



Photo-polymerization

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Abstract

The synthesis of functional polymers by photopolymerization thrives on the rich tradition of industrial photochemistry. Photo-induced polymerization can be broadly divided based on the initiation mechanism as radical, cationic, and anionic photopolymerization. A wide variety of initiators, photosensitizers, and polymerizable materials have been studied for various applications. This chapter is intended to be a primer to major concepts of photopolymerization. In the beginning of the chapter, physical aspects of light matter interactions are

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presented followed by photochemical pathways leading to reactions. In the subsequent sections radical polymerization is discussed by introducing different types of initiating systems and polymerizable materials. Within the section on radical polymerization, visible light polymerization and thio-ene photochemistry are also discussed. The section on thiol-ene looks at the fundamentals of thiol-ene reactions, their initiation, reactivity, and advantages over other radical driven polymerizations. Cationic polymerization is covered based on the material science of ionic and nonionic photoacid generators (PAGs). This section also discusses spectral broadening of reactivity in PAGs to visible wavelengths through electron transfer sensitization and free radical promoted cationic polymerization (FRPCP). Unlike radical and cationic polymerization there are little or no reports of commercial application of anionic polymerization. However, due to typical monomers employed in anionic polymerization and the control over the extent of polymerization afforded by this techniques makes it very attractive for functional applications. The section on anionic polymerization summarizes recent developments in this field. Finally in the section about two-photon initiated polymerization, we discuss the scope of nonlinear optical phenomena in photopolymerization.

1 Introduction

Photopolymerization became popular due to the wide-spread application of ultraviolet radiation for cross-linking of photoactive materials in various industries. Any polymeric species capable of undergoing a chemical change when exposed to light can be termed a photopolymer. Photopolymers started out as materials used in packaging and encapsulation of goods and printing technologies. Their early application in the industry was largely driven by the possibility of formulating photoactive materials that reduced the use of solvent while allowing for a remote triggering of chemical phenomena through irradiation. The subsequent growth of microelectronic industry with its demand for progressive miniaturization of components has led to the increased importance of photopolymers. In fact, the progression of microelectronics predicted by Moore's law would be hardly possible without negative photoresists. This was achieved due to the progress in the development, synthesis, and understanding of the chemistry of photopolymers and the resultant rational design. This has been the case with photopolymers applied to many different fields of activity. Need for efficiency and cost effectiveness has driven the development of the field in various directions.

Depending on how they chemically respond to light, photoresponsive polymers or their precursors can be divided into five classes [1]. The first class constitutes multifunctional monomers or oligomers containing functional groups that undergo radical, cationic, or anionic chain growth polymerization in the presence of a suitable photoinitiator (PI) leading to photo-crosslinked polymer networks (see Fig. 1a). When irradiated with a suitable wavelength, the PI initiates the polymerization reaction, leading to the addition of monomer or oligomers to form polymeric

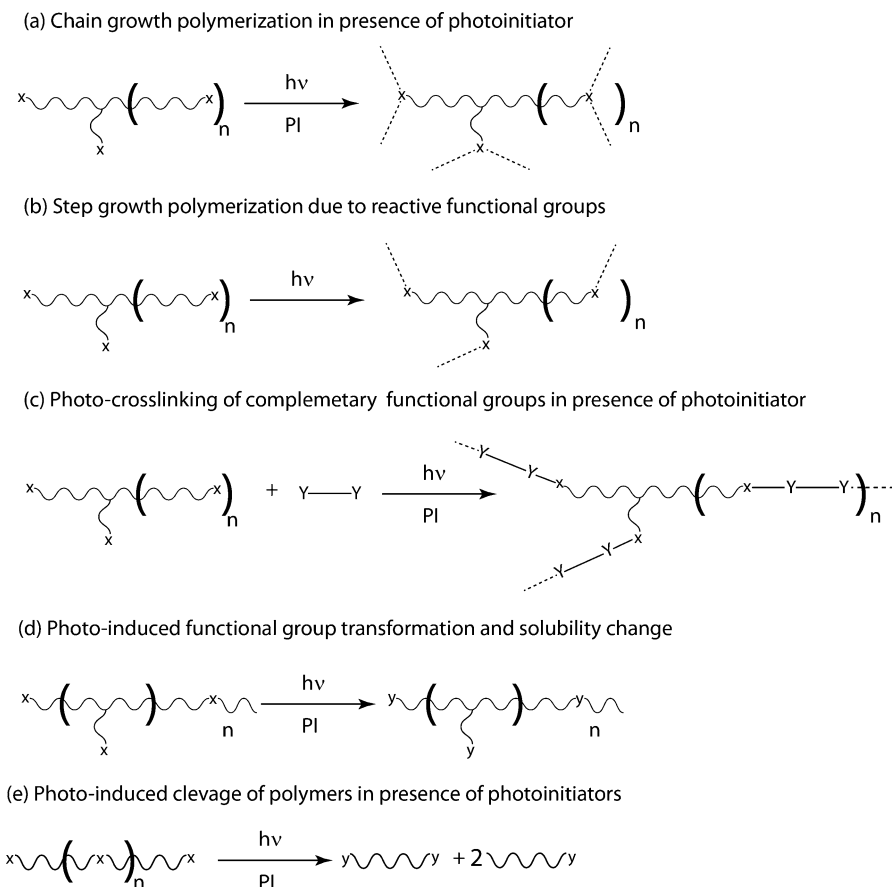


Fig. 1 Five different classes of photopolymers. (Reproduced from Ref. [1])

molecules. The second class of photopolymers consists of oligomers/monomers with integrated photoactive groups capable of initiating polymerization when irradiated with light (see Fig. 1b). In the second class of photopolymeric materials, there is no requirement of a PI. They typically undergo step growth polymerization where polymeric groups are added step by step (e.g., dimer then trimer then tetramer so on). The third class of photopolymer precursors involves component materials with complementary functional groups on them that interact with each other under irradiation in the presence of a suitable PI (see Fig. 1c). The fourth category involves photopolymers with functional groups which, in the presence of a suitable mediator (PI) and light, transform to another functional group with a difference in solubility (see Fig. 1d). The fifth class of photopolymer also undergoes a solubility change due to the photo-induced degradation of polymeric materials (see Fig. 1e).

This chapter deals with photopolymerization and materials for photopolymerization which can be included in categories (a–c) in Fig. 1.

Photopolymerization reactions are normally achieved by combining a number of different materials playing specific roles during polymerization. The combinations are often referred to as photopolymerizable formulations or just formulations. Formulations used for imaging applications are often referred to as photoresists. The most abundant component of a photoresist is a monomer or an oligomer with chemical functionalities capable of undergoing photoinduced chemical change. Different photopolymerization reactions are restricted to certain types of monomers/oligomers. For example, olefins and acrylic monomers/oligomers figure prominently in the materials for radical polymerization, while epoxides and vinyl ethers figure in cationic polymerization. The absorption of light and the initiation of the chemical reaction are mediated by a photoinitiator (PI).

Often another component called photosensitizer (PS) is present in the formulation. The photosensitizer is a molecule that is highly sensitive to light and plays a part in assisting the initiation of the photopolymerization. The PS has a higher sensitivity to a relevant wavelength and would serve to efficiently initiate the reaction in combination with the PI. The photoexcited PS molecule interacts with PI through energy or the electron transfer interaction. Apart from these components, photosensitive systems might contain inhibitor molecules aimed at nullifying the effects of spontaneous degradation of the high-energy bonds in initiators over time during their shelf life. For commercial applications, additional components meant to shape the physical properties of the photopolymerizable medium, such as viscosity, color, wetting, gloss, and matting, are also added to photosensitive systems.

A crucial factor governing the photopolymerization reaction is the choice of the light source. A wide range of optical sources like lamps, lasers, and sun light have been put to use depending on the requirement of the application. Recently, there have been numerous attempts to use sunlight to trigger polymerization, minimizing thus the cost of fabrication. Source like the Xe lamp and sunlight are broad spectrum sources that contain multiple wavelengths. Required wavelength can be filtered out of these sources by using filters. UV producing mercury lamps also converts a high amount of energy it takes up to heat. Mercury lamp emits at specific wavelengths. Doped mercury lamps emit in a range of wavelengths. Microwave lamp, excimer lamp, both continuous and pulsed laser sources are some other examples of the light sources used [2].

In the following chapter, we will discuss photopolymerization based on its modes of initiation. An exhaustive coverage of this broad topic is beyond the scope of the present chapter. Instead, we will focus on initiating the reader to the nuances of the field by providing insights into major developments. In the beginning, we provide a brief physical description of the light-matter interaction; the subsequent sections discuss various types of polymerization from the material perspective.

1.1 A Physical View of Photoexcitation

Photoinitiators and photosensitizers feature polar high-energy bonds between carbon and heteroatoms or metals. Polar bonds have a greater interaction with

electromagnetic radiation due to their strong interactions with the electrical field of light. When the intensity of radiation increases, the materials give rise to new phenomena which can be termed nonlinear optical (NLO) phenomena [3]. In essence, all optical processes are nonlinear, but they become relevant observables only when subjected to an intense radiation. The electric component of the electromagnetic wave is capable of attracting or deflecting the electronic cloud in a molecule, the resultant polarization in the molecule shows a linear behavior at lower intensities. However, in the presence of intense radiations, the polarization of the molecule shows a nonlinear response to light. The polarization (P) or the induced dipole moment (μ_i) of a molecule interacting with radiation can be written as follows (see Eq. 1):

$$P_i = \mu_i = \alpha_{ij}E_j \quad (1)$$

where α_{ij} is the linear polarizability tensor and E_j is the electric field associated with the electromagnetic radiation. The induced dipole moment of a molecule interacting with high intensity radiation can be written as follows (see Eq. 2):

$$\mu_i(E) = \mu_0 + \alpha_{ij}E_j + \frac{\beta_{ijk}}{2}E_jE_k + \frac{\gamma_{ijkl}}{8}E_jE_kE_l \dots \quad (2)$$

where μ_0 is the inherent polarizability of the molecule, α_{ij} is the linear polarizability of the molecule β_{ijk} , and γ_{ijkl} refers to the first and second hyperpolarizabilities. The terms E_i , E_j and E_k describe the electric field components of light. The first two terms explain the single-photon absorption of the molecule, while β_{ijk} and γ_{ijkl} describe the NLO interactions of the molecule with light in the microscopic scale.

For a bulk of molecules, the polarization can be written using Eqs. 3 and 4.

$$P = P_0 + P_i(E) \quad (3)$$

$$P_i(E) = \chi_{ij}^{(1)}E_j + \chi_{ijk}^{(2)}E_jE_k + \chi_{ijkl}^{(3)}E_jE_kE_l \dots \quad (4)$$

In Eq. 3, P_0 is the inherent polarization of a molecule and $P_i(E)$ the induced polarization where $\chi^{(n)}E$ is the nonlinear susceptibility tensor of $(n + 1)^{\text{th}}$ order. The first term in Eq. 4 describes the linear polarizability of the molecule. The terms $\chi_{ijk}^{(2)}$ and $\chi_{ijkl}^{(3)}$ are the bulk analogues of β_{ijk} and γ_{ijkl} , respectively, and are called first and second hyperpolarizability. A number of optical effects arise out of both the first and second hyperpolarizabilities, such as sum and difference-frequency generation, second-harmonic generation, direct four-wave mixing, optical rectification, parametric amplification, self-phase modulation, Kerr lensing, four-wave mixing, two-photon absorption, etc. [4]. In this chapter, we mainly discuss photochemical and photopolymerization triggered by the one-photon absorption (OPA) and two-photon absorption (TPA) excitation of molecules.

The range of wavelengths between 10 nm and 400 nm are defined as ultraviolet (UV) region of the spectrum. Almost all materials including air absorbs UV wavelengths between 10 and 180 nm making it difficult to work with it in the absence of a

vacuum, this range of wavelengths is called far UV region. Wavelengths between 180 and 280 nm constitute the middle-UV region, and those in the range 300–400 nm constitute the near UV region. The range of wavelengths between 200 and 400 nm has been most commonly used in photopolymerization reactions. The energy corresponding to this range of wavelengths can initiate electronic transition in a wide range of materials and cause bond rupture in organic molecules. For a given molecule, the scope of photophysical processes occurring on irradiation is defined by its frontier molecular orbitals, the absorbed wavelength, and the intensity of the light source. All potential photophysical processes during the evolution of a photoexcited molecule are summarized in Fig. 2. Common organic molecules feature σ -bonding molecular orbitals, σ^* antibonding molecular orbitals, π -bonding molecular orbitals, π^* antibonding molecular orbitals, and nonbonding orbitals (n). The transitions between these molecular orbitals (MOs) are subject to conditions of energy difference, symmetry, and occupancy of MOs. The most commonly encountered transitions in organic photoinitiators are $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions are localized transitions associated with active bonds in the molecule.

Another set of transitions called charge transfer (CT) transitions are found in the molecules containing extensive conjugation and strong donor and acceptor substitutions. In the CT transitions, the excitation energy is delocalized throughout the molecule. The NLO phenomena are particularly strong in the molecules with strong CT states. The simplest photochemical process in a molecule happens when it absorbs ultraviolet radiation, resulting in the excitation of an electron in its singlet ground state (S_0) to the first singlet excited state (S_1). Photoexcitation is a fast process that occurs at the timescale centering around 10^{-15} s. Alternatively, the absorption of two near IR photons can lead to a singlet excited state. The OPA- and TPA-excited singlet states may or may not be the same, depending on the symmetry of the molecule. They coincide in non-centrosymmetric molecules and differ in symmetric ones. The excited singlet state can follow any of the different paths outlined in Fig. 2, depending on the molecular orbitals and the source of radiation. In the presence of a high intensity laser or non-laser light sources, the excited electron can be further excited to a higher singlet state due to the phenomenon termed excited-state absorption (ESA). The probability of the ESA phenomenon depends on the intensity the light source.

Photoexcitation of a molecule results in the formation of chemically reactive species due to the redistribution of electronic cloud within the molecule. The heavy atoms in the molecule hold their positions (Franck-Condon principle), while the electronic cloud undergoes redistribution. The Franck-Condon principle restricts the inversion of the electronic spin during excitation due to the rules of quantum mechanics. Due to these restrictions, the initial geometry of the excited molecule is not the one that corresponds to an energy minimum (read stable). If an excited state is not immediately quenched after excitation, it undergoes vibrational relaxation to achieve energetically stable geometries, leading to the formation of triplet states [5]. The triplet excited states are more reactive than singlet excited states and lead to

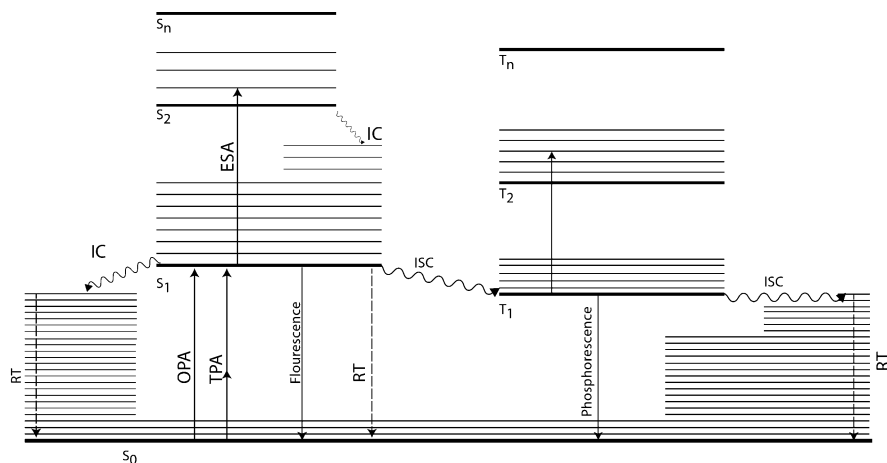


Fig. 2 The fate of the photophysical properties associated with an excited molecule is summarized in the Jablonski's diagram. S_n stands for the n^{th} singlet energy level of the molecules, T_n stands for the n^{th} triplet energy level of the molecule. *OPA* one-photon absorption, *TPA* two-photon absorption, *ESA* excited-state absorption, *ISC* inter system crossing, *IC* internal conversion, *RT* radiationless transfer of electrons

the products that are otherwise inaccessible [6]. Photoexcitation of PI can lead to the following eventualities.

- (i) The excited molecules undergo vibronic relaxation to reach a stable geometry, followed by a release of energy into solvent.
- (ii) The excited electron can undergo intersystem crossing to give a triplet state which further undergoes vibrational relaxation to reach an energy minimum.
- (iii) The emission of energy from the singlet or the triplet excited state, leading to luminescence, fluorescence, or phosphorescence.
- (iv) The excited molecule can undergo excitation quenching through interaction with other molecules; further, the molecule can return to ground state through radiationless thermal or vibrational processes.
- (v) Singlet and triplet excited molecular states can herald photochemical reactions.

Thermally driven reactions go through the singlet excited state. The probability of intersystem crossing and triplet formation in photochemical reactions lead to the formation of the products that are otherwise inaccessible. The use of photoexcitation for driving the reaction also leads to energy-rich excited states. Frequently, such excited states also feature electrons occupying nonbonding molecular orbitals. A photoexcited molecule is susceptible to three different primary photochemical pathways (see Fig. 3a). The first pathway involves the formation of a chemically reactive intermediate (RI) which then leads to the product. The second photochemical pathway leads to the formation of a funnel intermediate by the excited molecule, the funnel intermediate then leads to a product. IUPAC defines a photochemical funnel intermediate as a molecular

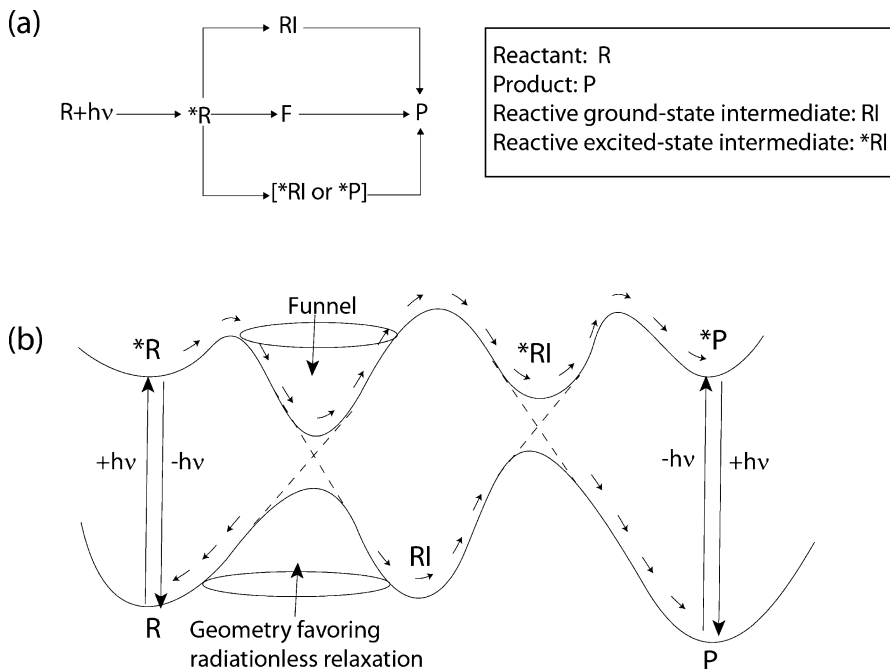


Fig. 3 (a) The photochemical pathways taken by the photoexcited molecule. (b) Potential energy surfaces of a photoreaction from photoexcitation to the formation of the product [8]

structure by means of which the excited-state reactant or intermediate is delivered to the ground state to initiate product formation [7].

The term funnel intermediate itself comes from the local shape of the potential energy surfaces of the ground and excited states (see Fig. 3b) [8]. For many organic reactions, the structure of the funnel can take the form of a conical intersection or a singlet-triplet crossing. The third pathway involves the formation of an excited intermediate state RI^* or an excited state product P^* that eventually gives rise to the product.

Most photoinitiators work through the primary photochemical pathway which progresses through the formation of a reactive intermediate, RI. The RIs formed can include radicals, biradicals, or zwitter ions that then directly or indirectly play a part in the initiation of the polymerization reactions. The role of photosensitizer is primarily that of a mediator in the photoinitiation process. The energy or electron transfer between the photosensitizer and the photoinitiator depends on their frontier molecular orbitals. The LUMO level of the sensitizer should be above the HOMO level of the initiator; when the energy difference is larger, the probability of energy transfer increases. Apart from this, the phase of the polymerizing medium governs the interaction between the photosensitizer and the photoinitiator. In samples permitting flow of materials, diffusion plays a key role in the dynamics and fate of the excited photosensitizer. The transfer of energy between the sensitizer and the initiator could take place through a coulombic interaction or by swapping of a high-energy electron [8].

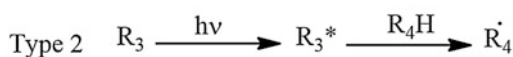
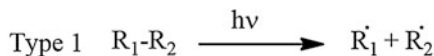
2 Radical Photopolymerization

Radical photopolymerization reactions are initiated by the generation of a free radical (R^\bullet) by a photoexcited photoinitiator (see Fig. 4). The generation of R^\bullet may proceed through the unimolecular process (Type 1) or the bimolecular process (Type 2). The first photochemical pathway outlined in Fig. 3b is responsible for the generation of the free radical. During its course, radical polymerization proceeds through different distinctive steps (see Fig. 4). During the propagation step, the free radical reacts with the monomer/oligomer to give rise to a radical bearing monomer or oligomer (RM^\bullet) called a macroradical. The macroradical then proceeds to grow by addition to more monomers. The reaction proceeds through the propagation step and eventually terminates through coupling or disproportionation reactions.

The presence of inhibitors, such as dissolved oxygen or other added components capable of consuming the radicals in the polymerizing medium, has a detrimental effect on the initiation process. Reactive species formed during initiation react with inhibitors, leading to a period of almost no polymerization reaction at the beginning (see Fig. 5). This phase of the reaction is termed the induction phase. Upon the total consumption of the inhibitors through reactions, the initiating species react with

Fig. 4 Different stages of free radical polymerization

Generation of initiating species



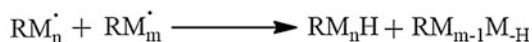
Initiation



Propagation

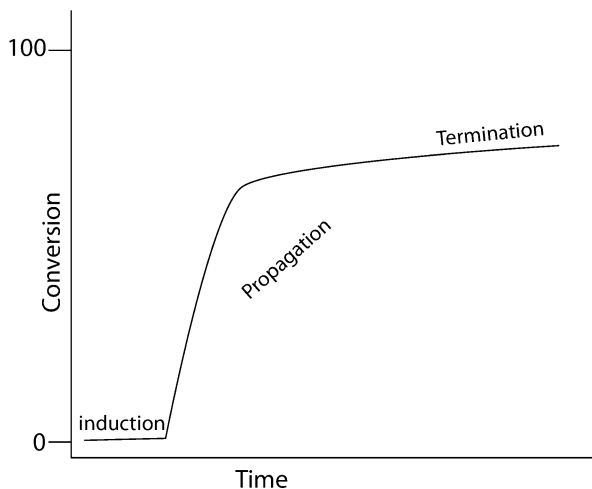


Termination



R^\bullet : Radical
 M : Monomer
 RM^\bullet : Macro Initiator

Fig. 5 Conversion of monomer versus time during photopolymerization



monomer forming a macroradical. The diffusion of the macroradicals throughout the medium leads to a rapid increase in the rate of polymerization until it reaches a maximum.

The development of polymerization is associated with a change in viscosity and refractive index of the polymerizable medium. Viscosity of the polymerizing medium progressively increases to the point where monomers are trapped between growing polymer chains. At this point, the polymerization reaction is terminated by the limited diffusion of the monomer. Due to this, photopolymerization reactions never run to 100% conversion of monomer. A graphical representation of the progression of photopolymerization can be seen in Fig. 5. The induction period is the relatively flat part at the initiation region.

2.1 Photoinitiators

Photoinitiation occurs when the absorption of photon leads to the generation of a free radical. This process is governed by the stability of the photoexcited state, as well as by the energy of the bonds within the excited molecule. As mentioned above, free radical photoinitiators can be classified into two types, based on the number of molecular species involved in the process. Type I photoinitiators constitute a unimolecular process accompanied by a rapid bond cleavage upon the absorption of light. Type II photoinitiators involve more than one molecule. A simple Type II photoinitiator consists of a bimolecular system involving an initiator and a co-initiator. The initiator is first excited into a long-lived triplet state, followed by an electron-transfer or a hydrogen-abstraction reaction with a co-initiator.

Type I photoinitiators are prominently benzoyl compounds; they undergo C–C cleavage at α , β , or γ positions on photoexcitation. The dissociation energy of the C–C bond next to the benzoyl is less than the energy of excitation of the molecule.

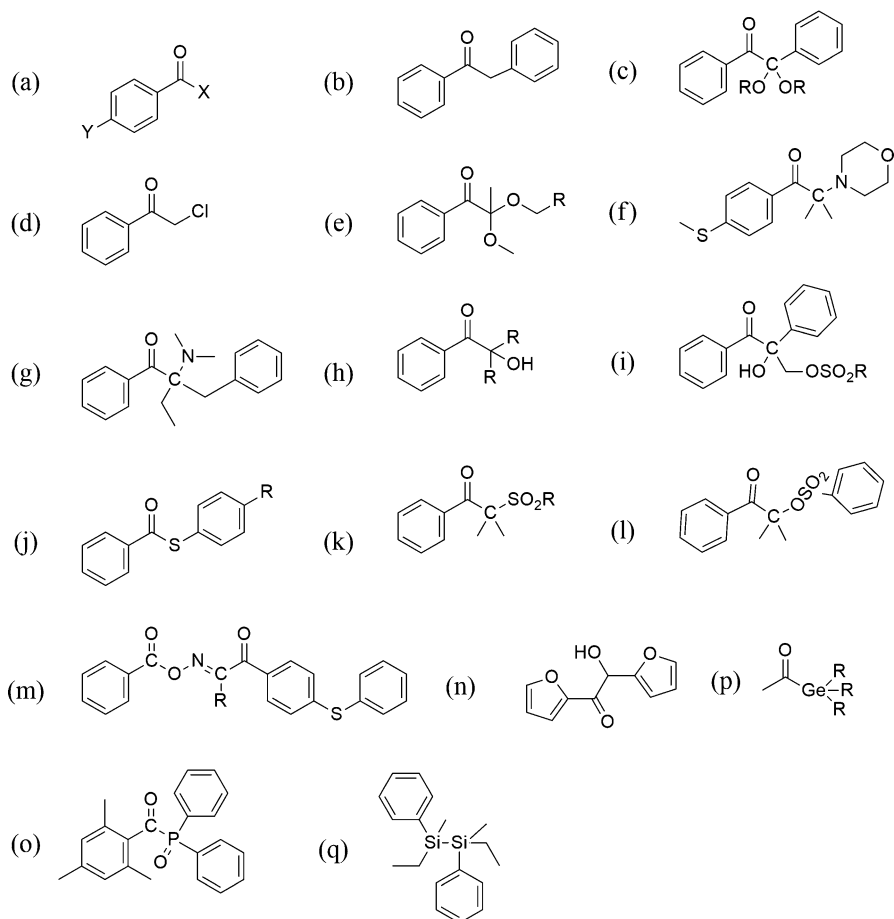
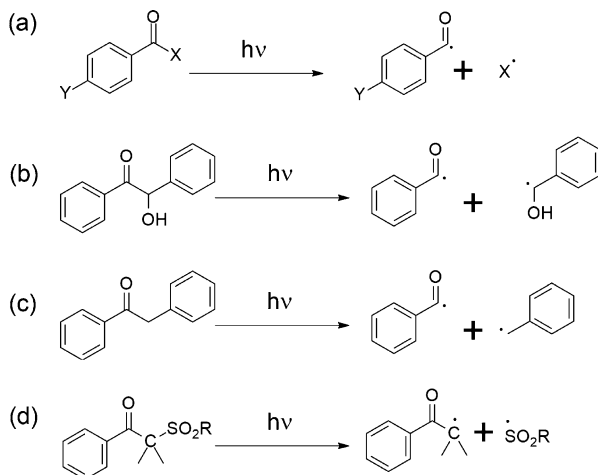


Fig. 6 (a) A model Type I photoinitiator followed by different typical examples; (b) benzoin derivatives; (c) benzoin ether derivatives; (d) halogenated ketones; (e) dialkylacetophenone; (f) morpholinoketone; (g) aminoketone; (h) hydroxyalkylacetophenones; (i) ketone sulfonic ester; (j) thiobenzoate derivatives; (k) sulfonylketone; (l) oxosulfonylketone (m) oxime ester; (n) furan hydroxyl alkyl ketone derivative; (o) organometallic ketone; (p) 2,4,6-trimethylbenzoyl diphenylphosphine oxide; (q) organosilanes

The carbonyl chromophore constitute three important molecular orbitals, namely n (nonbonding orbital on oxygen), π (bonding), and π^* (anti-bonding) molecular orbitals on carbonyl double bond. The $\pi \rightarrow \pi^*$ is a high-energy allowed transition and $n \rightarrow \pi^*$ transition is a low-energy forbidden transition. Both these transitions can give rise to singlet and triplet states on excitation. A model Type I radical photoinitiator is shown in Fig. 6a. The substituted groups X and Y influence the optical properties of the benzoyl compounds through electronic interactions, such as electronegativity, +I or -I effects, and delocalization. Some examples of Type I photoinitiators are shown in Fig. 6.

Fig. 7 Photocleavage of type I radical photoinitiator (a) model compound undergoing cleavage at α -carbon; (b–c) benzoin derivatives undergoing photoexcited α -cleavage; (d) sulfonyl ketone derivative undergoing β -cleavage on photoexcitation



The photoinduced cleavage of a model type 1 PI molecule can be seen in Fig. 7a. The rest of Fig. 7 shows the generation of radicals in two benzoin derivatives. The cases in Fig. 7a–c demonstrate cleavage at α -carbon. However, certain type 1 initiators, like sulfonyl ketones, sulfonyloxy ketones, thiosulfonyl ketones, and oxime esters, undergo cleavage at β -carbon upon photoexcitation (see Fig. 7d) [9–11]. The benzoyl radicals in type I photoinitiators are generated by the cleavage of σ bond oriented orthogonally to the π -orbitals of the aromatic group [2]. The substitution on the aromatic ring has little or no effect on the reactivity of the benzoyl radical. Radicals centered on carbon add at a high rate to monomers like acrylate. The nucleophilicity of the radical influences its addition to monomers. In the case of an alkyl radical, the tertiary carbon exhibits the highest nucleophilicity, followed by secondary carbon and primary carbon. Alkyl radicals with -OH substitution are more nucleophilic and would show a greater addition to electron deficient monomers like methacrylates. Carbonyl or nitrile substituted alkyl radical show a greater addition to electron rich monomers. The addition of benzoyl radical to the double bond on a monomer is around two-orders or magnitude (~ 100 -fold) higher as compared a radical centered on an alkyl carbon. Both these species are equally vulnerable to dissolved oxygen in the photopolymerizable medium. Most of the PIs in Fig. 6 feature benzoyl moiety, indicating the prominence of this group in developing useful photoinitiators. There have been several attempts to engineer compounds that do not contain this group in order to address the control over the excitation dynamics or choice of monomers. In compound Fig. 6n, the phenyl ring is substituted with the electron rich five-membered ring furan. Compound in Fig. 6p is organometallic germanium derivative where the germanium atom is attached to a ketone, during photo exposure the Ge–C bond undergoes cleavage to give initiating species. The substituted disilane derivative in Fig. 6q when irradiated undergoes cleavage at the Si–Si to give highly reactive silyl radicals. The advantage of using silyl radical as an initiating species is its ability to overcome oxygen inhibition of polymerization. The ambient oxygen has been shown to play an active part in accelerating the addition of the silyl

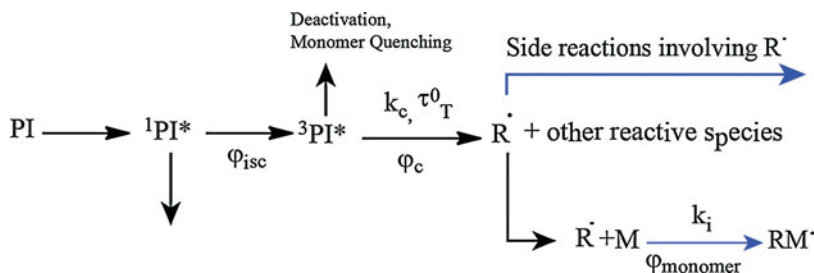


Fig. 8 Reactions governing the excitation and evolution of the photoinitiator

radical to monomers [2, 12, 13]. Another factor governing the effective action of the initiator is the effect of solvent on the stability of the photoexcited transition state. The stabilization of a charged transition state by a polar solvent can lead to an increase in cleavage of the photoinitiator and hence increase the reaction with the monomer.

The mechanism of photopolymerization can be studied through different techniques, such as chemical trapping [14], nuclear magnetic resonance (NMR) [15], time resolved Fourier Transform-Infrared (FT-IR) measurements [16, 17], laser flash photolysis [18], electron spin resonance (ESR) spectroscopy [19–21], chemically induced dynamic nuclear polarization (CIDNP), chemically-induced dynamic electronic polarization [CDEP] [22], femtosecond pump-probe experiments [23, 24], ultrafast fluorescence quenching [25], time-resolved stimulated emission [26], femtosecond-stimulated raman experiments [27], photothermal and photoacoustic methods [28], etc. For further details on the characterization and study of the kinetics of photopolymerization, the readers are referred to previous works [29–33].

Reactions leading to the formation of the macroradical RM^\cdot can be seen in Fig. 8. The rate of polymerization for the early stages of radical polymerization in a deaerated medium can be written as follows (see Eq. 5):

$$R_p = (k_p/k_t^{0.5}) R_i^{0.5} [M] \quad (5)$$

where the rate constants k_p and k_t correspond to propagation and termination steps of polymerization (see Fig. 8), respectively.

$$R_i = I_a \varphi_i \quad (6)$$

Here R_i is the rate of initiation that depends on the amount of absorbed light, I_a , and photoinitiation quantum yield φ_i which defines the efficiency of photoinitiation taking into account all the side processes that could occur during photoexcitation. The initiation quantum yield φ_i describes the number of initiation events associated with the absorption of a photon (or photons, e.g., two-photon-initiated polymerization). It is given by the product of the quantum yield of intersystem crossing φ_{isc} , quantum yield of initiating radical φ_c which is the number of free radical species formed as a result of the absorption of a photon and the quantum yield of the macroinitiator formed by the initial reaction between the initiator radicals and the

monomer ϕ_{monomer} . For a Type I initiator that undergoes cleavage in its triplet state, the initiation quantum yield is given by Eq. 7 [2].

$$\phi_i = \phi_{\text{isc}} \phi_c \phi_{\text{monomer}} \quad (7)$$

The bond cleavage of the photoinitiator is described by the product of ϕ_c and ϕ_{isc} (see Eq. 8) and is called dissociation quantum yield $\phi_{\text{dissociation}}$.

$$\phi_{\text{dissociation}} = \phi_{\text{isc}} \phi_c \quad (8)$$

The quantum yield of formation of radical R^\cdot depends on the rate at which triplets are generated by the photoinitiator k_c and the bimolecular quenching of the triplet by the monomer k_q . It is inversely proportional to the triplet life time τ_T^0 (see Eq. 9).

$$\phi_c = k_c / (1/\tau_T^0 + k_q[M]) \quad (9)$$

The quantum yield of the formation of the macroradical (RM) is denoted by ϕ_{monomer} (see Eq. 10). It depends on k_i , the initiation rate constant that governs the interaction between R^\cdot and monomer M , as well as k_r^0 the pseudo first-order rate constant which is sum of all rate constants leading to the disappearance of R^\cdot (see the processes represented by blue arrows in Fig. 8).

$$\phi_{\text{monomer}} = k_i [M] / (k_r^0 + k_i[M]) \quad (10)$$

Type II PIs form a long-lived triplet state on photoexcitation. Instead of undergoing cleavage, they interact with a co-initiator via a direct hydrogen transfer or an electron transfer reaction (see Fig. 9a). During the direct hydrogen transfer, the excited triplet state of the PI reacts with a co-initiator capable of donating a hydrogen radical to form a new radical species (PI-H $^\cdot$). This radical hydrogen adduct of the PI then initiates polymerization. Alternatively, the donor molecule (RH) forms an electron transfer complex with the photoexcited PI. The degradation of this charge transfer complex leads to PI-H $^\cdot$. Benzophenone initiates polymerization reactions through the formation of the charge transfer complex with amines. A wide range of amines are commonly employed as co-initiators. Other types of molecules, such as mercaptobenzothiazole, substituted silanes, germanes, silylamine derivatives, metal containing amines, boron derivatives, etc., have also been used. Examples of type II PIs and co-initiators can be seen in Figs. 10 and 11, respectively.

The initiation quantum yield for the type II initiators can be written as follows (see Eq. 11):

$$\phi_i = \phi_{\text{isc}} \phi_H \phi_R \phi_{\text{monomer}} \quad (11)$$

where ϕ_{isc} is the intersystem crossing quantum yield, ϕ_H is quantum yield describing the direct transfer of hydrogen, ϕ_R is the quantum yield of initiating radicals, and ϕ_{monomer} is the yield of the macroradical.

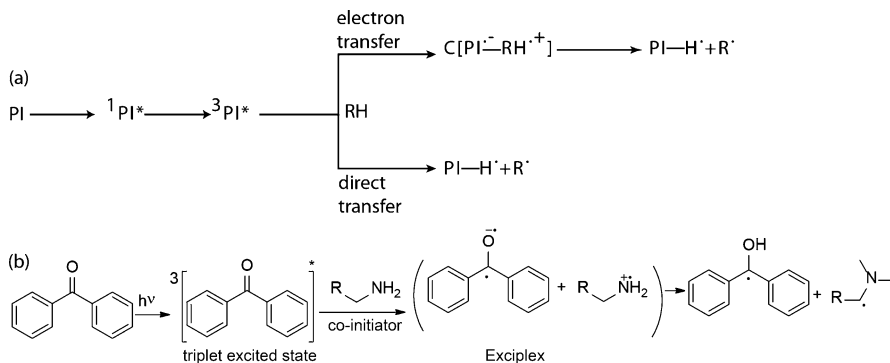


Fig. 9 Mechanism of initiation by type II initiators in the combination with an amine co-initiator

2.2 Monomers/Oligomers

Photopolymerization reactions involving a large variety of monomers/oligomers can be initiated by free radicals. This is because the radical is a neutral species stabilized through interactions with many common groups in monomers, such as halogen, phenyl, and many electron withdrawing groups. Radicals are nonspecific in their reactivity and interact with any available π -bond. Due to different rates of addition of the photogenerated radicals to the monomers, the reactivity of the monomers towards different initiators is variable [34]. Other factors, such as viscosity of the reactive medium, the thickness of the photopolymerizable film, the duration of irradiation, and the dark reaction after the light has been switched off, all govern the end results. Some prominent examples of molecules with chemical groups found in photoresists undergoing radical polymerization are provided in Fig. 12. Multifunctional monomers like epoxyacrylates, polyteracrylate, polytheracrylates, urethane acrylates, etc. are used in commercial formulations for photopolymerization (see Fig. 13).

Depending on the requirement of the application, photopolymerization can be carried out in solutions of monomers in suitable solvents, bulk monomers, or thin films. Due to the relative ease of following reaction and reactive species spectroscopically in solutions, reaction kinetics is often studied in solution. The propagating radical at a low concentration describes a second-order rate constant, while at a high concentrations, it is subject to a pseudo first-order rate constant. The termination reactions in solution phase photopolymerization are diffusion controlled [2, 35].

For many practical applications, polymerization takes place in bulk or thin films. Due to the effects of diffusion, the dynamics of polymerization can be entirely different in solution and in bulk. Owing to its ease of applicability for packaging of materials, photopolymerization has been intensely studied for decades. Despite this, determining the rate constants for addition of the radical produced by the initiator and a monomer is quite difficult. The viscosity of monomer in a bulk sample can be one or two orders of magnitude higher than the monomer solution.

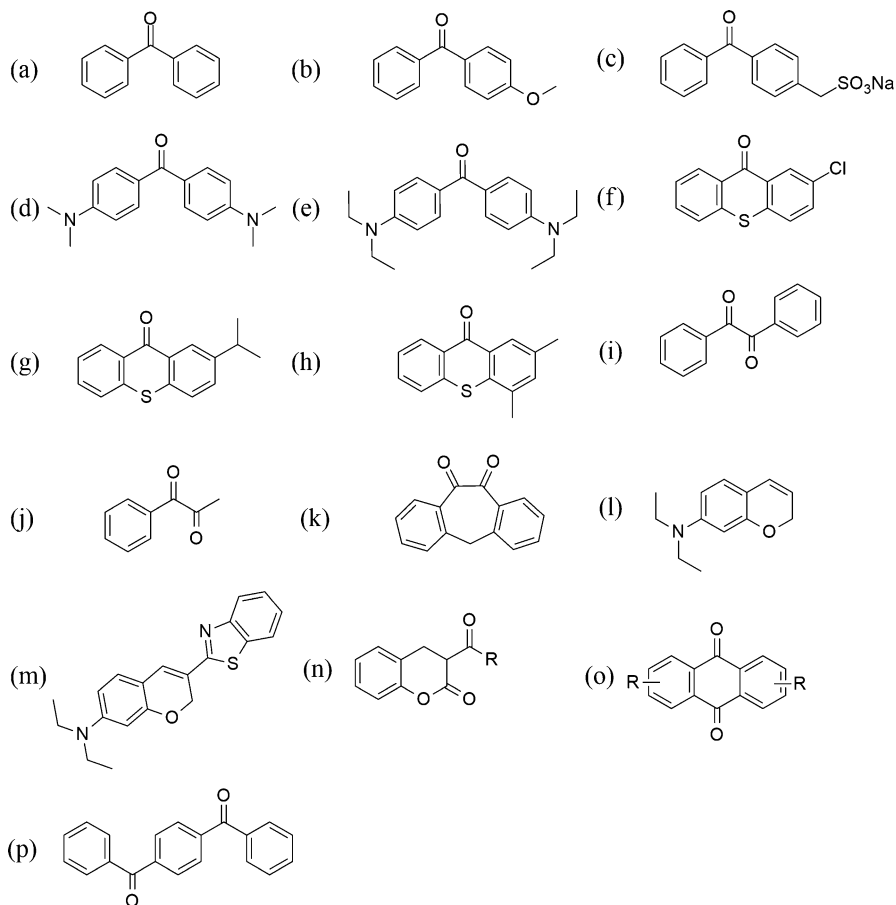


Fig. 10 Examples of type II photoinitiators: (a–e) benzophenone derivatives; (f–h) thioxanthone derivatives; (i–k) diketone (benzil) derivatives; (l–m) coumarin; (n) ketocoumarin; (o) anthraquinone derivatives; (p) terephthalophenone derivatives

The diffusion of the triplet radicals in the medium and its bimolecular quenching in the reactive medium are controlled by the viscosity of the reactive formulation. The rate constant for bimolecular quenching of the triplet radical by monomer (k_q) decreases with viscosity due to the decrease in diffusion, while it increases due to the increased presence of monomers in the bulk material. For a given monomer, the rate of polymerization increases with viscosity and then decreases. Viscosity also governs the cage effects involving the confinement of photogenerated reactive species by solvent molecules. For polymerization to take place, the radical has to escape the cage and react with monomers. In the solution phase, the cage effects are negligible; however, for increased viscosity, it is more difficult for a radical to escape the cage, resulting in a slower reaction [2, 35].

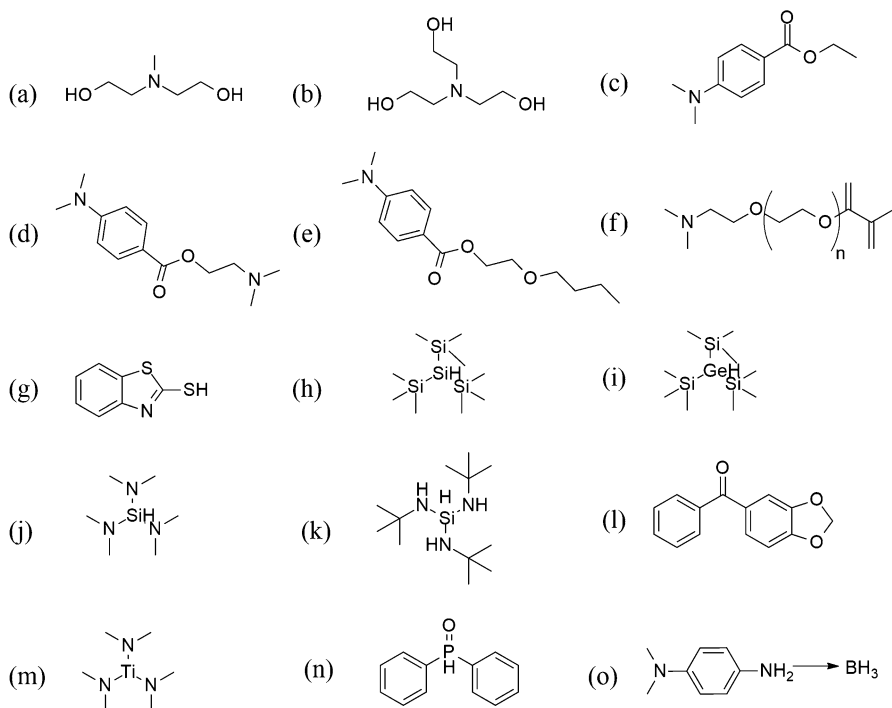
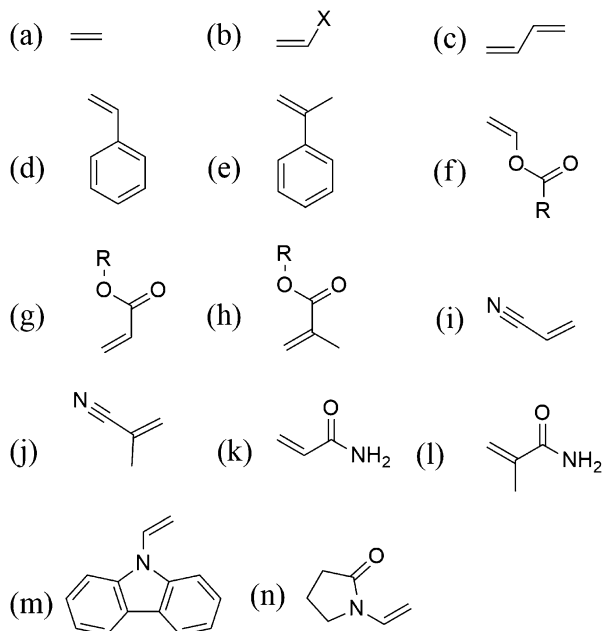


Fig. 11 Co-initiators for type II photoinitiators: **(a)** methyl diethanolamine; **(b)** triethanolamine; **(c)** ethyl 4-(dimethylamino)benzoate; **(d)** 2-(dimethylamino)ethyl 4-(dimethylamino)benzoate; **(e)** 2-butoxyethyl 4-(dimethylamino)benzoate; **(f)** amine containing polyether acrylate; **(g)** mercaptobenzothiazole; **(h)** tris(trimethylsilyl)silane; **(i)** tris(trimethylsilyl)germane; **(j–k)** silylamine derivatives; **(l)** acetal derivatives; **(m)** metal containing amines; **(n)** phosphorus containing co-initiator; **(o)** boron containing co-initiator

2.3 Visible Light–Sensitized Radical Polymerization

A molecule which can absorb visible wavelength and is capable of initiating a polymerization either by itself or in combination with other molecules can be termed a visible light initiator (or initiating systems, in cases when more than one molecule is involved) [36]. They are chosen for their high molar absorptivity at a visible wavelength or wavelengths, their specific interaction with monomers, and their long-lived excited states. Visible light initiating organic molecules can be constructed around UV photoinitiators by incorporating structural changes, such as those shown in Fig. 14a–d which are derivatives of Fig. 10f. The high-energy bonds in UV photoinitiators, when incorporated into molecules with extended conjugation, lead to visible light photoinitiators. The molecules in Fig. 14d are synthesized by incorporating benzophenone, thioxanthone, and pyrene on to a truxene moiety [37, 38]. The planar conjugated truxene moiety forms an efficient bridge for electrons, leading to a red-shifted absorption of the chromophore. The resulting molecules also show very high molar absorptivities, which makes them efficient initiators.

Fig. 12 Some common monomers/oligomers used in radical photopolymerization: (a) ethylene; (b) halogenated alkenes; (c) 1,3-dienes; (d) styrene; (e) *a*-methyl styrene; (f) vinyl ester; (g) acrylate; (h) methacrylate; (i) acrylonitrile; (j) methacrylonitrile; (k) acrylamide; (l) methacrylamide; (m) *N*-vinyl carbazole; (n) *N*-vinyl pyrrolidone



Due to their high interaction with light and stability of the photogenerated species, many organometallic compounds are highly suited for visible light photoinitiation. It should be noted that some organometallic molecules are cytotoxic and care should be taken on their selection in a photoinitiating system. The germane derivatives in Fig. 14i–k initiate radical polymerization in the presence of visible light due to free radicals generated by α -cleavage at the C–Ge bond [39–41]. An increase in the number of germanium atoms in the structure leads to a bathochromic shift in the absorption of the initiator. The photocleavage of germane initiators yield long-lived triplet species that are very efficient radical initiators [42]. Iridium complexes like those in Fig. 14l–m can be combined with suitable co-initiators to be used in free radical polymerization [43, 44]. The introduction of formyl moiety in the latter results in its higher extinction coefficient. Both compounds combine with tris(trimethylsilyl)silane and an iodonium salt to form a photoinitiator system for free radical polymerization. The mechanism of initiation is shown in Fig. 15.

2.4 Thiol-Ene Photopolymerization

Some of the earliest commercially available formulations for photopolymerization were based on photo-induced thiol-ene crosslinking. However, concerns over their shelf life, the odor of the thiols in the formulation, as well as the gradual degradation of the benzophenone photoinitiators used in these formulations causing discoloration led to their failure and disappearance. Many decades of ensuing research rectified the

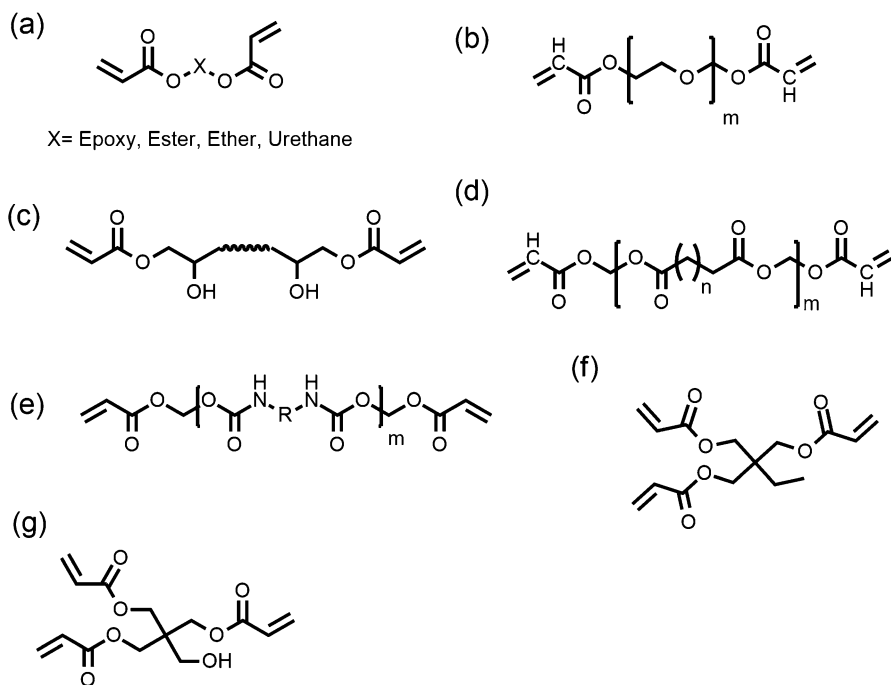


Fig. 13 (a) General structure of multifunctional monomers for free radical polymerization; (b) polyether acrylate; (c) epoxy acrylates; (d) polyester acrylate; (e) polyurethane acrylate; (f) crosslinker monomer trimethylolpropane triacrylate; (g) crosslinker monomer pentaerythritol triacrylate

above problems, leading to the reemergence of this very useful chemistry. The polymer network resulting from thiol-ene polymerization has been suggested as the most ideal from any free-radical polymerization [45, 46]. Since it has been tagged as a “Click reaction,” it has been extensively employed for the synthesis of functional polymers, hybrid materials, and microdevices [47–52]. Thiol-ene reactions are specific and proceed at mostly mild conditions making them attractive for a wide variety of chemical syntheses. Thiol-ene chemistry has been used in the synthesis of various monomers [53–56], polymers, or copolymers [57–65]. Thiol-ene additions are used as a method of direct synthesis or are used for post polymerization modification of polymers [66]. The versatility and mild conditions of thiol-ene reactions are very attractive for chemical modification of monomers, polymers and nanoparticles for biotechnological applications [66–70].

Thiol-ene photopolymerization shows a high curing speed with little or no oxygen and moisture sensitivity to give polymeric films with a very low shrinkage stress and a narrow glass transition temperature [45–47]. The mechanism of thio-ene polymerization shares the characteristics of both addition and condensation polymerization (see Fig. 16a) [46]. Some common enes and thiols that have been employed in thiol-ene polymerization reactions are shown in Fig. 16b.

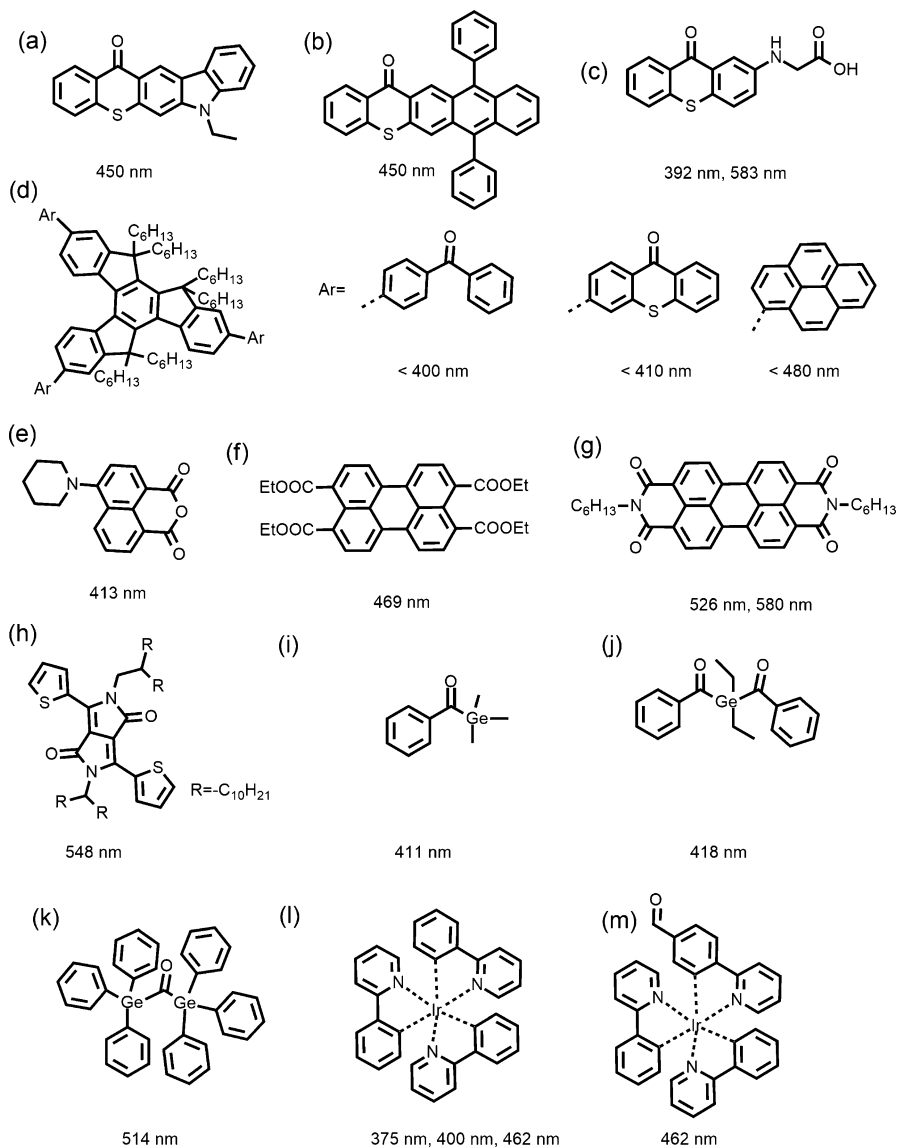


Fig. 14 Some examples of visible light photoinitiators; they are used either by themselves or in combination with other molecules to effect initiation. The absorption maxima or band width of activity are provided underneath each structure

The reaction is easily initiated by a radical photoinitiator and leads to a near quantitative addition of thiol to carbon-carbon double bond. Type I photoinitiators are favored for thiol-ene polymerization due to the improved hydrogen abstraction from thiols [71, 72]. Sterically, unhindered terminal enes show the highest reaction

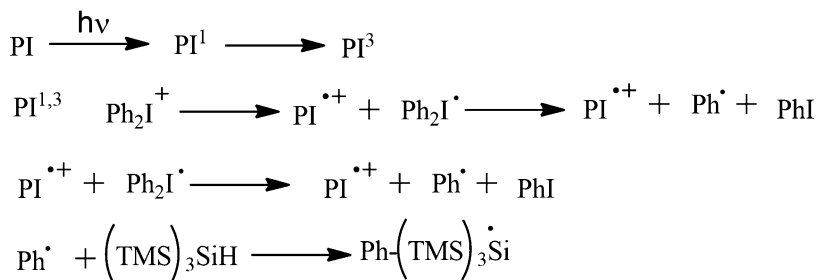


Fig. 15 Initiation of visible light photoinitiating combination; inorganic complexes play the role of the initiator

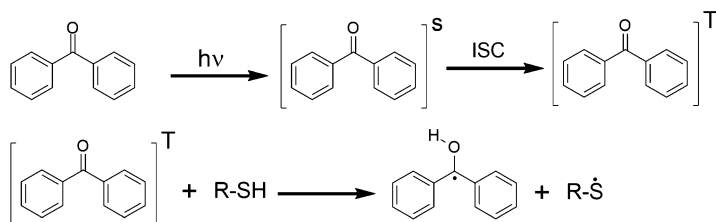
rates during thiol-ene photopolymerization compared to hindered enes [73, 74]. Electron rich or strained enes show higher reaction rates during photopolymerization with a particular thiol. Norbornene seen in Fig. 16b is an example of a strained ene as that undergoes rapid reaction with the thiyl radical leading to an addition product with reduced ring strain at the double bond. Hence, as compared to other enes, the reaction between thiyl and norbornene proceeds quite fast.

Vinyl ethers are examples of electron-rich enes that are highly reactive during thiol-ene polymerization. Conjugated dienes, methacrylates, styrene, and maleimides are examples of low reacting enes (see Fig. 16b) [46, 73]. Alkyl thiols, thiolglycolate esters, and thiol propionate esters have been used in thiol-ene reactions. Esters show a higher reactivity to alkenes, as compared to alkyl thiols. Common multifunctional thiols and enes used in thio-ene photopolymerization are shown in Fig. 17.

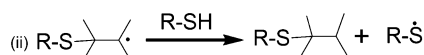
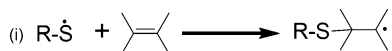
As shown in Fig. 16, the propagation of thiol-ene reaction proceeds in two distinct steps. The first step is called propagation involving the attack of the thiyl radical on the ene. The subsequent step is called the chain transfer step where the thiol-ene adduct radical abstracts hydrogen from a new thiol molecule to regenerate the thiyl radical. The chemical nature of the thiol and ene determines whether the propagation or the chain transfer step forms the rate-determining step during the reaction. Enes that are less reactive cause propagation to be the rate-limiting step. Thiols that structurally limit the abstractability of the hydrogen lead the chain transfer step to be the rate-limiting step. Unlike the conventional free-radical polymerization, a typical thiol-ene polymerization maintains a low cross-linking density characterized by the formation of low molecular weight oligomers for an extended period during the reaction. This, in turn, delays the gel point during polymerization, leading to ease of diffusion of species resulting in the buildup of a uniform network of polymers [75, 76]. In thiol-ene generated polymers, glass transition occurs over a small range of temperature, indicating the uniformity of the formed network. The narrow window of glass transition results in well-defined mechanical properties for the resultant polymers [77].

Thiol-acrylate and thiol-ene-acrylate formulations have been studied to diversify the properties of the thiol-ene crosslinked polymer. In the binary thiol-acrylate systems, multifunctional thiols are combined with traditional acrylate-based monomers. This

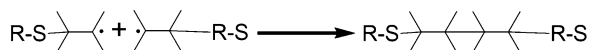
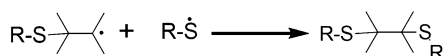
(a) Initiation



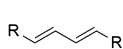
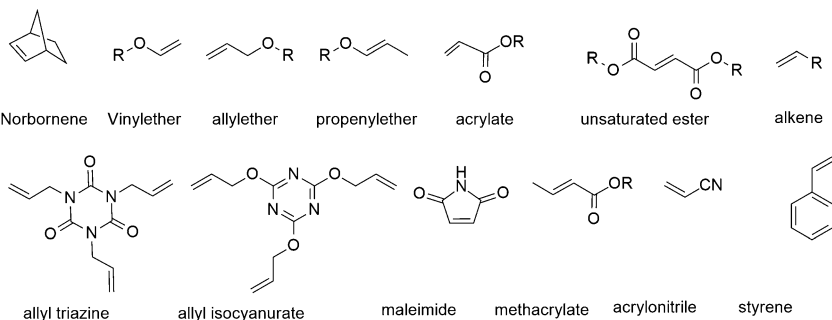
Propagation



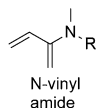
Termination



(b) Enes



Diene

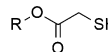


N-vinyl amide

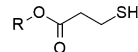
Thiols



alkyl thiol



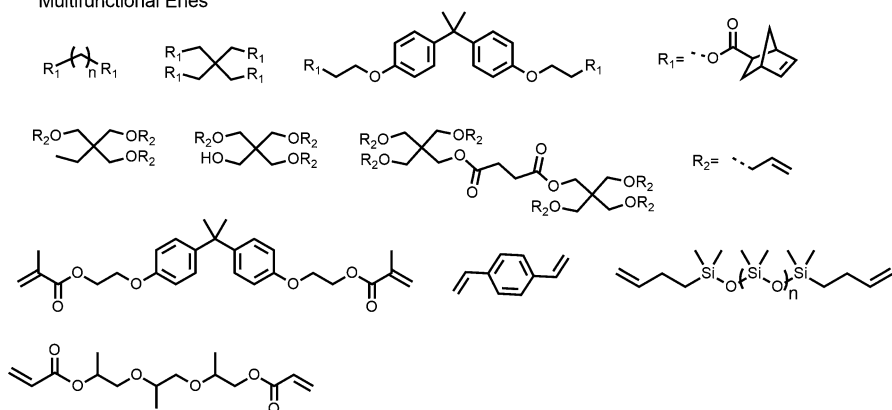
alkyl thioglycolate



alkyl mercaptopropionate

Fig. 16 (a) Thiol-ene polymerization, initiation, propagation, and termination steps and the examples of thiols and enes that could be employed in such reactions. The propagation step can be divided in two steps, namely, propagation (i) where the thiol radical adds to the double bond, and (ii) which involves hydrogen abstraction by the formed monomer radical from thiol is termed chain transfer step (ii). (b) Some enes and thiols that have been used in thiol-ene reaction

Multifunctional Enes



Multifunctional Thiols

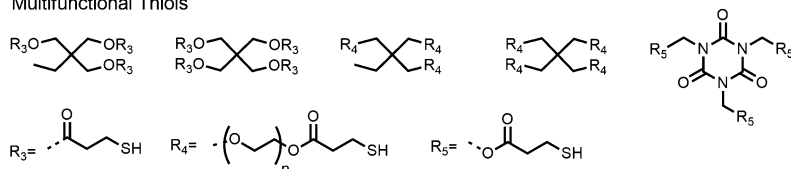


Fig. 17 Common multifunctional ene and thiol monomers employed in thiol-ene photopolymerization

combination leads to polymerization with low oxygen sensitivity, higher conversion, as well as delayed gel point without sizable compromise on the thermo-mechanical properties of the formed polymers, as compared to pure methacrylate polymers. The ternary combination of thiol, ene, and methacrylate is more robust than the binary combinations. Ternary mixtures result in polymers with the high glass transition temperatures similar to those in methacrylate polymers, while imparting the positive traits of thiol-ene polymerization in the system, such as oxygen inhibition and uniform polymerization [78]. With the careful choice of the monomers, there is the possibility of creating polymerization-induced phase separations. Phase separated double polymer networks could be interesting substrates for many applications. Thiol-ene polymerization of some thiol-ene-acrylate formulations results in the formation of two-phases and leads to a reduction in shrinkage stress. The ternary thiol-ene-acrylate formulations are less sensitive to stoichiometry of individual components and hence provide dexterity in designing polymers with desirable properties [78–81].

3 Cationic Polymerization

The oxygen sensitivity of radical polymerization is one of its major drawbacks requiring photocuring to be carried out under inert atmosphere. The high processing costs associated with maintaining inert atmosphere during applications lead to the

exploration of new chemistries capable of delivering effective photopolymerization under ambient conditions [82]. The discovery of photoacid generators enabled the use of chemical amplification reactions to carry out efficient polymerization without inter atmosphere. Chemical amplification refers to a single photochemical event leading to an increasing number of chemical events. Since each photochemical event leads to hundreds of chemical events during chemical amplification reactions, they can be used even with low doses of radiation. Ambient oxygen shows little of no effect on cationic polymerization. In cationic formulations, the photochemical reaction is initiated by a photoacid generator (PAG). A photoacid generator can be an ionic, nonionic, or organometallic compound [1].

3.1 Ionic Photoacid Generators

Photoacid generators (PAGs) are compounds that can generate acidic species on irradiation. Diaryl iodonium and triaryl sulfonium are among the earliest types of PAGs that were investigated for cationic polymerization [83–85]. The light-sensitive organic part of these PAGs features a heteroatom hosting a positive charge; PAGs are also associated with a metal complex anion that acts a counter ion. The counter ion combines with the photogenerated H^+ ion to form Brønsted acids (super acids) capable of catalyzing ring-opening polymerizations. Photoacid generators can be applied to ring-opening reactions of a wide variety of materials, such as multifunctional epoxides, oxetanes, vinyl ethers, cyclic ethers, cyclic acetals, cyclic siloxanes, etc.

Most common onium salt PAGs include iodonium derivatives, sulfonium derivatives, phosphonium derivatives, *N*-alkoxy pyridinium salts, etc. (see Fig. 18a–l). Some organometallic compounds are also used as cationic photo-initiators. Most PAGs absorb radiation in the UV region; however, their activity can be extended to longer wavelength by the use of photosensitizers by the application of free-radical promoted cationic polymerization [86]. Cationic photopolymerization is initiated by either the photogenerated acid or by a stable cation formed due to the photo-scission of the PAG.

Compounds (a–c) in Fig. 18 are examples of iodonium PAGs. The cationic and anionic species in the iodonium salt PAG play specific roles defining its properties. The onium cationic part defines the photochemistry of the PAG. It influences the absorption maximum (λ_{max}), the molar absorption coefficient, quantum yield, photosensitization, and thermal stability of the PAG. The anion determines the acid strength, initiation efficiency (during polymerization), and propagation rate constants (during polymerization). Once the photoacid is generated, the anion determines its role during polymerization. The importance of having non-nucleophilic counteranions was realized during the early investigation of diaryliodonium PAGs. The interaction of the photogenerated cationic species with a nucleophilic anion leads to the suppression of the initiating cationic species and hence the polymerization. In the presence of a suitable anion, the aryl and aryl iodine cationic species formed by photolysis of iodonium PAG can react with monomers, solvents, or impurities to give superacids of the form HMX_n (MX_n^- : BF_4^- , PF_6^- , AsF_6^- ,

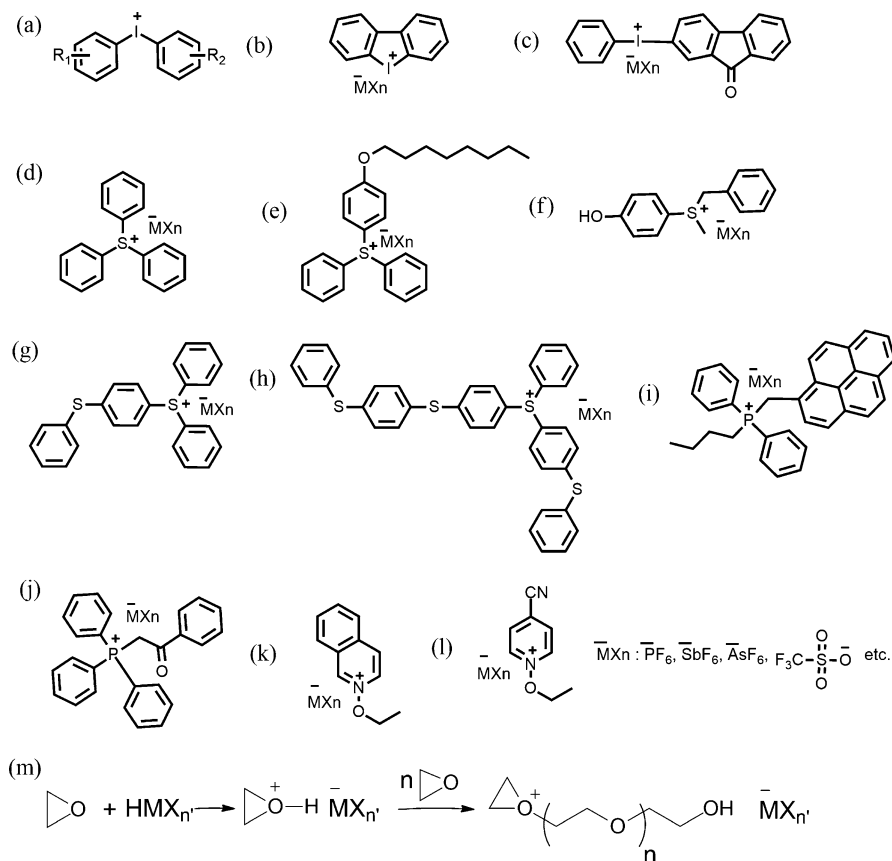


Fig. 18 Onium (ionic) photoacid generators and ring-opening polymerization: (a–c) Iodonium-based PAGs; (d–h) sulfonium-based; (i–j) phosphonium salts; (k–l) *N*-alkoxy pyridinium salts; and (m) ring-opening polymerization of epoxide monomer in the presence of photogenerated acid

SbF_6^- , $(\text{C}_6\text{H}_5)_4\text{B}^-$ etc.). For a series of onium salt with the same cation, the polymerization is dependent on the counterion. The extent of polymerization depends on the nucleophilicity and size of the counterion in the following order, $\text{SbF}_6^- > \text{AsF}_6^- > \text{PF}_6^- > \text{BF}_4^-$ [87]. These PAGs undergo photolysis with quantum yields in the range of 0.7–0.9. The λ_{max} and the intensity of absorption of iodonium PAGs can be engineered by substitutions on the aromatic ring. The super acids go on to initiate ring-opening polymerization reactions (see Fig. 18m) [82].

A simplified version of the mechanism of photolysis and photoacid generation in iodonium PAGs is shown in Fig. 19. A diaryliodonium salt undergoes photo-induced scission either through homolytic or through heterolytic cleavage (see Fig. 19). The photoexcited intermediate interacts with water or other protic solvents present during the reaction to give a strong Brønsted acid which can initiate cationic polymerization. In the viscous reaction media, the photogenerated species are subject to cage effects.

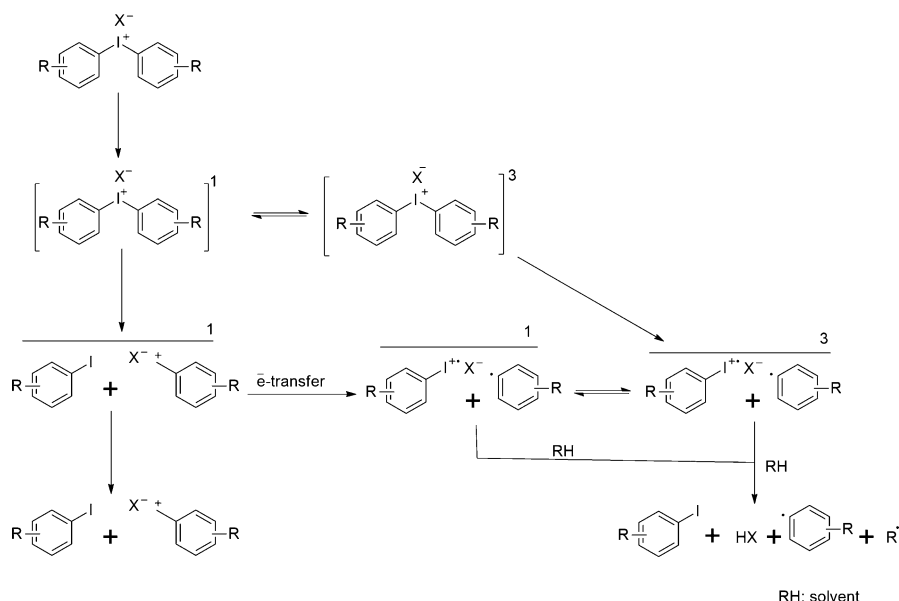


Fig. 19 Mechanism of photoacid generation in an iodonium salt PAG. Here RH is a protic solvent

Sulfonium-based PAGs form another important class of onium salt PAG. Compounds (d–g) in Fig. 18 are examples of sulfonium PAGs. They have a higher reduction potential, than iodonium PAGs, and hence show better thermal stability, allowing them to be used in formulation that is more shelf stable. The higher reduction potential also leads to a lower photosensitivity of the sulfonium-based PAG. The mechanism of photolysis of sulfonium PAGs closely resembles that of iodonium PAGs (see Fig. 20). Homolytic photo-scission pathway is more prominent in sulfonium PAGs, as compared to heterolytic cleavage pathway. Sulfonium PAGs show a longer wavelength absorption band at 305 nm. The substitution of thiophenoxyphenyl groups in compounds (g) and (h) in Fig. 18 increases the molar absorption coefficient of these compounds, as compared to compound (d). This makes them more sensitive photoinitiators. Ferrocenium-based PAGs form a newer class of organometallic initiators that are used mainly with monomers that could complex with iron atom in ferrocenium. They are mainly used for epoxide monomers. Some examples of ferrocenium PAGs and the mechanism of photo-initiation of ferrocenium PAGs are shown in Fig. 21.

3.2 Spectral Broadening

Spectral broadening refers to the technique of increasing the sensitivity of onium salt initiators to visible wavelengths to enable the use of new light sources in the near UV and visible regions of the spectrum. With the use of electron transfer sensitization,

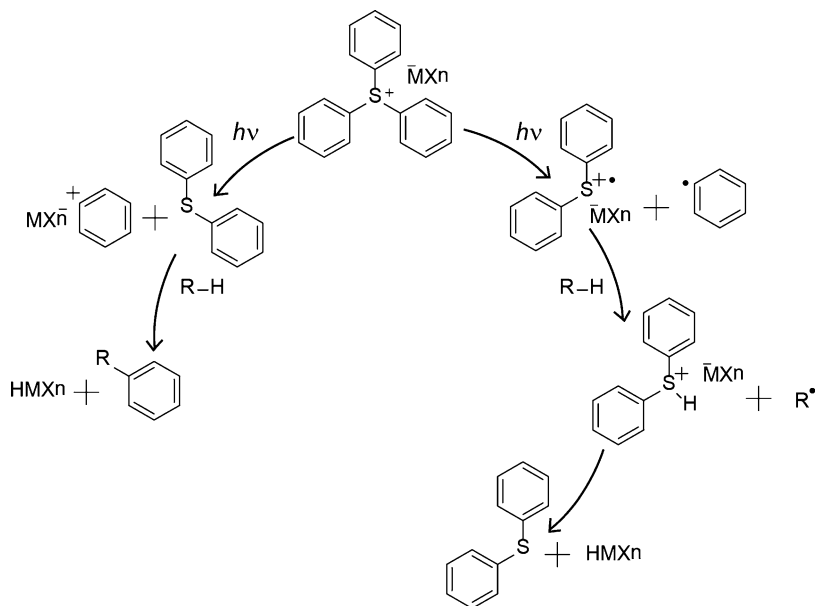
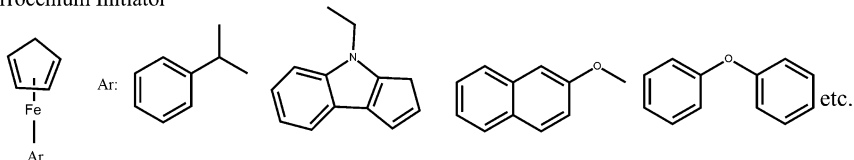


Fig. 20 Mechanism of photoacid generation in sulfonium salt PAG, here RH is a protic solvent

Ferrocenium Initiator



Mechanism of action of Ferrocenium Initiator

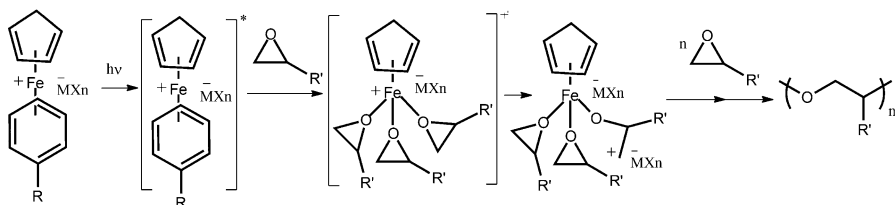
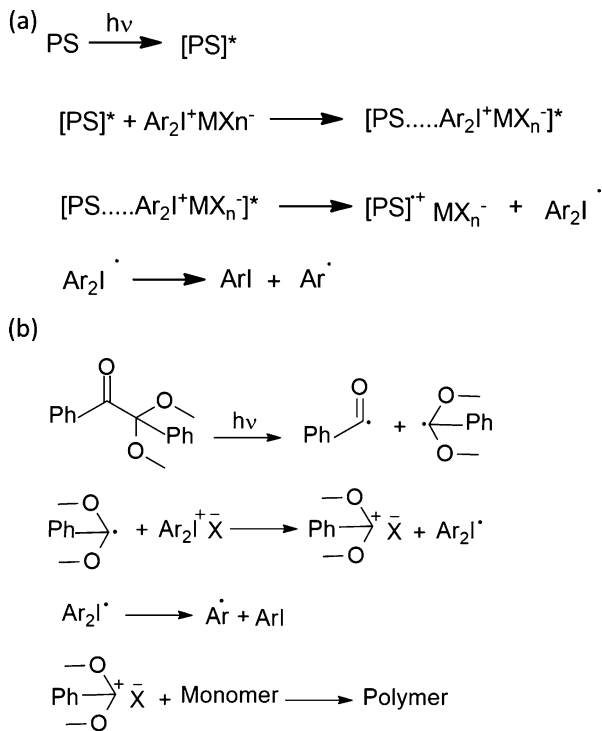


Fig. 21 Examples of ferrocenium photoinitiators and the mechanism of their action as cationic initiators

the absorption of both iodonium and sulfonium PAGs can be shifted to longer wavelengths [88]. Electron-transfer sensitization involves the combination of a photosensitizer (PS) with the PAG to achieve photoinitiation as shown in Fig. 22a. The photoexcitation of PS leads to an electron transfer reaction from PS to the PAG,

Fig. 22 (a) Mechanism of electron transfer sensitization in aryliodonium PAGs; (b) mechanism of free-radical promoted cationic polymerization



leading to the formation of an excited state complex (exciplex) followed by a reduction of the onium cation. This is followed by the irreversible decomposition of the resulting $\text{Ar}_2\text{I}^\bullet$ free radical; this process is very efficient and restricts back electron transfer to the photosensitizer from happening [84, 90]. The positively charged photosensitizer either directly initiates polymerization or generates photoacids through further reactions. Polyaromatic compounds, such as pyrene derivatives, atracene derivatives, carbazole derivatives, etc., are used as electron transfer sensitizers.

Free-radical promoted photosensitization of cationic polymerization (FRPCP) is another method for achieving spectral broadening. In FRPCP a radical initiator is added alongside the PAG. Free radicals formed by the radical initiator interact with onium salt PAG to generate a corresponding cation and $\text{Ar}_2\text{I}^\bullet$. The cation formed from the free radical initiator then goes on to initiate polymerization reactions. The $\text{Ar}_2\text{I}^\bullet$ undergoes a fast and irreversible decay. The mechanism for electron-transfer sensitization is shown in Fig. 22b. Typically, free radicals formed during FRPCP are oxidized to form species containing a positive charge capable of initiating cationic polymerization. A combination of aromatic ketone, disilane, and diaryliodonium salt is a typical example of a FRPCP initiator [89, 90]. Irradiation of the mixture leads to the formation of silyl radical which is then oxidized to give a positively charged initiating species. Acylgermanes like Fig. 14i can be used as a free radical initiator in

FRPCP [91–93]. They give germyl radicals on irradiation; these radicals are then oxidized to germanium ions which can initiate polymerization. Supramolecular complexes of iodonium PAGs-crown ethers and combination of onium salt and zinc halide have also been used for FRPCP [94–97]. Apart from this a combination of an organometallic compound of ruthenium, iridium, selenium or germanium with an organo silane and photoacid generator like those discussed in Sect. 6 can be used for initiating cationic polymerization in the near UV to visible wavelengths [39, 43, 93, 98–103]. These ambivalent initiating systems capable of initiating both radical and cationic polymerization have the potential to be used in complex photo-polymerizable materials.

3.3 Nonionic Photoacid Generators

Nonionic or nonsalt PAGs are another subclass of PAGs extensively studied in recent years. Unlike common onium PAGs, nonionic or nonsalt PAGs exhibit a broad wavelength activity and a good solubility in organic media and polymeric films. On irradiation, nonionic PAGs give rise to various organic acids, such as sulfinic acid, sulfonic acid, carboxylic acid, phosphoric acid, etc. [104, 105]. Some examples of nonionic PAGs are shown in Fig. 23. Under photoirradiation, nonionic PAGs generate organic acids capable of initiating polymerization. Compounds (a–i), except for (h) (see Fig. 23), generate sulfonic acids on irradiation [9]. Compound (f) in Fig. 23 generates a carboxylic acid on irradiation. Sulfone compounds (j) and (k) give rise to sulfinic acid on irradiation. Diphenyl selenide compound (m) in Fig. 23 yields a cationic radical capable of initiating polymerization in the presence of a photosensitizer [106]. The mechanism of photoacid generation in ortho-nitrobenzyl sulfonates, iminosulfonates, and N-hydroxyimide sulfonates is shown in Fig. 24a–c, respectively. Apart from the photoproducts shown in Fig. 24, there are other radical and ionic species that might be formed during the photoacid generation. These side products may or may not intervene in the progress of polymerization depending on the conditions during polymerization. Cage effects in the reaction medium, as well as the interaction of atmospheric oxygen with radical species generated during photoacid generation, can control the dynamics of polymerization. Compound (e) gives an 88% yield of *p*-toluene sulfonic acid in solution and 52–61% of the same compound in polymer films in air [107]. Interestingly, under vacuum conditions, due to the formation of ammonia by hydrolysis of imine, the yield of *p*-toluene sulfonic acid was found to be lower than both cases specified above.

3.4 Monomers for Cationic Polymerization

A wide range of functional groups are compatible to cationic polymerization (see Fig. 25) [82, 86, 109]. They include vinyl derivatives, vinyl ethers, various cyclic ethers, thiranes, cyclic esters, and cyclic siloxane derivatives. Apart from these,

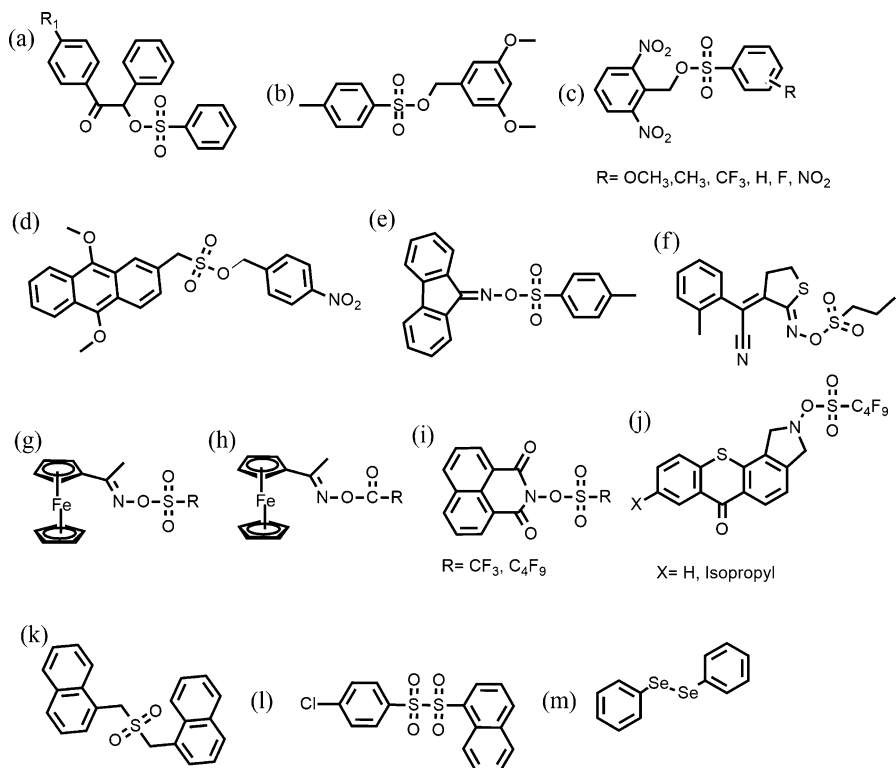


Fig. 23 Some examples of nonionic PAGs: (a–d) based on sulfonates; (e–f) iminosulfonates; (g) acetylferrocene oxime; (h) sulfonylferrocene oxime; (i–j) *N*-hydroxyimide sulfonates; (k–l) sulfones, and (m) selenide-based photoacid generators [106]

many unconventional monomers, such as benzoxazine, epoxy, end functionalized poly caprolactone, thiophene, etc. also undergo cationic polymerization [86, 110].

Practical application demands high reactivity, leading to a high cure speed, lack of oxygen inhibition, low-volume shrinkage, good mechanical properties, little or no toxicity, and good adhesion to various substrates from the monomer. The electron-rich carbon-carbon double bonds in vinyl ethers exhibit a higher curing rate than epoxy functionalized monomers. The high rate of conversion in vinyl ethers is also due to the low glass-transition temperature of the formed polymers [87]. Some examples of multifunctional epoxide monomers that can be polymerized by cationic photoinitiators are shown in Fig. 26a–d. Due to their extensive application in many different fields [1, 87], multifunctional epoxide monomers are the most important class of monomers in cationic polymerization. These monomers polymerize to form three-dimensional networks. The rate of photocuring increases rapidly for multifunctional epoxy groups, reaches a maximum, and then decreases. The presence of the soft counter ion associated with the photoacid minimizes the interaction between polymer chains containing cationic end groups. Cationic polymerization proceeds

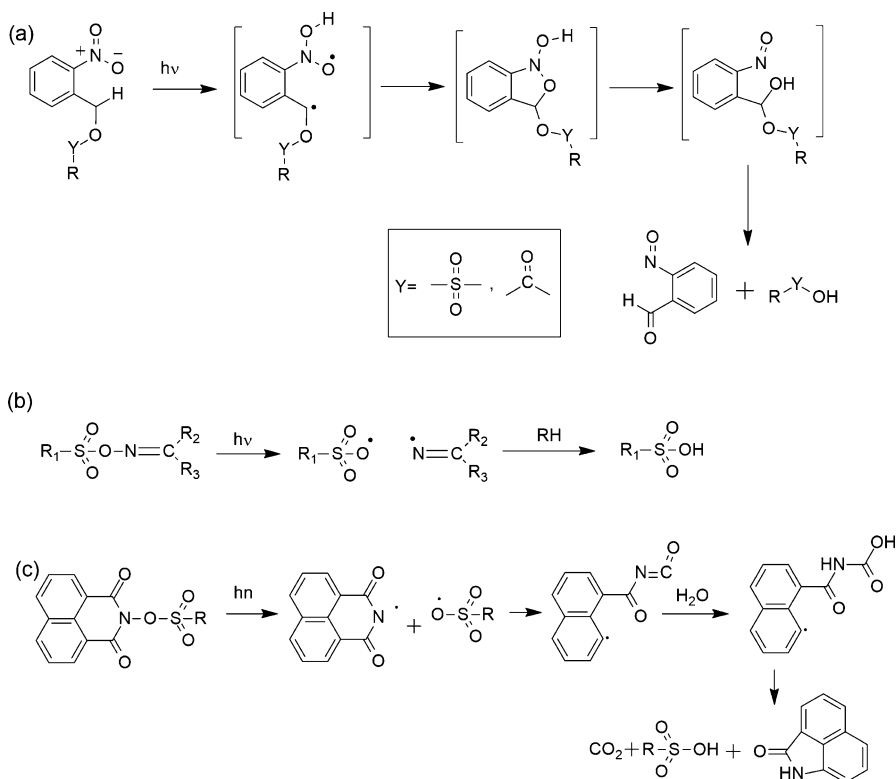


Fig. 24 The mechanism of photoacid generation in nonionic PAGs: (a) Orthonitrobenzyl sulfonates give rise to sulfonic acid and other photoproducts [103]; (b) iminosulfonates give rise to sulfonic acid and other photoproducts [107]; (c) *N*-hydroxyimide sulfonates give rise to sulfonic acid [108]

uninhibited in the dark state; after the light source has been switched off, this process can be accelerated by heating and is called a post-cure step.

The material requirement for applications dictates the design of monomers. The rate of curing of difunctional epoxides monomers was found to be inferior to that of difunctional acrylate monomers. Hence, there have been many attempts to increase the curing speed of the epoxy- based monomers through design. Of the different classes of monomers explored, cycloaliphatic epoxides were found to have the highest curing rates. Rapid polymerization in multifunctional epoxy monomers can lead to gel point, trapping large quantities of residual monomer inside the crosslinked network. This can be circumvented by prolonging the gel point during polymerization by the use of chain transfer agents that attack the cationic end of the polymer while initiating new polymeric chains [111]. Alcohols are among the most efficient chain transfer agents, the oxygen in the alcohol interacts with the cationic end of the growing polymer chain. This results in end-capping of the cationic chain. Further release of an H^+ ion from the alcohol terminated polymer chain initiates free

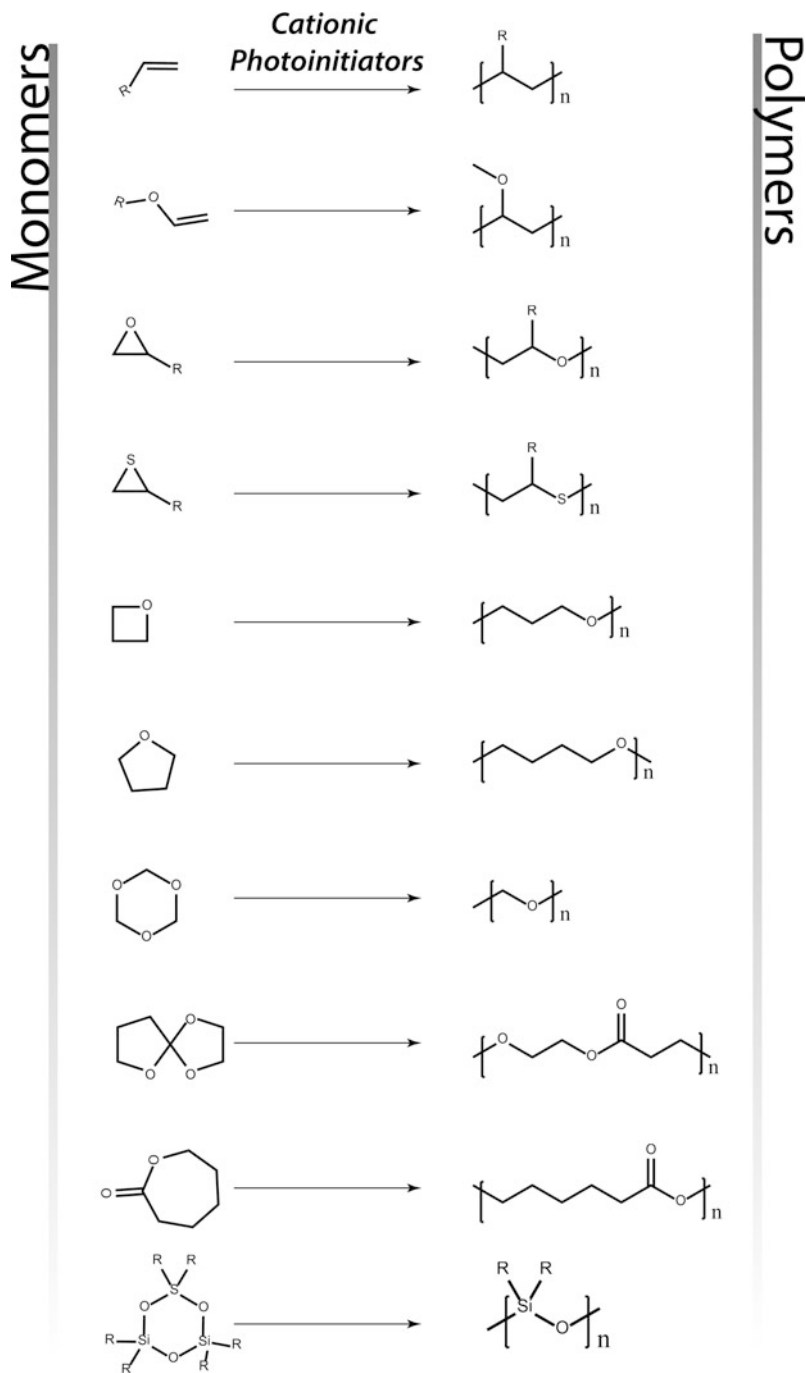


Fig. 25 Various monomers that can be polymerized by cationic polymerization; top to bottom: vinyl, vinyl ether, epoxy, thiirane, oxetane, tetrahydrofuran, 1,3,5-trioxane, 4,6-trioxaspiro[4.4]nonane, 6-caprolactone, hexamethylcyclotrisiloxane [82, 86]

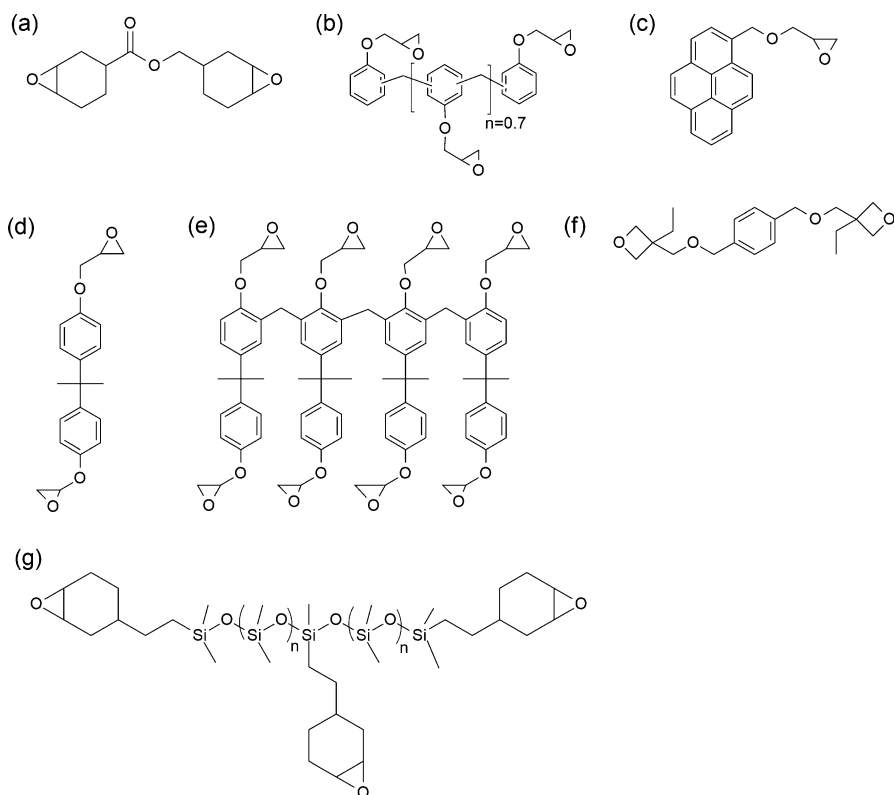


Fig. 26 Ring-opening polymerization in epoxide monomer; examples of multifunctional monomers that can be polymerized by cationic photoinitiators

monomers to progress the reaction. This method of activation of the growing polymer chain is called the activated chain-end mechanism [87, 112]. Apart from this, it has also been proposed that the monomer can be directly activated by alcohol, leading to the activated monomer mechanism [113, 114]. Both these mechanisms check the rapid growth of molecular mass or cross linking and delay the gel point, leading to higher conversions and better mechanical properties.

The high polymerization rates of multifunctional cycloaliphatic monomers make them popular for many commercial applications. Apart from the high curing rates, commercial applications demand high thermo-mechanical properties, chemical stability, abrasion resistance, adhesion, and solvent resistance. The presence of low molecular weight components in the cured polymer after photocuring can adversely affect its thermo-mechanical properties and increase its toxicity. The obvious low molecular weight materials in the cured polymers would be the photosensitizer, the PAG, or its photo-degradation products. Photosensitizers can be functionalized to be incorporated into the polymer; the epoxy functionalized pyrene molecule in Fig. 26c is one such example [115]. Another approach is the development of photosensitizers

attached to a polymer [116]. The photoacid generator can be substituted with long alkyl chains or bound to polymers to increase its molecular weight. The increasing substitution on the photoacid also dictates the diffusion of the photodegradation products from the PAG [117].

Volume shrinkage is one of the major problems faced by radical polymerizable acrylate photopolymers. Simple methyl methacrylate monomer shrinks by about 20–25% of its volume [118]. Multifunctional acrylate monomers show shrinkage lower than the above value (c.a. 10%), but shrinkage is still substantial to hamper application [119–121]. Shrinkage in multifunctional epoxide photopolymers is less than that of acrylate-based photoresists [122]. Some applications, such as dental fixtures, demand minimal shrinkage of the photocured structure. Volume shrinkage can be reduced by designing suitable monomers or a combination of monomers. For example, monomers (f) and (g) in Fig. 26 are used together to make rigid, solvent-resistant films with a low volume shrinkage [123]. Controlled addition of diol derivatives of compound (g) was found to decrease volume shrinkage. Epoxy functionalized hybrid silicone monomers, as the one in Fig. 26h, also undergo rapid polymerization, but yield soft elastomeric and transparent films [124]. Careful selection of monomers and initiators allows the engineering of properties in the final cured film or structure.

4 Anionic Polymerization

The idea of anionic photopolymerization has been around for a long time, but it has been only sporadically advanced over many years [125, 126]. In recent years, the interest in anionic photopolymerization has been renewed, mainly due to the control it provides over the composition and structure of the polymer. Monomers undergoing anionic polymerization should be able to stabilize a negative charge through inductive or resonance effects. Anionic photopolymerization reactions can be initiated by inorganic complexes of chromium, organometallic complexes of chromium, as well as tungsten, metallocenes, triarylmethyl derivatives, Zwitter ions, etc. [127–133]. Ethyl and methyl cyanoacrylates are the most widely studied monomers for anionic photopolymerization. Anionic photopolymerization is initiated by the formation of an anionic species by the photoexcited initiator as shown in see Fig. 27a [127, 129, 134–136]. The photogenerated anion adds to the carbon–carbon double bond in the monomer to generate an anionic adduct setting off the propagation reaction shown in Fig. 27b. Anionic polymerization of ethyl or methyl cyanoacrylates can be carried out in neat samples. Recently, ketoprofen has been used to initiate the polymerization of methoxy acrylate in neat as well as solutions in the presence of a mixture of sodium hydride and sodium hydroxide [137]. Ketoprofen initiated polymerization of methoxy acrylate is shown in Fig. 28.

Sila(I)ferrocenophanes can undergo photoinduced anionic ring-opening polymerization in the presence of a lithium or sodium salt of cyclopentadienyl [138–141]. Though such polymers have been previously prepared by conventional means, the photocontrolled reaction permits the use of ferrocenophanes with

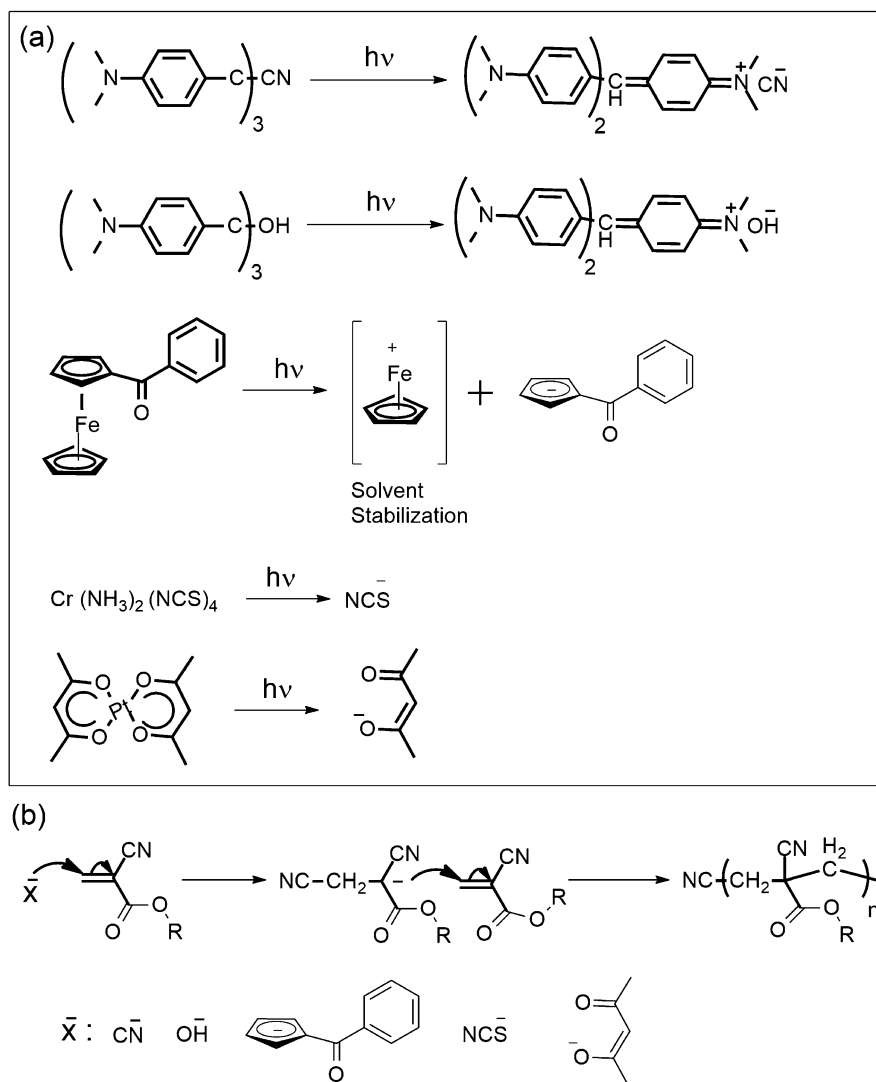


Fig. 27 Anionic photopolymerization of alkyl cyanoacrylate; (a) various photoinitiators; (b) the general scheme for anionic polymerization of alkyl cyanoacrylate [133]

sensitive functional groups as pendants [139, 142, 143]. The scheme in Fig. 29 elaborates the ring-opening polymerization of ferrocenophanes. The mechanism of the photoinduced anionic polymerization is not completely understood, but it is postulated that the strained sila bridge plays a role in weakening the bond between the cyclopentadiene and iron. This bond-weakening effect, alongside with photo-induced ligand to metal charge transfer, increases the electrophilicity of iron.

Fig. 28 Ketoprofen in the presence of NaH and NaOH can polymerize methoxyacrylate with high yields in both liquid and solid state polymerization. The initiation and propagation step of the anionic polymerization of methoxyacrylate can be seen here [137]

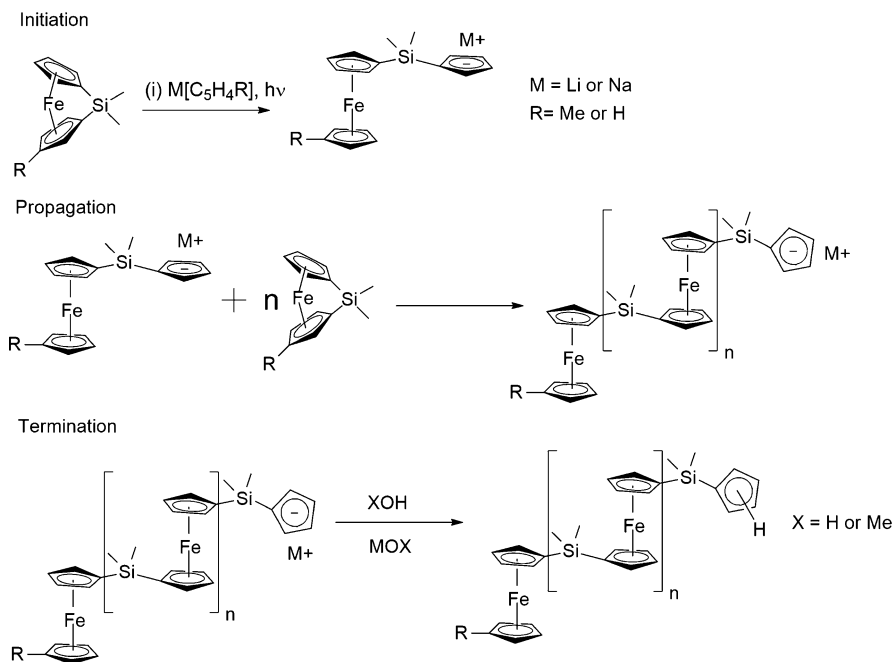
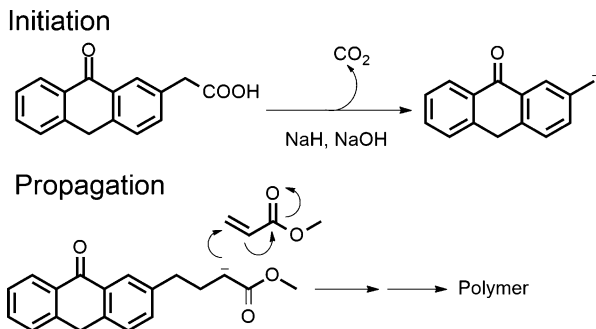


Fig. 29 Ring-opening photopolymerization of ferrocenophanes in the presence of lithium or sodium salt of cyclopentadienyl cation

The nucleophilic metal center then drives the formation of a reactive ring opened species containing cyclopentadienyl anion. This anion is stabilized by a positively charged metal counter ion and leads to the propagation of the ring-opening polymerization by addition of ferrocenophane monomers. The photoreactions are induced using wavelengths greater than 310 nm. This reaction proceeds only in the presence of light, which makes it convenient to add new monomers to make complex polymers [140]. Due to this remarkable control over the addition of monomers, polyferrocenophanes with low polydispersities and a high degree of control

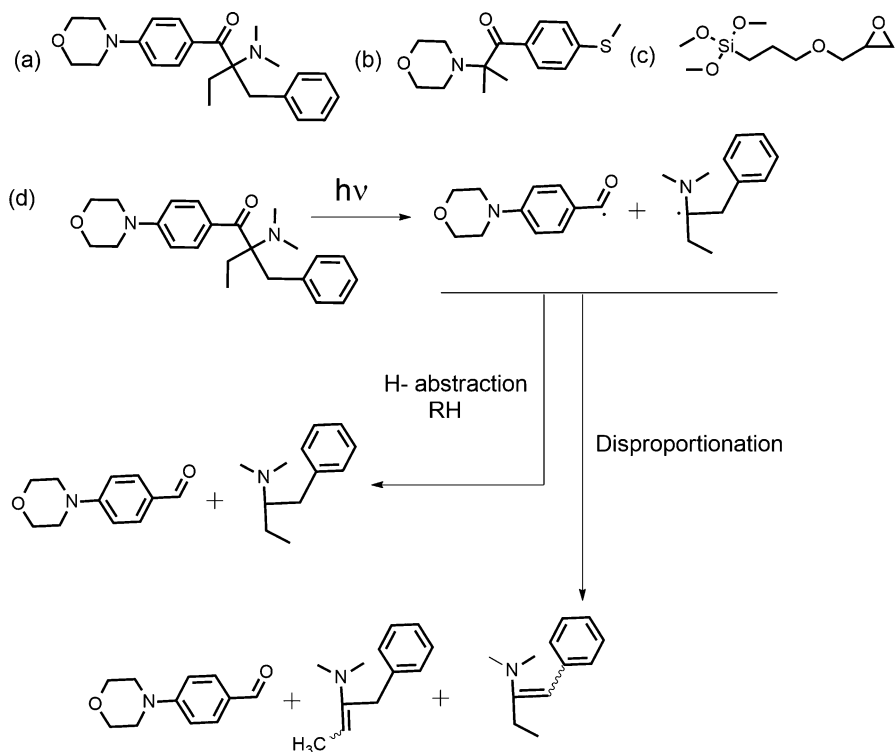


Fig. 30 Photoinitiation of photobase generator that could simultaneously initiate anionic and sol-gel polymerization

over the molecular weights can be obtained. The reaction can be terminated by the addition of a protic solvent which adds hydrogen to the growing negative end of the polymer. Photoinitiated ferrocenophanes have been applied to the synthesis of block copolymers, opening up the possibility of tailoring block copolymers properties suited for different applications [142, 144, 145]. Metal containing polymers and block copolymers synthesized from ferrocenophanes are highly promising functional materials for applications like high refractive index materials, charge transport materials, redox active gels, photoresists for electron beam, plasma etching as well as nanolithography, catalytic materials, etc. [146–156].

Photobases are photolabile compounds capable of releasing a powerful base on irradiation. They have a high reactivity with oxirane type monomers monomer [2, 104, 157]. A recent report featured the simultaneous photoinitiation of anionic and sol-gel polymerization of 3-(glycidyoxypropyl)trimethoxysilane (GPTMS) by an aminoketone based photobase generator [158]. The α -amino acetophenone-based photoinitiators are shown in Fig. 30a–b. They are both well-known type I radical photoinitiators. Upon photoexcitation, the cleavage of the excited photoinitiator yields highly reactive α -amino alkyl and benzoyl radicals.

In the absence of monomers capable of yielding radicals, they undergo H-abstraction and disproportionation, leading to the formation of tertiary amines. The tertiary amino group could initiate both anionic polymerization and sol-gel reaction. The hybrid monomer GPTMS in Fig. 30c undergoes cationic polymerization at the epoxy functional group and sol-gel reaction at the alkoxy silane groups. The aromatic groups around the tertiary amine in the initiator make it stable towards base-sensitive compounds in the patterning media and hence ensure longer shelf stability. After photocleavage, there is a steric release at the amine leaving it highly reactive [11]. The polymerization was carried out in neat monomer with 4 wt% of the photoinitiator. The photoirradiation of the sample was followed by a thermal curing step which was used for the complete drying of the polymerized film. The control over structure and functionality provided by anionic polymerization makes it very desirable for the synthesis of functional materials. A wider application of known techniques and an exploration of new initiating systems and monomers are required to meet this potential.

5 Two-Photon Induced Polymerization

The discussions up to this point have dealt with photopolymerization reactions initiated by the absorption of single photons. Under the condition of a very high-intensity radiation, it is possible for molecules absorbing in UV or visible radiation to simultaneously absorb two lower energy near-IR photons to get excited. This phenomenon is called two-photon absorption. Two near-IR photons of the same or different wavelengths can be absorbed during two-photon absorption. As defined previously, two-photon absorption is a third-order nonlinear optical effect. The energy level to which the electron is excited during a two-photon absorption would be determined by the symmetry of the molecule. In non-centrosymmetric molecules, the lowest two-photon allowed energy level coincides with the lowest one-photon allowed energy level. In a centrosymmetric molecule, the first allowed two-photon energy level is lower than the first one-photon allowed energy level. Two-photon process is an intensity-dependent phenomenon that is confined to the focus of a tightly focused laser beam. Because of this strong confinement, two-photon absorption can be used to initiate spatially confined chemical reactions. Photopolymerization reactions initiated by two-photon absorption are called two-photon polymerization (TPP). Two-photon lithography (TPL) is a lithographic technique based on TPP.

Two-photon absorption has been used to initiate free-radical, cationic, and anionic polymerizations [159]. The efficiency of two-photon absorption by a molecule is described in terms of two-photon absorption cross-section (TPACS) expressed in the GM units ($1 \text{ GM} = 10^{-50} \text{ cm}^4 \text{ s/photon-molecule}$). Due to the low TPACS of common free radical and cationic photoinitiators, early efforts were focused on designing two-photon absorbing molecules with high TPACS. Efficient organic two-photon absorbing (TPA) molecules contain electron-accepting and electron-donating groups bridged by conjugated aromatic constructs of diverse

arrangements. Two-photon absorbers can be dipolar [160–163], quadrupolar [160–172], triagonal [173–177], multibranched [178, 179], dendritic [180–182], oligomeric [170, 183, 184], or polymeric molecules [185–188]. Some typical examples of two-photon sensitizers are shown in Fig. 31.

Two-photon sensitized radical polymerization can be initiated by either a single molecule or a combination of two or more molecules. Single molecules that initiate two-photon polymerization do so from a charge separated excited state. In a two-component initiating system, the excited two-photon absorbing (TPA) molecule interacts with another initiator through electron or energy transfer. Compounds like those shown in Fig. 31 can be combined with previously discussed radical initiators to give efficient initiating systems.

Two-photon absorbing unimolecular initiators for cationic polymerization are rarer than one-component radical initiators [189–191]. Examples of one-component photoinitiating systems used in cationic TPP are shown in Fig. 32. One-component cationic initiators have faced some design challenges due to conflicting electronic criteria for efficient two-photon absorption and photoacid generation [191]. More research is required to reach a molecular understanding of efficient two-photon sensitized photoacid generation from a single molecule. The evidence available so far indicates that PAGs constructed around quadrupolar molecular motifs show a high efficiency as compared to the dipolar ones. Most reports on two-photon initiated cationic polymerization involve two-component initiating system constituting a two-photon absorber and a cationic photoinitiator that interacts with the TPA molecules [192]. Given the availability of the TPA molecule, two-component PI systems can be easily formulated and used. For many applications where high-resolution microstructures are not required, common commercial UV initiators can be used in combination with commercially available PAGs. Two-photon sensitized polymerization is growing in popularity due to the availability of commercial lithographic systems operating with femto-second and picosecond lasers as light sources [193]. TPL has seen a wide adaption in the structuring of biologically relevant microstructures' changes to hardware and light sources are currently driving the maturity of this technique towards commercialization. The recent demonstration of ultra-fast fabrication techniques is a game changer and is poised to revolutionize the applications of TPL in the near future.

6 Scope and Outlook

The application of photopolymers and photopolymerization continues to develop and expand based on the demand of new materials. The demand for sub ten nanometer to few ten nanometer components in electronic circuits has driven the demand for extreme UV (EUV) lithographic systems and materials. The high energy of EUV radiation can cause ionization of materials and excited electrons from inner energy levels. This scenario presents new challenges to the material chemist [194–197]. A new class of photoresists based on nanoparticles is being studied for EUV patterning [198–203]. The emergence and the growth of 3D printing is also a

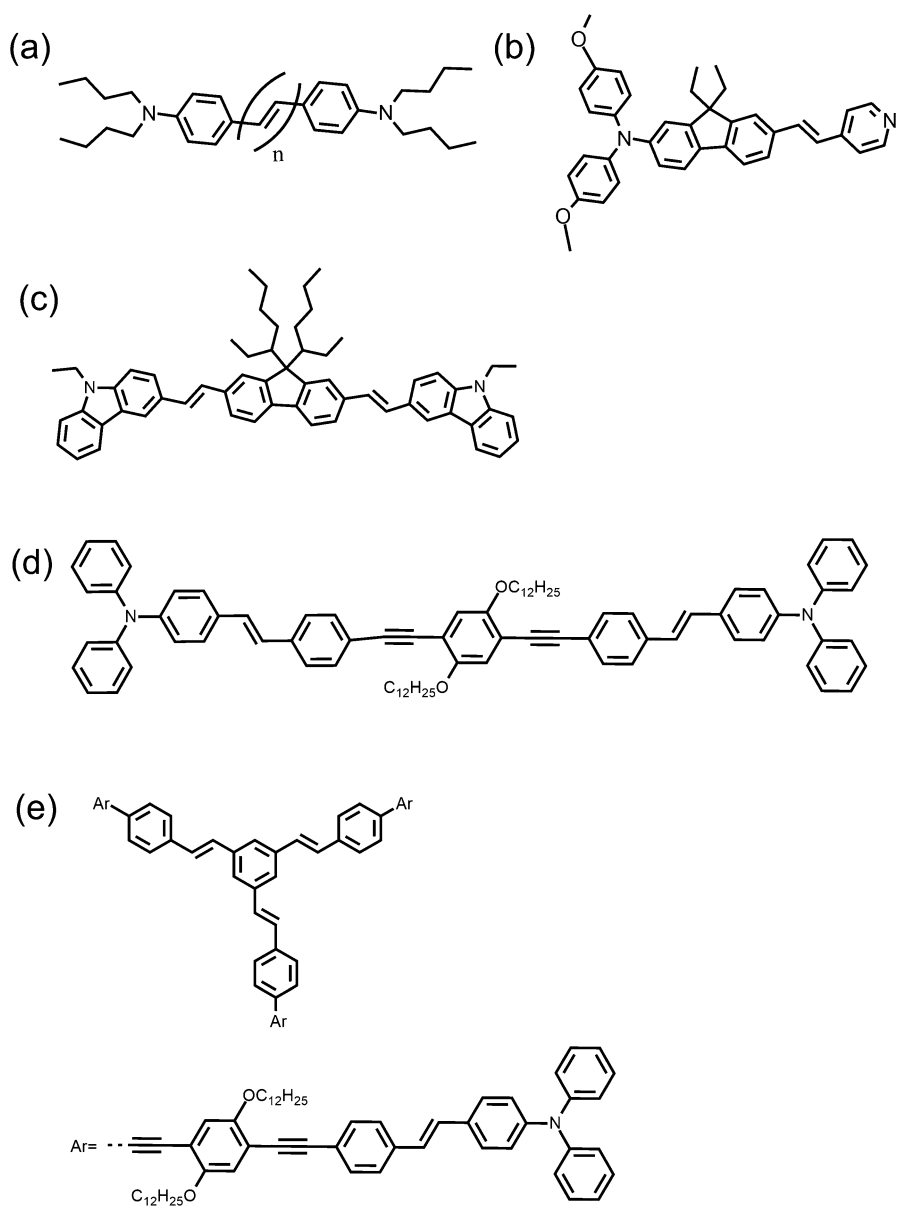
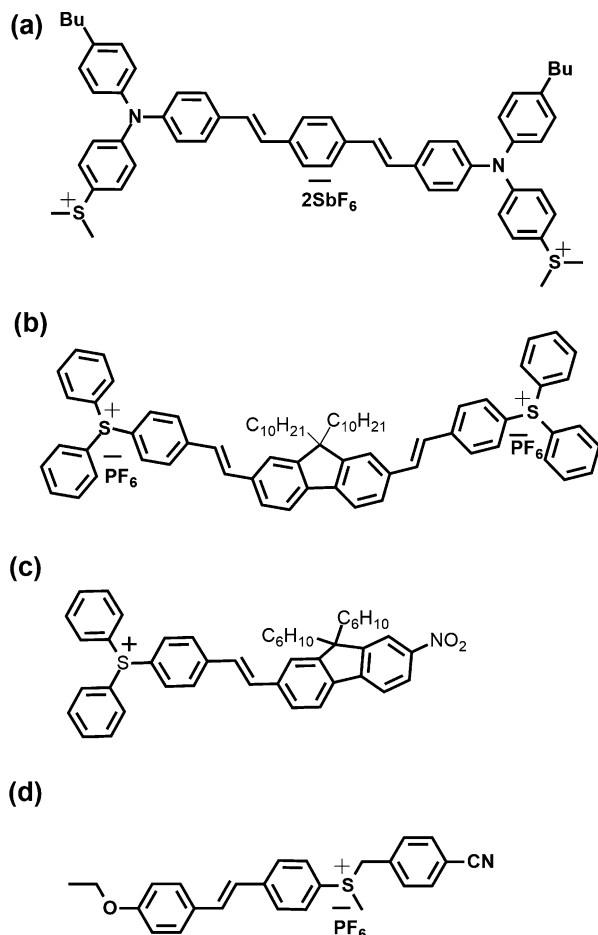


Fig. 31 Examples of two-photon sensitizers; (a) and (b) are examples of dipolar molecules, (c) and (d) are examples of quadrupolar molecules; and (e) is an example of a triangular molecule

Fig. 32 Examples of unimolecular TPA initiators for cationic TPP



major driver behind the growth of novel photopolymerization systems. Recently, De Semione et al. reported ultrafast 3D printing of monolithic 3D structures by engineering the oxygen inhibition of polymerization at the interface between the photopolymer and the cured structure [204]. The development of fast two-photon polymerization and holographic systems demand polymer precursors showing fast response to light and undergoing controlled polymerization [205, 206]. Material demand from medical and industrial applications has led to the development of new photopolymerizable materials [207–210]. The research into medical implants has spurred the growth of many new soft materials which are biocompatible or can be combined with biomaterials to give photo processable materials [211–215]. Human industrial activity and its effect on the environment has been a concern since the turn of the twenty-first century. This concern has contributed to need and awareness of sustainability in the sciences. Many research groups are starting to address the environment in their research for new photopolymers [216–224]. Photopolymers

will continue to play a major role in the future; research into nanomaterial based resists mentioned above may lead to new functional films and microstructures. Large-scale industrial application will continue to be driven by conditions of cost effectiveness. High value applications like microelectronics, biotechnology, health, and space provides a lot of space for growth and development.

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