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Progress in the Development of Polymeric and Multifunctional Photoinitiators

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Abstract:

UV-curing technology has been developed and widely used in industry for 6 decades. However, the migration of low-molecular-weight photolysis is today an important drawback in many application fields such as food packaging materials, leading to unpleasant secondary features such as odor, blooming and contamination. Therefore, many efforts have been devoted to design polymeric photoinitiators (PPIs) and multifunctional photoinitiators (MFPIs) to overcome these drawbacks. This review introduces the development and the challenges of UV-curing technology and the state of the art of PPIs and MFPIs, in which methodologies of synthesis and characterization are meticulously discussed. Moreover, a novel classification, based on the molecular structure, has been drafted for all the PPIs conventionally reacting through photodissociation or photoreduction. Most of the PPIs and MFPIs have excellent photochemistry properties, some of which have extra properties such as amphiphile, self-floating and biocompatibility. Examples of well-defined structures are discussed in the section on MFPIs.

Keywords: photopolymerization, polymeric photoinitiator, multifunctional photoinitiator, free radical, migration

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Abbreviations

AA	Acrylic acid	MK	Michler ketone
ABPE-10	2,2-Bis[4-(acryloxypolyethoxy)phenyl]propane	MMA	Methylmethacrylate
AM	Acrylamide	MW	Molecular weight
AMP-10G	Phenoxy ethyleneglycol acrylate	NMP	Nitroxide mediated polymerization
AN	Acrylonitrile	NVP	N-Vinylpyrrolidone
An	Anthracene	PDI	Polydispersity index
ATRP	Atom transfer radical polymerization	PEG	Poly(ethylene glycol)
BA	Butyl Acrylate	PEGDA	Polyethyleneglycol diacrylate
BP	Benzophenone	PETA	Pentaerythritol tri-, tetra- acrylate
CEVE	2-Chloroethylvinyl ether	PI	Photoinitiator
CHO	Cyclohexene oxide	PPGDA	Poly(propylene glycol) diacrylate
DBC	Double bond conversion	PPI	Polymeric photoinitiator
DEAB	4,4' Bis (diethylamino) benzophenone	PU	Polyurethane
DMAB	4-(Dimethylamino) benzophenone	Py	Pyrene
EA	Ethylacrylate	RAFT	Reversible addition fragmentation chain-transfer
EPOX	(3,4-Epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate	RASFF	Rapid Alert System for Food and Feed
HCPII	Hyperbranched and cross-linked polymeric photoinitiator	RDRP	Reversible-deactivation radical polymerization
HDDA	Hexanediol diacrylate	St	Styrene
HEMA	2-Hydroxyethyl methacrylate	TDI	Toluene-2,4-diisocyanate
HMPP	2-Hydroxy-2-methyl-1-phenyl-propanone	THFA	Tetrahydrofurfuryl acrylate
IPDI	Isophorone diisocyanate	TMPTA	Trimethylolpropane triacrylate
ITX	Isopropylthioxanthone	TPGDA	Tripropylene glycol diacrylate
LFP	Laser flash photolysis	TPO	Trimethylbenzoyldiphenylphosphine oxide
LOD	Limit of detection	TX	Thioxanthone
LOQ	Limit of quantification	UV	Ultraviolet
LPPI	Linear polymeric photoinitiator	VCHD	4-Vinylcyclohexene dioxide
MFPI	Multifunctional photoinitiator	VOC	Volatile organic compound
		VP	1-Vinyl-2-p

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1. Introduction

Economy, efficiency, ecology and energy are the “4E” principles of modern industrial development. UV-curing technology is widely studied among coatings, adhesives and inks manufacturers, because of its compliance with these principles. Compared to thermal curing system, UV-curing process has attractive advantages such as high-speed, low energy consumption and low-solvent formulation [1-2]. Between the two main types of UV-curing mechanism (radical-type and cationic-type), the radical-type systems are the most widely used in UV-curing application so far in virtue of their higher reactivity [1,3].

Radiation curing has gained popularity in the packaging printing industry over the last decades, since it was commercialized in the late 1960s. Using ultraviolet (UV) energy to trigger polymerization of resins onto a substrate, UV-curing technique has been used in inks and coatings for food packaging printing, such as breakfast cereal boxes, milk and fruit juice cartons, frozen dinner cartons, ice cream and frozen dessert packages, as well as flexible film wraps. UV curing affords distinct advantages: fast curing, room temperature operation, high quality end products and low cost. In addition, UV curing technology is generally performed under room temperature conditions and thus allows the application of inks and coatings on heat sensitive substrates. Moreover, UV-cured formulations can be directly applied to the outer surface of the package without the use of solvents, hence reducing drying time and eliminating solvent exposure to workers.

In UV curing, acrylate monomers and oligomers are predominantly used to form a polymer resin due to the rapid reaction rates and the high degree of optical clarity of the end products. The acrylate monomers are primarily used as diluents, to impart the rheological properties necessary for the printing and coating process [4]. Many types of curable acrylate monomers are available commercially. For instance, there are acrylate monomers like tripropylene glycol diacrylate

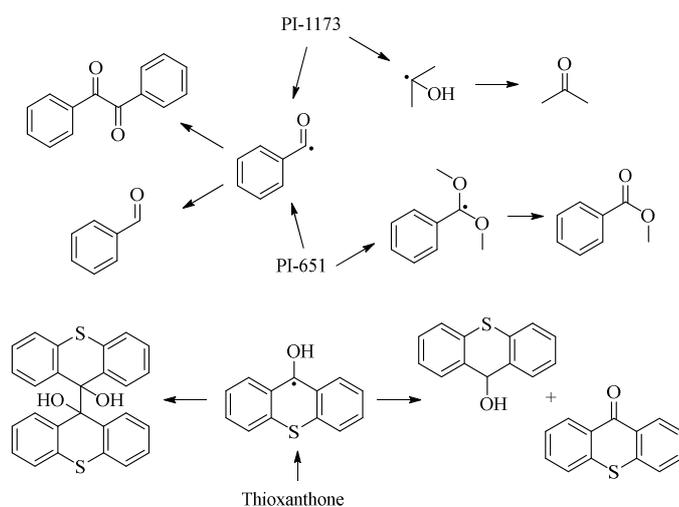
(TPGDA), trimethylolpropane triacrylate (TMPTA), hexanediol diacrylate (HDDA) and pentaerythritol tri-, tetra acrylate (PETA) etc.

Photoinitiators (PIs), the agents that absorb the UV energy and form free radicals that initiate the polymerization reaction, are the key compounds in UV-curing formulations. According to the free radical forming mechanism, the PIs can be classified to Type-I PIs and Type-II PIs [1-2]. Type-I PIs lead to photodissociation, creating two radicals that may both initiate the polymerization reaction. Type-II PIs undergo photoreduction reaction by reaction with an electron or hydrogen donor. Thus, they require an additional co-initiator, such as a tertiary amine, ether, ester, or thiol for the formation of initiating radicals and low reactive ketyl radicals [3,5].

Generally, the higher reactive radicals initiate the polymerization reaction and are therefore locked into the growing polymer chains after the polymerization process. Nevertheless, some of the photoproducts of PIs may exhibit varied physical and chemical properties, which can be detrimental to the efficiency of photoinitiation and the performance of the cured product. The photoproducts of both Type-I and Type-II PIs may undergo further rearrangement, combination, oxidation and decomposition due to the instability of the radicals (Scheme 1). Some of these small molecular by-products may be colored or odorous and be inclined to migration in the polymer networks [6]. The migration of the PIs fragments could bring about odor and blooming of coatings, which present problems in materials used for food packaging. A further concern are residual amounts of PIs, either as remainder of the UV-curing process or due to incomplete purification, since PI species are prone to migrate through the porous paperboard and secondary packaging to the food or beverage. They also can remain in the paperboard after the outer print layer is removed, and thus PIs can appear in new packaging made with recycled paperboard fibers [7].

In the last decade, several notifications reported through Rapid Alert System for Food and Feed (RASFF) in the EU were related to the PIs used for food packaging. More than one hundred notifications issued RASFF concerned the migration of PIs from food packaging since 2000. The first one corresponded to the detection of isopropylthioxanthone (ITX) in baby milk in 2005 [6,8]. That well-known “isopropylthioxanthone case” (2005) and the “benzophenone and 4-methylbenzophenone cases” (2009) led to serious consequences [8]. Soon after these events, considerable interest has been focused on side effects due to photoinitiators in the food industry, including the migration process, the analytical methods for migration and the toxicity of the photoproducts.

It is important to precise that the term “migration” also accounts for the transfer of chemicals compounds from the package to the food. Also, throughout the paper we are interested in PIs among the different components of the photopolymerizable formulations used for food packaging. A variety of factors have been shown to affect migration from the printed surface through the paperboard and to the food itself (direct contact), or from the paperboard through the vapor phase to the food (indirect contact) [7-8]. These factors include set-off [9-10], the vapor pressure of the UV photoinitiator [11], time and temperature of food storage [9-10,12], porosity and types of materials used for primary and secondary packaging, the fat and moisture content of the food, and whether the UV photoinitiator is present or not in recycled materials used to form new packaging.



Scheme 1. Several examples of secondary reactions of photoinitiators.

PIs with high molecular weight (MW) are believed to be a promising solution to the above problem, among those polymeric photoinitiators (PPIs) and multifunctional photoinitiators (MFPIs) are major topics of discussion. The idea of grafting the PIs on a high MW molecule is aimed at anchoring the odorous or toxic photoproducts. Previous review articles introduce the synthesis and performance of various macromolecules bearing Type-I or Type-II PI groups such as benzoin ether and thioxanthone [13]. However, there have been increasing numbers of PPIs and MFPIs with all sorts of molecular structures. Therefore, the existing definition and classification of these PIs needs to be reappraised.

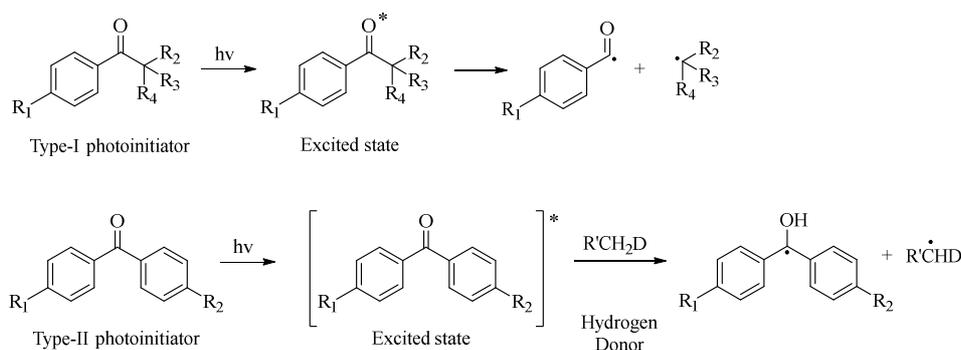
Many efforts have been devoted to the development of PPIs and MFPIs including synthesis routes, photoinitiating performances and structural functionalities. This systematic review introduces the recent advances of PPIs and MFPIs, and drafts an innovative categorization for them. PPIs are distributed according their molecular structure into three classes: linear polymeric photoinitiator (LPPI), hyperbranched or cross-linked polymeric photoinitiator (HCPPI), and multifunctional photoinitiator (MFPI). In the scope of this discussion, the initiation systems of

low-MW Type-II PI with polymer hydrogen donor and the self-photoinitiation of monomer bearing PI group are not included, notwithstanding their prosperous application.

2. Classification of polymeric photoinitiators

Many different strategies can be used to develop new polymeric photoinitiators leading to a wide variety of structures. Therefore, when dealing with PPIs, it is convenient to separate a) the photoinitiator moiety, which is quite often based on well-known low molecular weight photoinitiators and b) the polymeric backbone that does not influence the absorption of light and the mechanism of reaction.

Concerning the photoinitiator moiety, one has to say that most of the polymeric photoinitiators are based on well-known low molecular weight photoinitiators. Therefore, the photoinitiation mechanisms are expected to be quite similar to the parent molecules. From that point of view, photoinitiators are generally divided into two families: Type-I and Type-II photoinitiators.



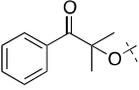
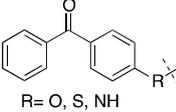
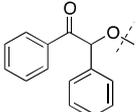
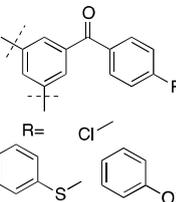
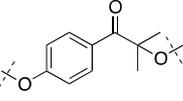
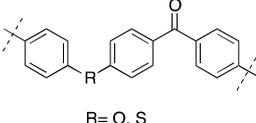
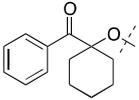
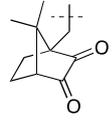
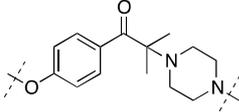
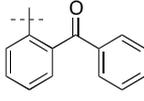
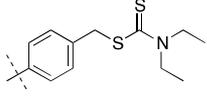
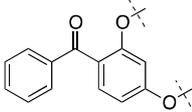
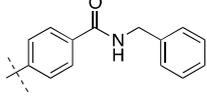
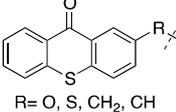
Scheme 2. Reaction mechanisms of Type-I and Type-II photoinitiators.

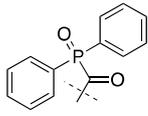
Type-I PIs absorb radiation and undergo bond cleavage from an excited state providing initiating radicals, while Type-II PIs undergo hydrogen abstraction from a coinitorator (hydrogen

donor), which results in two free radical species (Scheme 2). The photoinduced homolytic cleavage of Type-I PIs could occur at the α -position (major) or β -position (minor) of carbonyl group, depending on their bond strengths. As for Type-II PIs, a co-initiator, such as tertiary amine, ether, ester, thiol, etc., is needed to donate hydrogen to the triplet state PI, producing a low reactive ketyl radical and a highly reactive donor radical [3,5].

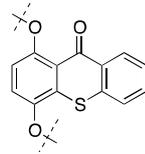
Table 1. Structures of photoinitiator moiety in PPIs and MFPIs.

L: LPPIs, H: HCPPIs, M: MFPIs

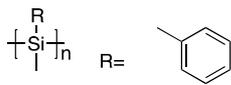
Type I			Type II		
PI group	λ_{\max} (nm)	Ref.	PI group	λ_{\max} (nm)	Ref.
	280, 330	L [14-19] H [20] M [21-22]	 R= O, S, NH	280~290, 340~350	L [23-35] H [36-40] M [41-44]
	275, 320	L [14,16,45]	 R= Cl, S-phenyl, O-phenyl	250~280, 315~325	L [46-49]
	280, 325	L [14-16,50-53] M [54-56]	 R= O, S	315~325	L [46,57-59]
	280, 320	L [60-61] H [20]		468	L [62-63]
	290, 320	L [64-65]			L [66]
	300, 340	H [67]		246~248, 308	L [68]
		L [69]	 R= O, S, CH ₂ , CH	380~390	L [70-76] H [77-78] M [79-83]



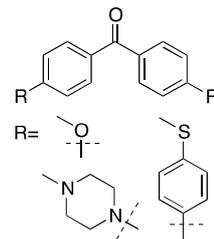
390 L [84-85]



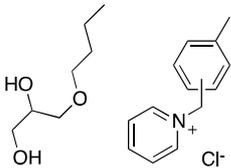
320, 400 L [86-90]



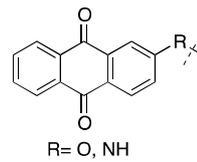
260~270,
330~340 L [91-94]



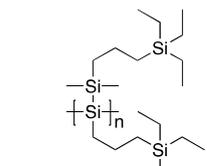
295, 348 L
[25,95-100]



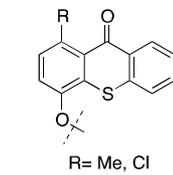
270, 330 L [101]



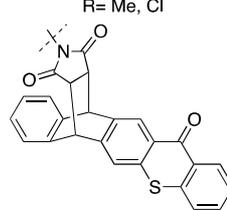
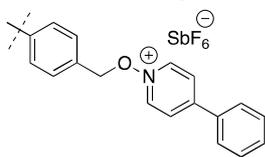
329~339 L [102]
M [44]



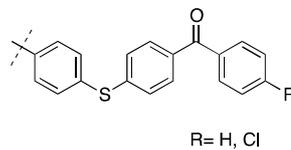
310 L [103]



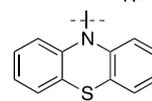
388~399 L [70,104]



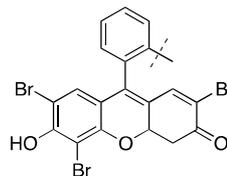
380~390 L [105-106]



251~258,
317~323 L [107-108]



254~259,
311~316 L [109]



H [110]

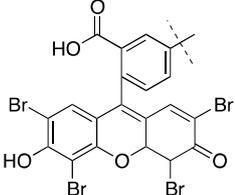
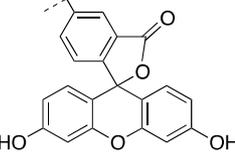
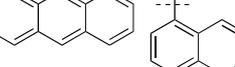
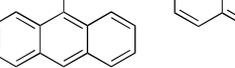
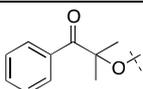
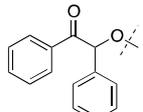
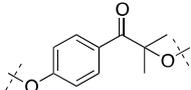
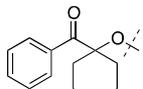
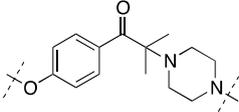
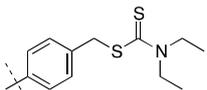
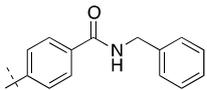
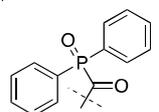
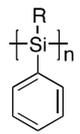
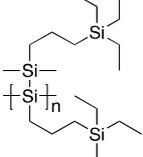
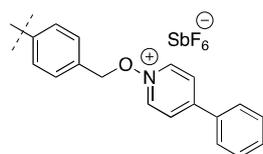
		M [111]
	495	L [112]
	334~348, 400~404	L [66] M [41]
		

Table 1 collects the different photoinitiator structures that have been used to synthesize PPIs, while Table 2 includes the DBC of acrylate monomers that initiated by those PPIs. The photochemistry of these photoinitiators groups is well known and will not be discussed as the reaction mechanism have been described elsewhere [1-3,5].

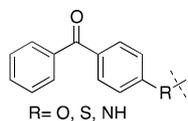
Next to the photoinitiator moiety, the polymer backbone plays an important role. Indeed, the ease of synthesis, the viscosity, and the solubility properties will control the effectiveness of the PPI. For sake of clarity, it is worth classifying the different kind of polymeric structures that could be found in the literature.

Table 2. Structures of photoinitiator moiety in PPIs and MFPIs and the final DBC of the employed monomers. L : LPPIs, H : HCPPIs, M : MFPIs

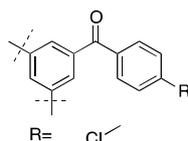
PI group	Monomer	Final Conversion (%)	Ref
	L: MMA H:EA	14.5-21.0 88.0	15-16 21
	L: MMA CHO	14.0 16.0-22.0	16 45
	L: MMA AN AM HDDA M: TMPTA Ebecryl 605	15.0-21.0 17.5 17.0-28.2 65.0 45.0 69.2-95.0	16,51-52 50 50,52 53 54 55-56
	L: MMA St H: EA	46.0-49.0 10.0 88.0	60 61 20
	L: HDDA	30.0-40.0	64-65
	H: MMA	50.0	67
	L: MMA St	12.0-40.0 15.0-34.0	69 69
	L: HEMA HEMA/H2O HDDA/BA	48.0-82.0 102.0-116.0 4.0-20.0	84 84 85
	L: AM/H2O HEMA AA	80.0-100 >90.0 >90.0	94 94 94
	L: TMPTA	59.0	101



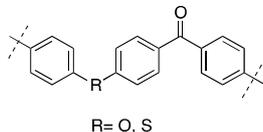
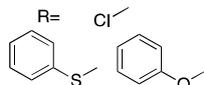
L: MMA 56.0-79.0 103



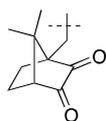
L: TMPTA 20.0-55.0 24,26,33-34
 HDDA 60.0-95.0 26,32,35
 TPGDA 40.0-90.0 27-29,31,33
 MMA 0.5-30.6 32,35
 THFA 98.0 33
 TEGDMA 50.0-72.0 32-35
 PETA 30.0 38
 HEMA 85.0 35
 H: TMPTA 44.1-58.9 38
 HDDA 44.3-76.2 39-40
 M: EPOX 90.0 41
 TMPTA 20.0 41



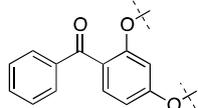
L: EA 9.4-15.4 46
 PPGDA 59.8-86.2 46
 TMPTA 32.6-59.9 46-49
 PU prepolymer 28.7-97.3 47-49



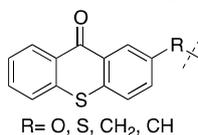
L: EA 11.3-15.3 46
 PPGDA 41.5-80.3 46,58
 TMPTA 36.5-53.9 46-58
 PU prepolymer 61.3-86.7 57



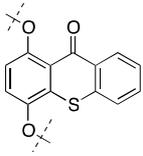
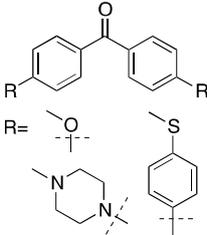
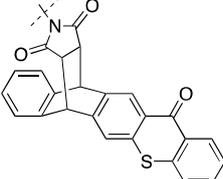
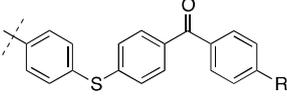
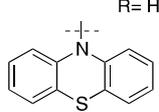
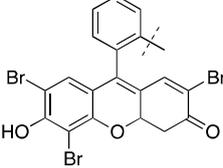
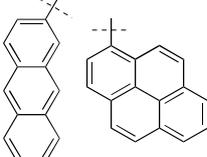
L: HDDA/BA 3.0-65.0 63



L: PPGDA 85.4-93.4 68
 TMPTA 63.2-68.0 68



L: TMPTA 30.0-60.0 71
 MMA 5.3-28.8 72,75
 AM 85.7-100.0 74,75
 NVP 14.0-26.1 75
 HEMA 27.7-48.0 75
 H: AM 62.3-83.4 77
 PEGDA 85.4-87.1 77
 A-BPE-10 78.7-86.0 77
 M: AM >20.0 79
 MMA 0-41.5 80,82
 TMPTA 60.0 80
 AM >50.0 81
 A-BPE-10 54.7-89.4 83

	L: MMA	>25.0	75,88
	PPGDA	9.9-51.7	87,89
	TMPTA	31.8-54.1	87,89-90
	AM	54.2	90
	ABPE-10	79.3	90
	L: PPGDA	65.8-76.2	95
	AMP-10G	20.0-78.5	97
	A-BPE-10	74.1-88.8	98,100
	TMPTA	40.5	98
	HDDA	12.0-65.0	99
	PEGDA	66.7-94.2	100
	L: MMA	0.3-20.0	105
	AA	70.0	106
	AM	69.0	106
	HEMA	73.0	106
	VP	72.0	106
	L: HDDA	71.2-98.1	107-108
	TMPTA	45.6-76.3	107-108
	L: CEVE	95.0	109
	VCHD	80.0-90.0	109
	H: St	2.2	110
	AM	87.4	110
	AN	38.4	110
	AA	4.8	110
	EPOX	55.0-80.0	41

The classification in this review is based on the variety of molecular configurations of photoinitiator moieties and backbones (Figure 1). Since the photoinitiator groups are the substantial parts in PPIs and MFPIs, a discussion of the backbone structures has not been the interest of researchers. In most cases, the motivation for considering the backbone structure would be related to the ease of synthesis of the respective structure. This will be discussed in the

following sections. Nevertheless, some peculiar backbones either have certain functionalities [51,55-57,86-87] or affect the photochemistry of the photoinitiator groups [102].

LPPI refer to the linear polymer bearing PI groups either as “in-chain LPPIs” which include the PI as a part of the linear chain or as “side-chain LPPIs” in which the PI is connected to the polymer backbone as a pending group.

Highly cross-linked polymeric photoinitiator (HCPPI) refers to uncountable PI groups grafted either on hyperbranched polymer or on polymeric cross-linked network. By contrast, multifunctional polymeric photoinitiator (MFPI) refers to defined number of PI groups locating at relatively low-molecular-weight core or dendrimer.

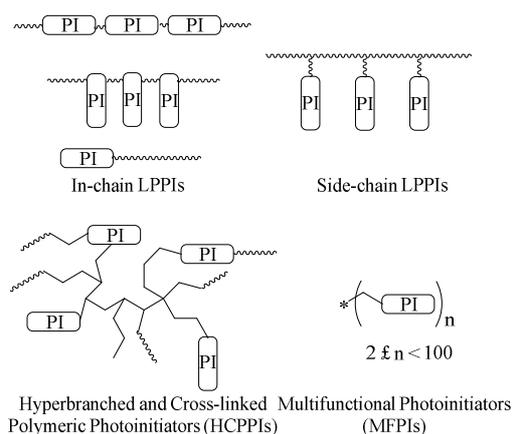


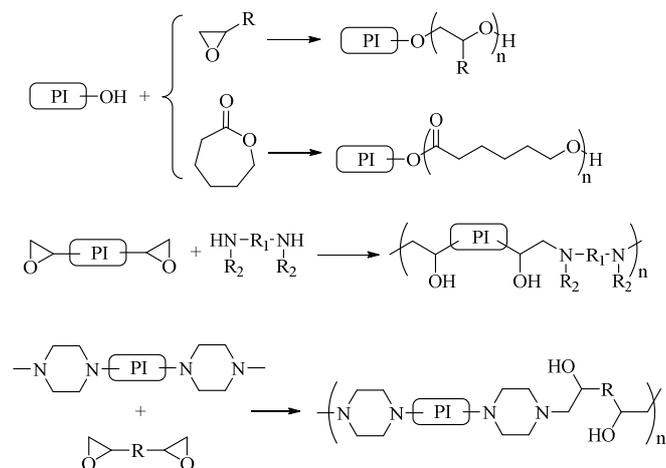
Figure 1. Structural distinction of in-chain LPPI, side-chain LPPI, HCPPI and MFPI according to the classification of this review.

3. General methodologies of synthesis of PPIs

The first question when one designs the synthesis route of a new PPI would be: how to install an effective PI on a polymer and preserve it during the preparation step? This question implies two different ways of constructing PPIs, which are represented by “preserve” and “install”. Generally, PI groups can survive in most of the non-photoinduced polymerization as part of starting formulation, and be located in polymeric structure, which is one way to construct PPIs. Grafting PI groups on a ready-made polymer is another way to prepare PPIs, which is unrestricted in polymerization method but demands particular functional groups on both polymer and PI. In accordance with those ideas, several methods have been explored and used in preparation of PPIs.

3.1 Ring-opening polymerization (M1)

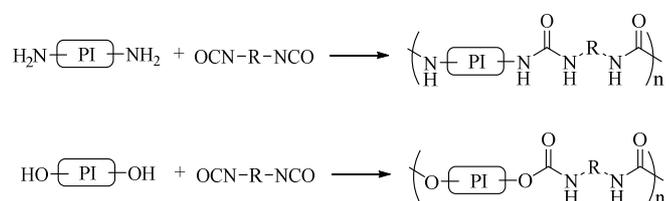
Ring-opening polymerization is one of the most versatile methods in living polymerization. Epoxides and lactones are the most popular cyclic monomers for synthesis such PPIs. Additionally, PPIs can have different functionality depending on the structure of the starting PI moiety (Scheme 3). For example, employing 1-hydroxycyclohexyl phenyl ketone, known as a commercial PI “Irgacure 184”, as a starting hydroxyl source, Degirmenci [14,16] synthesized poly(ϵ -caprolactone)s via ring-opening polymerization catalyzed by $\text{Sn}(\text{Oct})_2$ with PDIs lower than 1.50. Recently, D,L-lactide has also been used as a ring-opening monomer to prepare “mid-chain” PPIs [19]. A novel biobased and environmental friendly LPPIs of poly(D,L-lactide) homopolymer and tetrablock poly(D,L-lactide)-poly(ϵ -caprolactone) copolymer with controlled molecular weights and narrow molecular weight distributions via M1 were prepared. Jiang et al. modified thioxanthone [88] and benzophenone [68,95,98] to difunctional monomers, and then synthesized a series of PPIs with PI groups in the repeat units.



Scheme 3. Resin-like PPIs formed from ring opening polymerization.

3.2 Alcoholysis/aminolysis of isocyanates (M2)

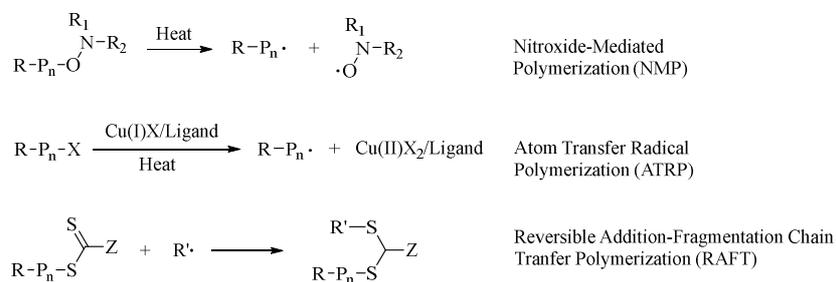
Isocyanates have been widely used in preparation of oligomer, thanks to the high reactivity with hydroxyl and amino groups. In addition, this reaction does not require any catalyst and produces no by-product. This makes these reactions quite suitable for industrial manufacturing. When modified with two hydroxyl or amino groups, PIs can copolymerize with commercial isocyanates such as IPDI and TDI, forming PPIs with polyurethane or polyurea backbones (Scheme 4). Wei et al. [46-49,59] designed a two-step copolymerization among hydroxyl, amino and isocyanate compounds, preparing varied PPIs with both benzophenone derivatives and amino coinitiators on the back bones (Scheme 8b).



Scheme 4. Resin-like PPIs formed from alcoholysis/aminolysis of isocyanate.

3.3 ATRP from bromo-substituted PIs

The methods M1 and M2 mentioned above are both facile methods that should be considered in industrial manufacturing. From a laboratory standpoint, controlled reversible-deactivation radical polymerization (RDRP) affords easy way to control the PPI structure. Among those approaches, atom transfer radical polymerization (ATRP) has been employed in synthesis of PPIs. In the basic ATRP equilibrium, redox-active transition metal complexes are involved as catalyst, among which the $\text{Cu}^{\text{I}}/\text{L}$ and $\text{X-Cu}^{\text{II}}/\text{L}$ are the most often used [113]. Additionally, alkyl halides act as initiators and dormant species that periodically react with the catalyst. Due to that specific equilibrium, polymers formed via ATRP bear haloalkanes after the removal of the catalyst system, which are the tiniest “tails” in RDRP family. Not only narrow molecular weight distribution [14-15,61], and block copolymer [16,69], but also possibility of further end group modification [114-115] can be achieved with ATRP. In the case of PPIs preparation, although there are other techniques, such as the well-known reversible addition fragmentation chain-transfer (RAFT) and nitroxide mediated polymerization (NMP) in RDRP to satisfy the similar requirement on general circumstance, the photo- or thermal stability of their dormant species are incomparable to those of ATRP in photosensitive system, which can be the reason why reports of RAFT and NMP are seldom seen on the topic of PPIs (Scheme 5).



Scheme 5. Chemical properties of dormant species of different RDRP approaches.

3.4 Click chemistry

Click chemistry had been an advanced tool in both polymerization and polymer modification. By simple and fast procedures, various products have been synthesized at high yield. More and more reactions are being found to match the concept of click chemistry, offering more options for construction of macromolecules (Figure 2).

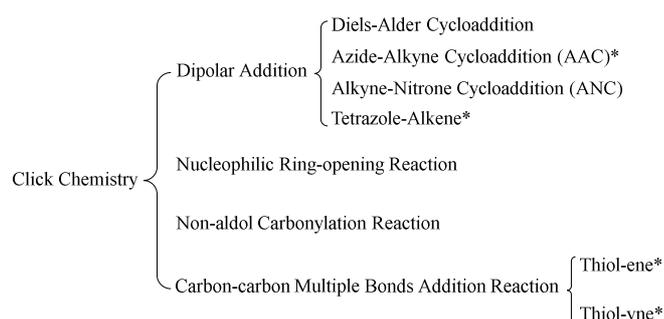
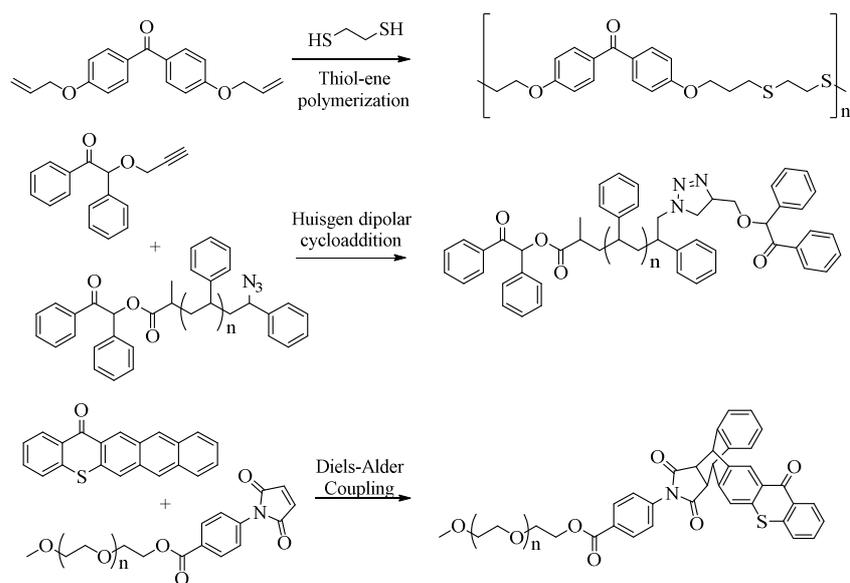


Figure 2. Classification of Click Chemistry (* photo-induced reaction has been reported).

In preparation of PPIs, the most classic example of polymer click reaction is thiol-ene polymerization, which was applied by Temel et al. to synthesize benzophenone-based PPI [99]. Moreover, copper(I)-catalyzed Huisgen dipolar cycloaddition was employed for grafting PI groups to polymer end group by Degirmenci *et al.* [45] Diels-Alder reaction is also one of the important click reactions to modify polymer end groups with PI groups (Scheme 6) [106].



Scheme 6. Click reactions for synthesizing polymeric photoinitiators.

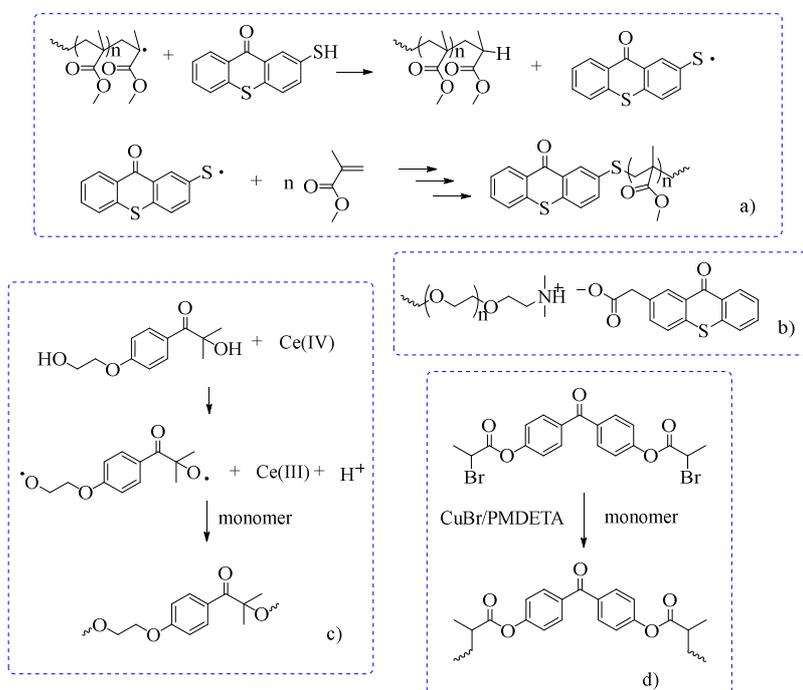
4. Linear Polymeric Photoinitiators (LPPIs)

Linear polymers are among one of the most common type of macromolecules in both scientific and industrial area. Introducing photoinitiators (Type-I or Type-II) to linear polymers is a facile way to obtain PPIs, for example, by polymerization of monomers bearing PI groups. In this way, the PI groups can be located in the backbone or the side chain of the polymer as part of the repetitive unit. Besides, modification of end-group is another route to prepare LPPIs. Nevertheless, the convenience of synthesis is not the only merit of LPPIs. The structural nature of linear polymer also benefits to the properties and the application of LPPIs.

4.1 In-chain LPPIs

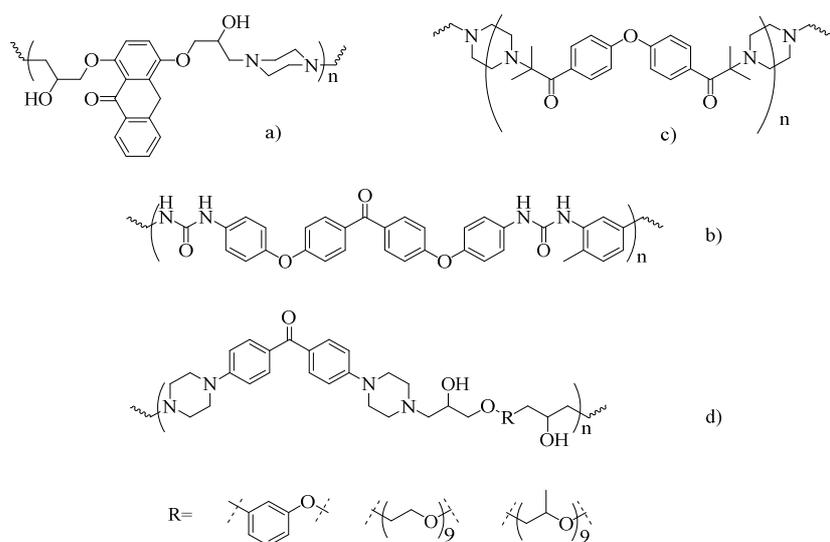
According to our definition of in-chain LPPIs, it is obvious that the conjugation system of PI is part of the polymer backbone. Most of these LPPIs bearing Type-I PI groups, in this case, would be degraded along with photolysis of PI groups.

The facile methodologies mentioned had not hindered the development of synthesis of In-chain LPPIs. Karasu *et al.* [73] adopted 2-mercapto thioxanthone as a chain transfer agent in polymerization of styrene (St) and methyl methacrylate (MMA), leading to the formation of polymers with thioxanthone (TX) end groups (Figure 7a). More recently, Yilmaz *et al.* [75] reported a similar PPI prepared by counterion incorporation of TX and polymer, which can be applied in either organic or aqueous system (Figure 7b). Degirmenci *et al.* [50-52] developed a Ce(IV)/HNO₃ redox initiation system to prepare polymers with PIs in mid-chain (Figure 7c). In this case, 2-hydroxy-1-[4-(2-hydroxyethoxy) phenyl]-2-methyl propan-1-one, was used as initiator due to its dihydroxyl functionality. Also benefit from the hydroxyl functionality, 4-hydroxybenzophenone and 4,4'-dihydroxybenzophenone were modified with 2-bromopropionyl bromine by Temel *et al.* [25] followed by ATRP to form end-functionalized and mid-functionalized polymers (Figure 7d).



Scheme 7. Exemplary structures of LPPIs.

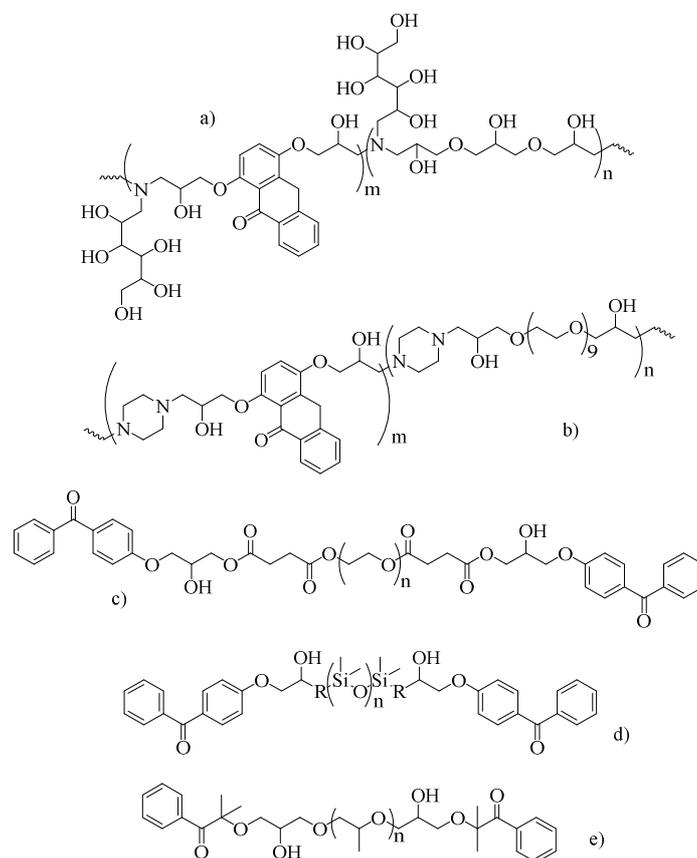
Linear polymers bearing photosensitive conjugated groups in the backbone consequentially have property differences, both with respect to photodynamic and in thermodynamic properties, to common polymers. Jiang and Yin synthesized a PPI containing in-chain TX and coinitiator amines, which had a red-shifted maximum absorption (from 396 nm to 399 nm) and a weaker fluorescent (Scheme 8a) compared to the corresponding TX model compounds (M1) [86]. They also modified that PPI with acrylate and styryl as the side groups, resulting blue shifts of absorption peaks (from 399 nm to 395 nm) [87]. Wei *et al.* [57] also reported a similar result (M2). Ye *et al.* [64] designed an oligomeric photoinitiator containing α -aminoalkylphenone chromophore (M1), which was found to have great thermal stability with a decomposition temperature higher than 300°C (Scheme 8c). The photoinitiating behavior of the oligo(α -aminoketones) was also investigated (M1) [65]. Similarly, Wen *et al.* [97] synthesized several polymeric Michler's ketone photoinitiators (M1), demonstrating that the chain flexibility of LPPIs influences the photoinitiation efficiency (Scheme 8d). The difference in photoinitiation performance between LPPIs and their low-molecular-weight counterparts could be even greater, according to the work of Wei *et al.* (M2) [58]. They found that the LPPI they prepared had high photoefficiency ($R_{p,max} = 2.733 \times 10^2 \text{ s}^{-1}$ and $2.085 \times 10^2 \text{ s}^{-1}$), while its counterpart, 4-amino-4'-[4-amino-thiophenyl]benzophenone, could hardly initiate the photopolymerization.



Scheme 8. Some of the LPIIs synthesized via step-growth polymerization.

The organic photoinitiators have been endowed with extraordinary properties by being located to polymer backbone. Suffering from their hydrophobicity, most organic radical photoinitiators are inapplicable to waterborne systems, which is the trend of UV-curing material development fulfilling the requirement of decreasing VOC. However, amphiphilic polymers provides one way to reach that goal (Scheme 9a-c). Thioxanthone had been introduced to water-soluble polymer (M1) [89] and amphiphilic block copolymer (M1) [90]. Wang *et al.* (M1) [33] utilized epoxy-modified BP as the end-capping agent in the polymerization of poly(ethylene glycol) (PEG), which is the typical representative of hydrophilic polymers, to obtain a series of one-component Type-II amphiphilic LPIIs. Wen *et al.* (M1) [100] found that the Michler's ketone LPIIs had different maximum absorption in CH_2Cl_2 and H_2O . Other researchers have discovered more exciting application of in-chain LPIIs. Polymeric gradient materials have attracted much attention in recent years. Gradient distribution of photoinitiators is a promising solution for overcoming the O_2 inhibition of UV-curing process. Polysiloxane has been chosen to be the backbone of "self-floating" LPIIs (M1) [28,31]. Zhang and co-workers (M1) [29]

investigated the floating ability and photoinitiation kinetics of polysiloxane BP LPPIs with different silicone chain lengths. They also found that this polysiloxane LPPI has good control of wrinkling on UV-cured films (Scheme 9d). Seok et al. (M1) [17] introduced an acetophenone functionalized oligomeric LPPI to the preparation of polymer-dispersed liquid crystal film, which exhibited both driving voltage and high contrast ratio (Scheme 9e). Jiang *et al.* [96] synthesized a novel negative photosensitive polyimide with good photolithographic properties via polyimidization, the synthesis of which implied a new idea of coupling conjunction structures with PI groups.

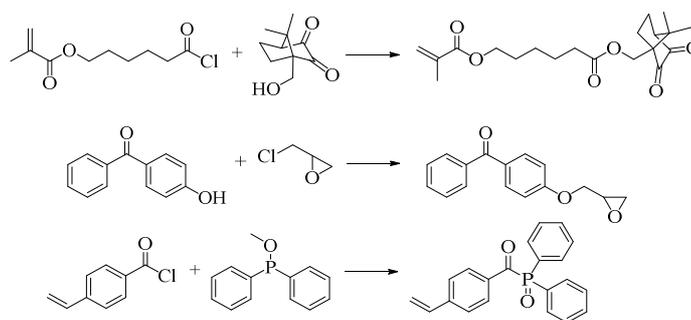


Scheme 9. LPPIs with additional properties: amphiphilic (a-c), self-floating (d) and matrix forming in liquid crystal (e).

4.2 Side-chain LPPIs

Moving the chromophores to the side-chain of polymers reduces the difficulty of preparing

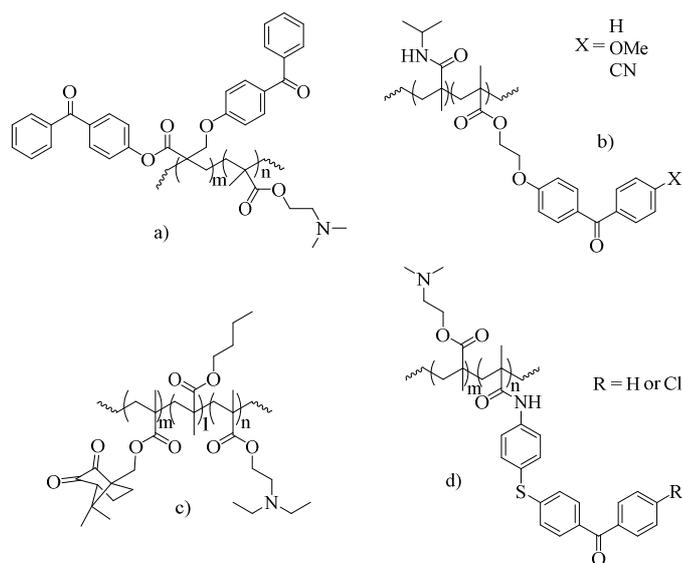
LPIs. Some reactive groups such as acrylate [62-63,70,104], styrene [84] and epoxy (M1) [27,71], can be grafted to varied low-molecular-weight PIs or photosensitive conjugated molecules leading to “polymerizable photoinitiators” (Scheme 10). By means of either thermal polymerization [105] or more advanced synthetic techniques such as ATRP [72], researchers can fabricate side-chain LPIs with ordinary backbones. Most of the work described in this chapter employed these methods. Nonetheless, modification of functionalized polymers is another facile and interesting route. Castelvetro *et al.* [85] performed phosphorylation of benzoic acid side-chain-functionalized polymer, to synthesize LPI with acyl phosphine oxide PI, on the side chain. Durmaz and co-workers [103] introduced phenyl pyridinium ions into poly(styrene-co-chloromethylstyrene) with AgSbF₆, followed by photo-induced grafting polymerization of MMA. The research groups of Arsu and Yagci grafted anthracene-thioxanthone [105] and BP [24] to the side chain of polystyrene via click reactions. Gomurashvili and Crivello [109] employed both homopolymerization of PI monomers and modification of polymer to prepare varied side-chain LPIs.



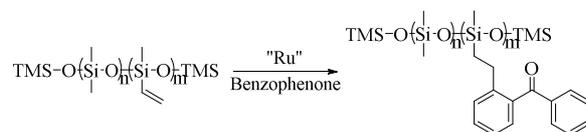
Scheme 10. Examples of “polymerizable photoinitiators”.

Since the structural feature of side-chain LPIs facilitates the synthesis of them, many research interests focus on the photochemical properties. Similar with the phenomenon described above, red shifts of the absorption were also observed in BP side-chain modified homopolymer

(from 252 nm to 289 and 294 nm) [35] and copolymer (from 267 nm to 289 nm) [32]. Cesur et al. [53] found that the BP based side-chain LPPIs they synthesized were particularly efficient compared to BP (Scheme 11a). Taking advantage of the laser flash photolysis (LFP) system, Allonas *et al.* [62] reported the excited-states properties and photoreactivity of PMMA with camphorquinone (CQ) in the side chain (Scheme 11c). Another series of PMMA based side-chain LPPIs bearing BP derivatives were found to have different quantum yields in different solvents in Encinas's group [23] (Scheme 11b). When Wang et al. [107] bonded phenyl sulfide to BP in the side-chain of a polymer and investigated its photoinitiation behavior, they found that the BP derivative, known as a typical hydrogen-abstracting chromophore (Type-II PI), underwent C-S bond cleavage as a photofragmenting chromophore (Type-I PI), and initiated polymerization in the absence of any hydrogen donor (Scheme 11d). Moreover, this LPPI can also perform hydrogen abstraction in the presence of hydrogen donor. A study of one-component thioxanthone-based side-chain LPPIs came more recently. Avci et al. [76] have employed both thioxanthone groups and hydrogen donors on the side-chain of polymer via copolymerization. The solubility and photoinitiating activity of the LPPIs have been characterized.

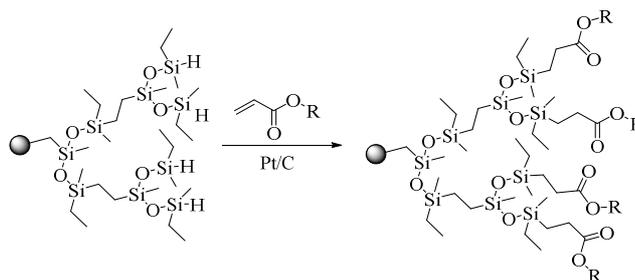


Scheme 11. Example LPPIs for which the kinetic of photoinitiation had been studied.



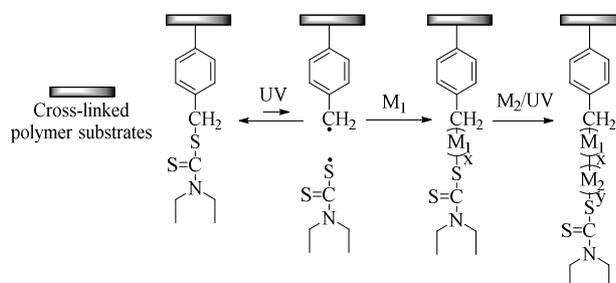
Scheme 12. Ru-catalyzed anti-Markovnikov addition of vinyl-substituted polysiloxane with benzophenone. [66], Copyright 2004. Reproduced with permission from John Wiley & Sons Inc.

Most applications of side-chain LPPIs are similar to the in-chain ones, among which the application in hydrophile system has been the popular aspect so far [74,84,102,104]. Seok et al. [18] also developed a side-chain LPPI for liquid crystal film. Nevertheless, there had been several particular applications, which make side-chain LPPIs worth being discussed independently. Mabry and Weber [66] synthesized benzophenone-modified and anthracene-modified polysiloxanes by using Ru-catalyzed addition of an ortho C-H bond of the two Type-II PIs across the C-C double bonds of vinyl-substituted siloxanes (Scheme 12). Those PI groups on the side-chain underwent crosslink reaction when heated to 300 °C. Lee et al. [112] reported a systematic investigation of a series of photoreducible side-chain LPPIs for use in polymerization-based amplifications (Scheme 13). They coupled neutravidin, a deglycosylated product of native avidin from egg whites, to the LPPIs by dehydration condensation between carboxyl side group and amino functional compounds. This was used to recognize biotin-labeled DNA immobilized on glass chip surface and found that the number of PIs on macroinitiator had a great effect on the signal strength. Buller et al. [30] prepared a set of photo-crosslinkable copolymers based on oligo(ethylene glycol) methacrylate bearing 2-(4-benzoylphenoxy)ethyl methacrylate as a photosensitive crosslinking unit. Subsequent UV irradiation of spin-coated films onto silicon substrates led to biocompatible polymer films with broadened swelling-deswelling transition without hysteresis, which indicates the potential application in the



Scheme 14. Illustration of the hydrosilylation of hyperbranched organosilane.

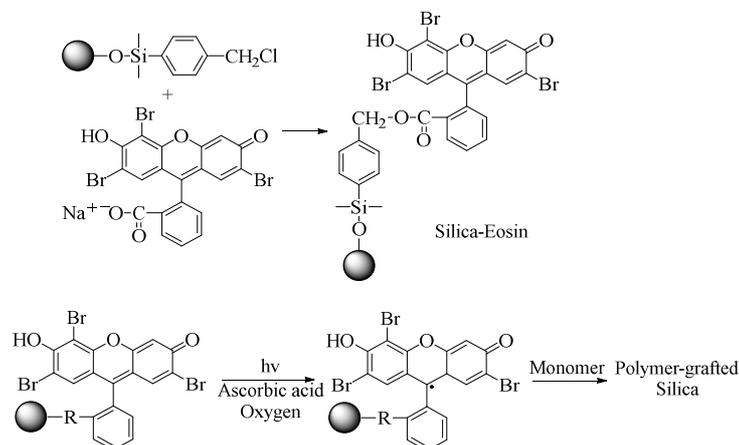
A red-shifted UV absorption in the HCPPI products was observed due to the introduction of alkyl. Xie et al. [40] designed an A_2B_3 monomer system for the synthesis of hyperbranched polymer, which contains hydrogen donor for the Type-II PIs located on the terminal groups. Moreover, a commercial hyperbranched polymer, which consists of hyperbranched polyester and polyether, was adopted by Shi and coworkers [38-39]. The UV-vis spectra of these research show an obvious red shift of π - π^* absorption from ~ 250 nm of BP to ~ 280 nm of PPI.



Scheme 15. Cross-linked polymer networks bearing dithiocarbamate photoiniferter. [67], Copyright 2002.

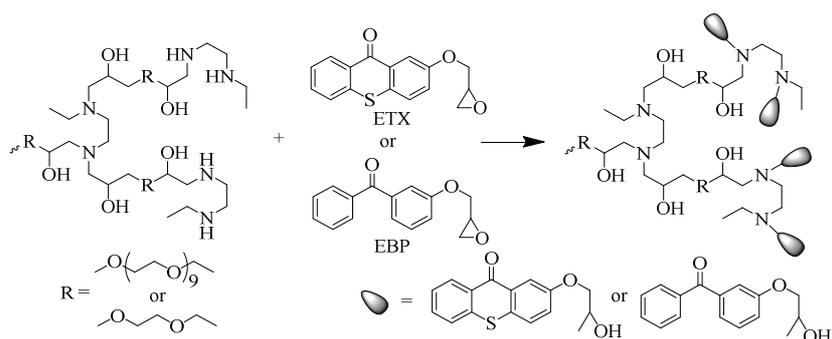
There are more choices for the core substrate to be grafted by the PIs. Luo et al. [67] synthesized a monomer photoiniferter bearing acrylate and dithiocarbamate. In the present of this monomer photoiniferter, a mixture of acrylate monomers was polymerized under UV irradiation to form polymer network, where the dormant species of the photoiniferter persisted (Scheme 15). Satoh et al. [110] reported another interesting instance. They immobilized eosin moieties on a

nanosized silica surface, followed by photografting of various vinyl monomers under visible light at room temperature in the presence of a reducing agent and oxygen (Scheme 16). The wettability of polymer-grafted silica surface, determined by the penetrating rate of water, was also discussed.



Scheme 16. Synthesis and photoinitiation of silica-eosin. [110], Copyright 2005. Reproduced with permission from John Wiley & Sons Inc.

Recently, hyperbranched poly(ether amine) has been used as novel backbone for one-component polymeric type II photoinitiators [78]. By introducing thioxanthone (TX) or benzophenone (BP) moieties into the periphery of the hyperbranched polymer comprising the hydrophilic PEO short chain and coinitiator amine moieties in the backbone (Scheme 17). Due to its flexible, amphiphilic and hyperbranched structure, the synthesized HPIs could be dissolved very well not only in many organic systems including acrylate monomers, but also in water with high solubility of 10 wt%.



Scheme 17. Synthesis of one-component water-soluble hyperbranched poly(ether amine) containing thioxanthone or benzophenone photoinitiators.

6. Multifunctional Photoinitiators (MFPIs)

Among the varied kinds of PIs with high molecular weight, multifunctional photoinitiators MFPIs, which have defined number of functional groups, have been the Cinderella of industry due to the difficulty of remaining structural homogeneous in mass production. In order to prepare MFPI with high degree of functionality, dendrimer has been utilized as the core moiety. Even though the methodology of synthesizing MFPIs is similar to those of synthesizing hyperbranched PPIs, the structural regularity and the countability of functionality of MFPIs make them distinctive.

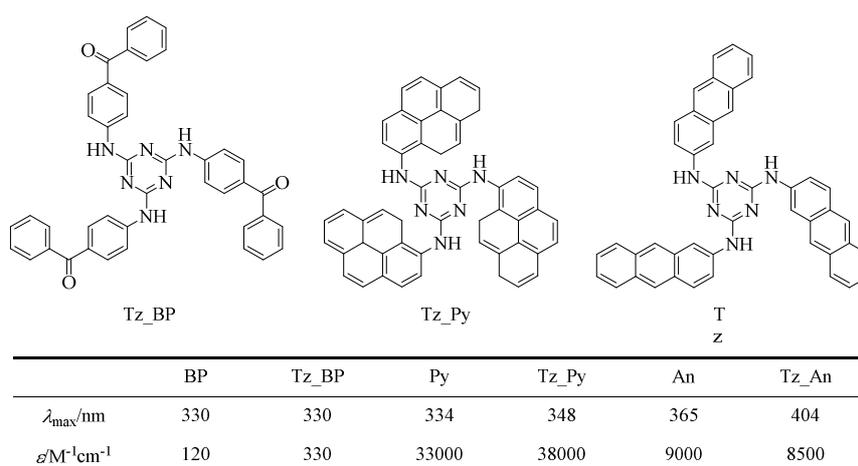
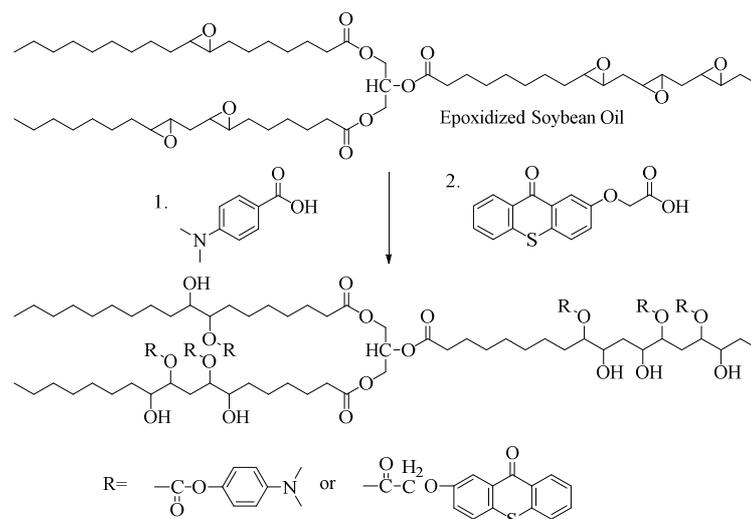


Figure 3. Trifunctional photoinitiators based on a triazine skeleton and their photochemical properties

compared with benzophenone (BP), pyrene (Py) and anthracene (An) respectively. [41], Copyright 2012. Reproduced with permission from the American Chemical Society.

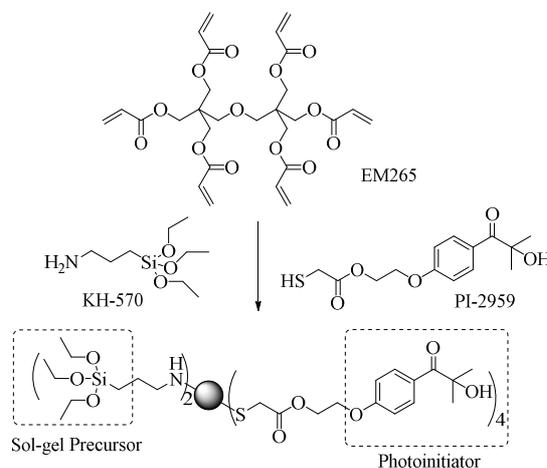
Simple molecular bis-/tri-functional PIs are, to an extent, expedients for industrial demand for low migration due to their synthetic facilitation. Ye et al. [54] prepared a novel difunctional PI, which can be regarded as two commercial PIs 2-hydroxy-2-methyl-1-phenyl-propanone (HMPP) strapped by an ether group. The synthesis process they employed was Friedel-Crafts acylation between phenyl and acyl chloride, which was similar to the manufacturing of HMPP but engendering a difunctional product. Allonas and coworkers [55] studied more bis-functional HMPP-based PIs with different linking bond, and investigated their excited-state processes. Difunctional compounds such as toluene-2,4-diisocyanate (TDI) [42] and acryl chlorides [43] were also adopted as the coupling agents of PIs. Tehfe et al. [41] synthesized three tri-functional Type-II PIs, which had large conjugate structures (Figure 3). Their light absorption properties were significantly improved by the strong molecular orbital coupling. Different light sources have been employed, such as Xe-Hg lamp (UV-visible light), halogen lamp (mostly visible light) and LED lamp (365 nm), to investigate their photoinitiation behavior. Luo et al. [83] presented a “green” idea that epoxidized soybean oil could be used as the promising intermediate for preparing MFPIs (Scheme 18).



Scheme 18. Illustration of the grafting of epoxidized soybean oil with type-II photoinitiators and coiniciators. [83], Copyright 2012. Reproduced with permission from 'Elsevier Science Ltd.

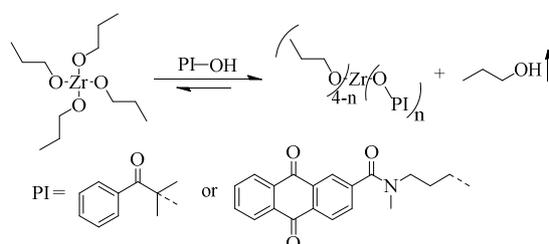
As the functionality increases, the PIs in this family become more and more alike to dendritic polymer. Grafting PIs to an existing dendrimer have been a favored technique to some researchers [21]. Jiang and coworkers had been working on introducing thioxanthenes to dendrimer poly(propylene imine)s, the products from which had interesting properties, containing hydrogen donors [79-80] and being water-compatible [81]. Kaastrup and Sikes [111] chose poly(amidoamine) dendrimers functionalized with eosins as MFPIs applied for photopolymerization-based signal amplifiers. Nevertheless, the candidates of so-called “scaffolds” in MFPIs are not restricted to dendritic polymers. Hu and Shi [56] employed a hexafunctional acrylic compound “EM265” as the core of a new MFPI. After modification of a commercial PI (2-hydroxy-1-[4-(2-hydroxyethoxy) phenyl]-2-methyl propan-1-one) and the subsequent addition reactions, the MFPI containing both acetophenones and ethoxysilanes had been prepared, which could also be used as a sol-gel precursor (Scheme 19). Cyclodextrin has attracted strong interests of researchers for its application in food, pharmaceutical, chemical and agricultural industry. As a multifunctional compound with distinctive structure, cyclodextrin can be

chemically attached to PIs, according to Balta et al. [82] They also investigated its photoinitiated properties in aqueous medium.



Scheme 19. Illustration of a multifunctional photoinitiator with sol-gel precursors.

Due to the synthesis difficulty and structural variety of HCPPIs and MFPIs, most of the research only demonstrated the ability of photoinitiation in common formulation under certain conditions. Nevertheless, more details on the properties of HCPPIs and MFPIs are required. In the report from Chen *et al.* [36], the extractability of the hyperbranched polyglycerol PPIs in UV-cured samples had been evaluated by HPLC. After the extraction of acetonitrile/H₂O solution of the samples with ultrasonic bath, the content of the residual BP and the coinitiator in the HCPPI samples were found much less than the samples with low-molecular-weight correspondent PI system.



Scheme 20. Synthesis of type I and type II MFPIs via ligand substitution of organozirconium.

Recently, a novel synthesis route for coupling photoinitiator groups to one MFPI was discovered by Zhou et al. The ligand groups on the organozirconiums can be substituted by other analogues under a mild condition, which can be a conventional PI [22] or its derivatives [44]. This kind of MFPIs can have good performance in migration and overcoming oxygen inhibition, while their photoinitiation activities have few advantages comparing to their low-molecular-weight analogues (Scheme 20).

7. Migration testing for measuring UV photoinitiators

In order to assess the migration potential of UV inks and coatings on food packaging prints, appropriate analytical methods are necessary in the packaging industry. Several groups of scientists have published their analytical methods for detecting UV-curable monomers and by-products with the migration potential into foods, since the late 1990s. Most of the studies reports migration tests on low molecular weight PIs. However, it is interesting to discuss the methodology and results reported in the literature as this could be easily adapted to PPIs or MFPIs.

As known, UV-curing formulations are complex mixtures and PIs are a very heterogeneous group of molecules with very diverse physicochemical properties, so analytical procedures need to be modified as a function of the molecule or group investigated. Moreover, different side-products can be generated by photocuring reactions under irradiation making the analysis even more complex.

An analytical method for detecting BP in carton board was extensively investigated by Anderson *et al* [116]. They developed GC-MS method using BP-*d*₁₀ as an internal standard to quantify BP, which might migrate from carton-board into foods. The limit of detection (LOD) was 0.01 mg/kg and the limit of quantification (LOQ) was 0.05 mg/kg. BP was detected in the

carton board samples (0.01-7.3 mg/kg) and the food samples (0.01-5.7 mg/kg). In addition, they calculated the mass fraction of BP migration for different temperatures (room temperature and chilled/frozen temperature) and different contacts (direct and indirect contact). They revealed interesting reduction effects of low temperature and indirect contact. They found that there was a six-fold reduction in migration for indirect contact compared with direct contact and a six-fold reduction for chilled/frozen storage compared with ambient storage and 40-fold reduction for the two contact conditions (indirect contact and chilled/frozen storage) combined. Based on these results, the authors concluded that 1–2 % of the BP in the packaging migrated to the food. For foods where the BP levels were below the specific migration limit of 0.6 mg/kg, levels in the corresponding packaging ranged from 5 to 7 mg/kg [116,117]. Other studies have investigated levels of BP in the packaging of a variety of food products [118-121].

Emission of volatile organic compounds (VOCs) during UV curing processes and from UV-cured products would be of special concern in terms of indoor pollution. Salthammer *et al.* [122], investigated the VOCs produced during the photochemical process, for instance photoinitiators, their by-products and monomers, with a specially designed chamber including UV lamps and a purge-and-trap system. The collected VOCs were analyzed by GC-MS. The major VOCs found in their UV-curing processes were benzaldehyde, cyclohexanone and benzophenone. Unpolymerized acrylate monomers, TPGDA and HDDA were also detected from the chamber. It is worth noting that the odor issue was not scientifically addressed in the studies related to PPIs or MFPIs.

Johns *et al* [10], investigated migration of impregnated BP from carton board to foods during frozen storage (-20 °C) and then microwave heating using solvent extraction followed by GC-MS. BP was detected in some carton board samples suggesting the use of UV-cured inks with BP as the main PI. In addition to the BP migration study, migration of model ink

components, which were impregnated in cardboards, was investigated. Among the model components, using more volatile substances showed higher migration rate than using fewer volatile substances. However, microwave heating of the food lowered migration levels of more volatile substances because of volatilization. Their study suggests that if the concentrations of low molecular weight volatiles are controlled by proper UV-curing process and if physical transfer of high molecular weight components via reverse side transfer phenomenon is taken care of, migration levels of printing ink components would be kept low in the frozen storage condition.

Castle *et al.* [123] investigated the migration of residues of dialkylamino benzophenone including Michler ketone (MK), 4,4' bis (dimethylamino) benzophenone, its analog, 4,4' bis (diethylamino) benzophenone (DEAB), and the monoamino form of MK, 4-(dimethylamino) benzophenone (DMAB), from paper and board food packaging materials. MK is not recommended for use in printing inks intended for carton board food packaging in the UK because MK is a potential carcinogen. However, in some other countries, MK is still being used. Their study was designed to assess the potential migration of MK, DEAB and DMAB in imported materials for food packaging. The samples, mainly printed carton boards, were extracted with ethanol, followed by the analysis of the extracts with HPLC and GC-MS. MK, DEAB and DMAB were detected from paper and board food contact materials. Also, MK was detected in imprinted materials. Their results suggest that the origin of the residues is from the use of recycled fibers. In addition, they analyzed some samples in which the highest concentration of MK was detected, but no measurable migration of MK at less than 2.0 pg/kg food was found.

In the literature, liquid chromatography (LC) and GC are the most commonly used techniques to analyze food and/or food contact materials. High-performance LC (HPLC)-based

methods found in the literature have been summarized [6]. LC is the most elected technique due to the low volatility of PIs: when coupled to a diode array detector and/or fluorescence detection, it is the most extensively used for quantification purposes; when coupled to mass spectrometry, it can be used for confirmatory purposes or both identification and confirmation. However, LC-MS and LC-MS/MS are now commonly used to detect various substances. GC is very common for determining semi-volatile PIs such as BP and derivatives. Moreover, different detectors can be used, among which the MS detector is the most common [124].

8. Perspectives and outlook

UV-curing techniques play an important role because of their potential to facilitate environmental benign materials fabrication. A large amount of work has been done on the synthesis of low migration PIs as mentioned in this review, most of which was achieved in laboratory but not facile in industry. Among those methodologies and structures of low migration PIs, polymerizable photoinitiators can be the candidate to fulfill the expectations of low migration, facile synthesis and industrial applicability. With a slight modification on the formulation or the process, for instance, those polymerizable PIs mentioned in Scheme 10 can be used as both the PI and one of the monomers in UV-curing formulation. And the photochemistry products of them can be immobilized in the cured network, resulting in minimum migration. Furthermore, this immobility also works for leftover PI groups and most of the by-product fragments. Some intermediates of LPPIs described in previous chapters can be used to testify the immobility in cured product, since their efficiency of photoinitiation had been confirmed. One challenge that can be expected in molecular design is the reactivity of the monomer groups in polymerizable PIs, which is the critical factor in “fastening” PI groups (and their photochemistry products) in the cured network. Apart from employing monomer groups with high reactivity

ratios to in the preparation of PIs, modifying the PIs with functional groups that reactive to acrylate, such as amino or thiol, can be logical methods to prepare polymerizable PIs.

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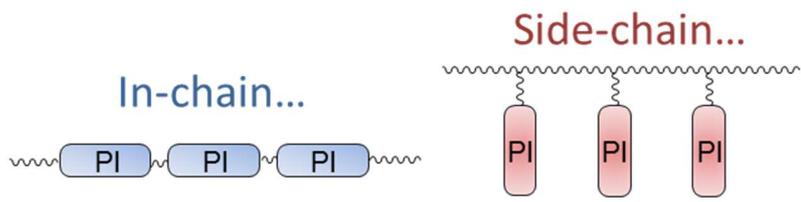
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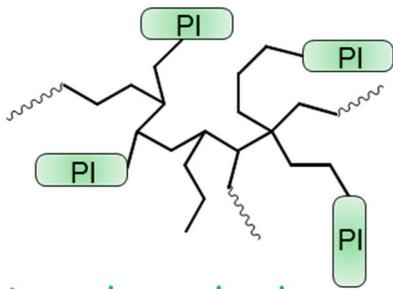
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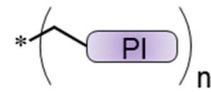
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... polymeric photoinitiators



Multifunctional...



Hyperbranched or cross-linked...