzylidene ketones in dichloromethane. Reproduced with permission of Ref. [204]

Steady state photolysis experiments done in acetonitrile for the two-component dye/TEOA systems revealed for the best candidates i.e. TPA-C and CZ-C, the photolysis to occur in two distinct steps. Thus, a fast decrease of the absorption intensity within 10 s was first observed, followed in a second step by a slower decay rate. It was thus suggested that an isomerization reaction of the benzylidene ketones was first occurring, followed in second step by the expected reaction with TEOA. Finally, upon elongation of the irradiation time, a complete bleaching of the solution was observed, favorable to get colorless photopolymers. By using the classical Rehm–Weller equation, the Gibbs free energy change (ΔG) for the intermolecular electron transfer between the photoexcited dye and TEOA could be determined and proved to be negative, indicative of the favorable process for the photoinduced electron transfer.

2.2. Asymmetrically substituted benzylidene ketones for one-photon photopolymerization

If the synthesis of symmetrically substituted dyes is an easy work, the synthesis of asymmetrically substituted structures is more difficult and, in this field, only one structure has been reported since 1991.[321] 1-(4-(Dimethylamino)phenyl)-5-phenylpenta-1,4-dien-3-one (ABA) was notably used as photosensitizer for the sensitization of a diphenyliodonium salt (Iod) and the FRP of methyl methacrylate (MMA) (See Figure 34). Due to the presence of a unique dimethylamino group, absorption of ABA was located in the 350-500 nm range, therefore blue shifted compared to M2K (See Figures 4 and 5) for which an absorption ranging from 350 up to 550 nm could also be determined in acetonitrile.

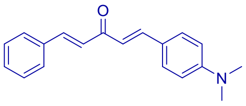
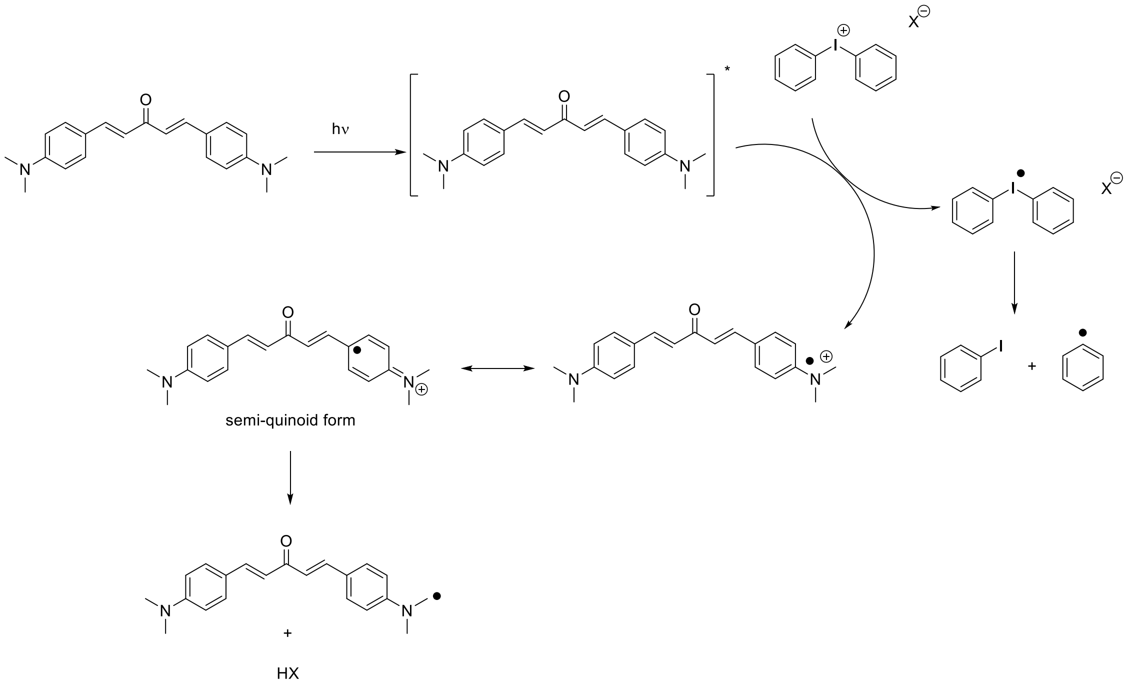

ABA

Figure 34. Chemical structure of the asymmetrically substituted benzylidene ketone ABA.

Comparison of the photoinitiating ability of ABA with that of M2K upon irradiation with a xenon lamp revealed M2K to clearly outperform ABA in terms of polymerization rate and final monomer conversion. Steady state photolysis experiments done in acetonitrile for the two-component M2K/Iod revealed for the appearance of an absorption band at 714 nm, corresponding to the semi-quinonoid form of the radical cation of M2K, which can rapidly evolve and generate α-aminoalkyl radicals according to the mechanism depicted in the Scheme 5. As interesting feature, if formation of the semi-quinoid form of M2K was detected in solution, this peak was not observed during photopolymerization, meaning that the semi-quinoid form is rapidly converted as an initiating species. Conversely, in the case of ABA and due to its asymmetric structure, less α-aminoalkyl radicals can be produced, adversely affecting its photoinitiating ability.



Scheme 5. Mechanism involved in the formation of a semi-quinoid form and the generation of initiating radicals.

3. Future opportunities

Even if major advances have been obtained with benzylidene ketones as photoinitiators of polymerization, numerous works remain to be done. Indeed, at present, no water-soluble benzylidene ketones have been developed, despites the crucial need for such photoinitiators. Indeed, the development of greener, sustainable, lower-cost and energy efficient polymerization processes is the focus of intense research efforts.[2,322–324] Even a few examples of benzylidene ketones-based monocomponent systems have been proposed, an efficient strategy to develop monocomponent photoinitiators consists in developing photocleavable structures that can generate radicals upon homolytic cleavage of a specific bond. In this field, numerous Type I photoinitiators have been reported in the literature, as exemplified with benzylketals, hexaaryl biimidazoles (HABIs), phosphine oxides, trichloromethyl-*S*-triazine glyoxylates, α-aminoalkylacetophenones, α-haloacetophenones, benzoin derivatives, hydroxyacetophenones, *o*-acyl-α-oximino ketones, acyloximino esters or [325] At present, no Type I photoinitiators based on benzylidene ketones have been reported in the literature, despite the appropriate light absorption properties.

4. Conclusion

To conclude, benzylidene ketones have been the focus of numerous studies due to their unique ability to act as one and two-photon photoinitiators. Several attempts were carried out to improve the two photon absorption properties consisting in replacing the vinylene spacer by vinylic ones or by extending the number of double bonds. If historically, benzylidene ketones were used as two-photon photoinitiators, recent developments during the last two years are only devoted one-photon photoinitiators. Interestingly, almost all benzylidene ketones were capable to bleach during irradiation, enabling to produce colorless coatings. Phenyl-free structures of high reactivity were also proposed, addressing the toxicity issue pour polyaromatic structures. Besides the promising results obtained with these dyes, a great deal of work still remains to be done concerning benzylidene ketones. Notably, water-soluble dyes have not been developed yet, what could be of crucial interest for developing more environmentally friendly polymerization processes. Similarly, Type I photoinitiators such as oxime esters have not been developed yet, what could constitute an interesting approach for the simplification of the photocurable resins.

Acknowledgments

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Conflicts of Interest

The authors declare no conflict of interest.

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