

LIGHT INDUCED PROCESSES FOR THE SYNTHESIS OF POLYMERS WITH COMPLEX STRUCTURES

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Abstract: Light induced reactions are based on the absorption of light that excites the electrons of a molecule and can, under favorable circumstances, lead to dissociation, isomerization, abstraction, electron or energy transfer, and bond formation. These reactions have been the subject of many studies in various fields including organic chemistry, molecular biology, electronics etc. Light induced reactions can advantageously be utilized in the field of polymer chemistry. Among them, light induced polymerization is of enormous commercial importance. Techniques such as curing of coatings on wood, metal and paper, adhesives, printing inks and photoresists are based on photopolymerization. There are some other interesting applications, including production of laser video discs and curing of acrylate dental fillings. In this chapter, general methods for the light induced polymerization processes involving radical and ionic reactions are described. Special emphasize is devoted to their application to more complex macromolecular structures such as block, graft and star copolymers, and polymer nanocomposites based on clay and metal.

Keywords: Photoinitiated free radical polymerization; Photoinitiated cationic polymerization; Block copolymers; Graft copolymers; Polymer/metal nanocomposites; Polymer/clay nanocomposites

1. Introduction

Polymerization initiated by light induced processes, referred as photopolymerization, has found many applications including printing inks, adhesives, surface coating, microelectronics, printing plates and 3D microfabrication. In these applications, a photosensitive molecule, as a polymerization initiator, is

excited by irradiation leading to the formation of reactive species capable of converting liquid monomer mixtures into solid structures. Besides energy, cost and environmental considerations, light induced processes have the advantage of providing homogeneous conditions and high reactivity that cannot be achieved by conventional systems.

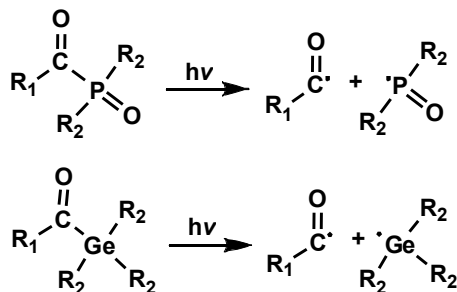
Light induced polymerizations are used not only in the formulations containing bi- and multi-functional monomers leading to the formation of cross-linked networks, but also synthesis of linear and complex macromolecular structures such as block and graft copolymers, and star polymers. Additionally, the photopolymerization strategy can be of general use in the syntheses of metal and clay/polymer nanocomposites. Both radical and cationically acting systems have successfully been employed, and the mechanisms of initiation have been studied in detail. Compare to the cationic mode, free radical photoinitiation is in more advanced state because of the availability of wide range of monomer formulations and photoinitiators with broad spectral sensitivity in UV and visible range. Many efforts have been paid to develop photoinitiators for both polymerizations acting at different wavelength ranges.

In this paper, we describe photochemical routes for the synthesis of novel complex macromolecular structures and hybrid nanocomposites possessing linear and crosslinked polymeric structures as well as inorganic components. Such hybrid nanocomposites will be potentially attractive in size related bio, electronic and catalytic applications. Before discussing the preparation of such complex macromolecular structures, it is essential to present photoinitiating systems for the examples recently reported in the authors' laboratory.

2. Photoinitiating Systems

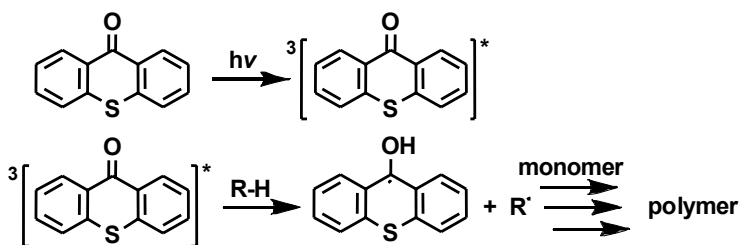
2.1. PHOTOINITIATING SYSTEMS FOR FREE RADICAL POLYMERIZATION

Photoinitiated radical polymerization may be initiated by both cleavage (type I) and H-abstraction type (type II) initiators. The radical generation processes of type I and type II photoinitiators are entirely different. While type I photoinitiators generate initiating radicals by a unimolecular cleavage reaction, type II initiators undergo bimolecular hydrogen abstraction reactions. The main cleavable photoinitiators include benzil dimethyl ketal, benzoin ethers, alkyl hydroxyphenyl ketones, dialkoxyacetophenones, benzylcyclohexanol, amino alkylketones, acylphosphine oxides and acyl germanes. Except for acylphosphine oxide and acylgermane photoinitiators, the cleavage takes place at carbon-carbon bond. Long wavelength and visible light active acylphosphine oxide and acylgermane photoinitiators undergo cleavage at carbon-phosphorous and carbon-germane bonds upon irradiation, respectively (Scheme 1).^[1, 2]



Scheme 1. Photoinduced cleavage of acylphosphine oxides and acylgermane initiators.

Photolysis of aromatic ketones, such as benzophenone, thioxanthenes, benzil, and quionones, in the presence of hydrogen donors, such as alcohols, amines, or thiols, leads to the formation of a radical produced from the carbonyl compound (ketyl type radical) and another radical derived from the hydrogen donor. The photopolymerization of vinyl monomers is usually initiated by the radical produced from the hydrogen donor. The ketyl radicals are usually not reactive toward vinyl monomers due to the steric hindrance and the delocalization of unpaired electron. The overall mechanism of the photoinitiation is represented in Scheme 2 on the example of thioxanthone.



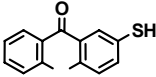
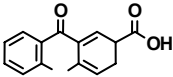
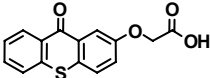
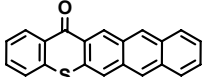
Scheme 2. Photoinitiated free radical polymerization by using thioxanthone.

One of the disadvantages of type II systems concerns high usage of high volatile and odorous amines as hydrogen donors.^[3] Poly(ethylene oxide) and poly(ethylene imine) based dendrimers of the following structures have been successfully used as polymeric hydrogen donors to replace low molecular weight amines in the formulations. As it will be shown later, these molecules act as precursors for graft and star copolymers (*vide infra*).

As part of our efforts to avoid problems associated with the amine hydrogen donors, we have recently reported several new thioxanthone derivatives as photoinitiators for free radical polymerization. Interestingly, these photoinitiators do not require an additional coinitiator, that is, a separate molecular hydrogen donor. The structures and the mode of action of such one-component photoinitiators are shown in Table 1.

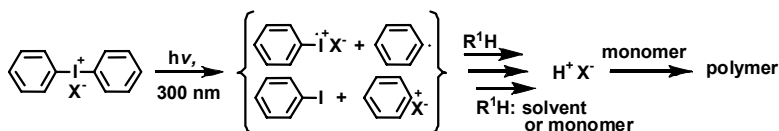
Besides hydrogen donors, photoinitiators themselves can be incorporated into polymeric structures. This way, the macromolecules having covalently bonded chromophoric groups overcome the problems associated with high volatility and high migration often observed with low molar mass analogous. The two recent examples concern attachment of thioxanthone photoinitiators into polymers as pendant groups by photoinitiator synthesis from the polymeric precursors^[9] and by taking advantage of two click reactions, namely Diels–Alder and 1,3-dipolar cycloaddition reactions.^[10]

TABLE 1. Thioxanthone based one-component photoinitiators.

Photoinitiator	Structure	Mode of action	Ref.
2-Mercaptothioxanthone		Hydrogen abstraction	[4, 5]
2-(9-Thioxanthone-2-thio)acetic acid		Hydrogen abstraction	[6, 7]
2-(9-Thioxanthone)acetic acid		Hydrogen abstraction	[6, 7]
Thioxanthone-anthracene		Endoperoxide formation	[8]

2.2. PHOTOINITIATING SYSTEMS FOR CATIONIC POLYMERIZATION

Although several non-salt structured cationic photoinitiators were reported, most of the photoinitiated cationic polymerization applications are based on onium-salt type initiators, namely diaryliodonium, triarylsulphonium and *N*-alkoxy pyridinium salts. Upon photolysis, these initiators undergo irreversible photo-fragmentation to produce cation radicals and Bronsted acids capable of initiating cationic polymerization (Scheme 3).^[11]



Scheme 3. Photoinitiated cationic polymerization by using iodonium salt.

Unfortunately, onium salts have absorptions at 300 nm regions which limit their use in various applications including curing of pigmented systems. In order to have longer wavelength activity particularly at visible range several indirect methods were proposed. Adaption of the initiating system to longer

wavelengths can be achieved in three ways: (i) oxidation of free radicals by onium salts (also called free radical promoted cationic polymerization), (ii) electron transfer between photoexcited sensitizer and onium salt, and (iii) electron transfer in photoexcited charge transfer complexes of certain onium salts.^[12] For example, we have recently shown that acylgermane based photoinitiators can successfully be used in free radical promoted cationic polymerization of appropriate monomers. Because of the fact that these free radical photoinitiators exhibit long wavelength characteristics (due to the well-known interaction of the lone pair of the carbonyl oxygen with the free d-orbitals of the germanium), the spectral sensitivity of cationic polymerization was easily extended to the visible range. As can be seen from Figure 1, typical onium salt, diphenyl iodonium salt is transparent at the visible range where acyl germane photoinitiator strongly absorbs the light.

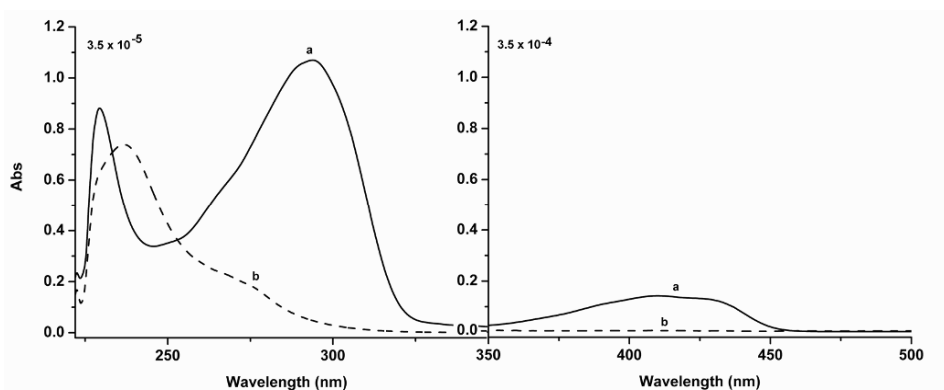
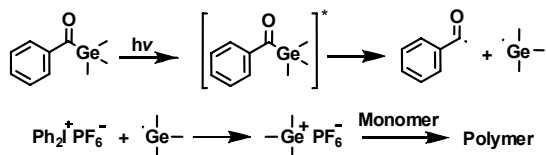


Figure 1. Optical absorption spectra of benzoyltrimethylgermane (BTG) (a) and $\text{Ph}_2\text{I}^+\text{PF}_6^-$ (b) in CH_2Cl_2 .

Typical acylgermane photoinitiator, benzoyltrimethylgermane (BTG) in conjunction with an iodonium salt was shown to be active in initiating cationic polymerization of various monomers at wavelengths up to 450 nm.^[13] Detailed polymerization and radical scavenging experiments revealed that trimethylgermyl radicals formed from the homolysis of carbon german bonds in the primary step undergo electron transfer reaction yielding germanium cations capable of initiating cationic polymerization (Scheme 4).



Scheme 4. Photoinitiated cationic polymerization by using benzoyltrimethylgermane in the presence of $\text{Ph}_2\text{I}^+\text{PF}_6^-$.

Polynuclear aromatic hydrocarbons can also induce photoinitiated cationic polymerization at long wavelengths. Quite unusual example of this type of photosensitization by using a dithienothiophene derivative, namely 3,5-diphenyldithieno [3,2-*b*:2,3-*d'*] thiophene (DDT), was recently reported.^[14] This compound, known as a precursor for conducting polymers, absorbs light at above 350 nm (Figure 2) and initiates the polymerization in the presence of iodonium salt.

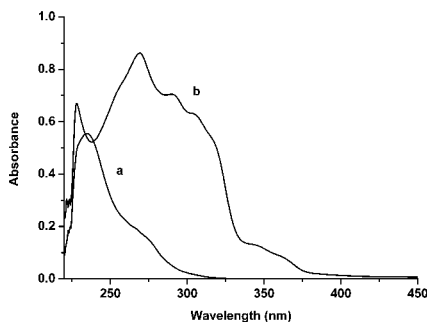
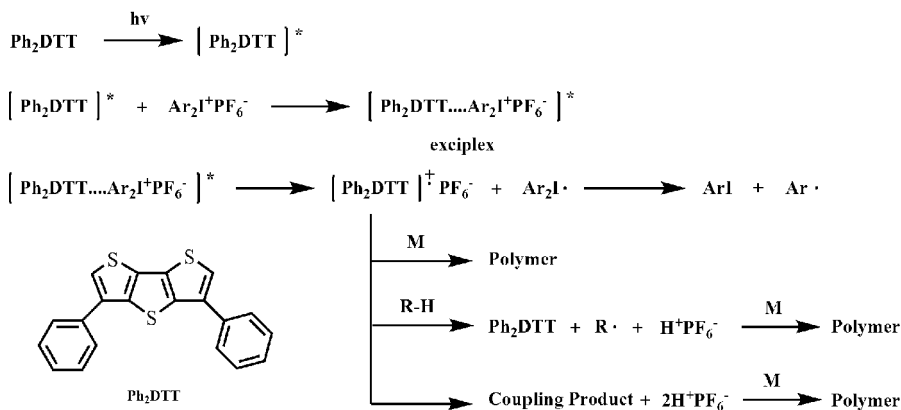


Figure 2. UV spectra of 3.5×10^{-5} M $\text{Ph}_2\text{I}^+\text{PF}_6^-$ (a) and 3.5×10^{-5} M 3,5-diphenyldithieno[3,2-*b*:2,3-*d'*]thiophene (DDT) (b) in CH_2Cl_2 .

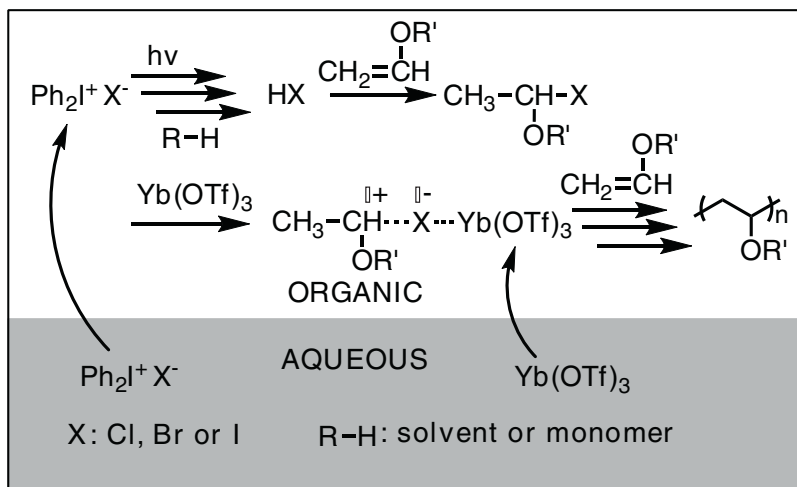
A mechanism (Scheme 5) involving formation of exciplex and subsequent electron transfer from excited DDT to iodonium ions was proposed.



Scheme 5. Photoinitiated cationic polymerization by using 3,5-diphenyldithieno[3,2-*b*:2,3-*d'*]thiophene (DDT) in the presence of $\text{Ph}_2\text{I}^+\text{PF}_6^-$.

How wide photoinitiated cationic polymerization can be used in different applications on an industrial scale depends on the economical and environmental advantages offered by the particular process involved. For example, vinyl ethers can be rapidly photopolymerized by cationic means which overcomes limitations of molecular oxygen inhibition and avoids problems related to monomer toxicity associated with the more conventional free radical polymerization of acrylates which are widely used in industrial applications. Recently introduced initiating system for the polymerization of this class of monomers, consisting of diphenyliodonium halides and a zinc halide Lewis acid further eliminates the use of toxic arsenic and antimonate based anions.^[15, 16] Such polymerization can successfully be performed in aqueous medium in the presence of the water-tolerant Lewis acid, ytterbium triflate.^[17] Obviously, this process would open new pathways for many applications employing water-borne systems. The polymerization consists of two-steps; (i) photoinduced adduct formation and (ii) subsequent propagation with the aid of Yb(OTf)₃ (Scheme 6). The fast polymerization exhibited an explosive character so that the monomer conversion and molecular weights of the resulting polymers are very dependent on the experimental conditions, such as temperature and stirring manner.

The following sections will focus on the light induced reactions in the synthesis of polymers with complex structures. Subjects to be discussed include: (i) block and graft copolymers by photopolymerization, (ii) star polymers by photopolymerization, and (iii) *in situ* synthesis of metal or clay/polymer nano composites by light induced processes.



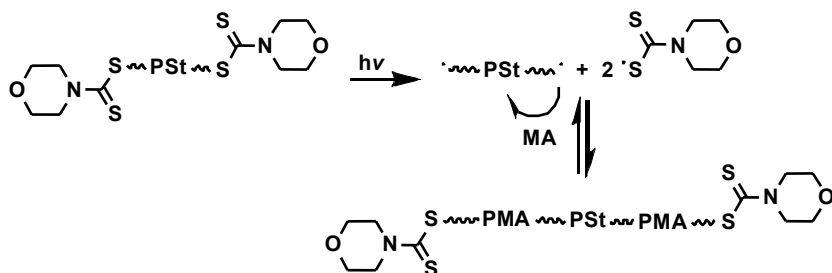
Scheme 6. Photoinitiated cationic polymerization of vinyl ethers in aqueous medium.

In general photoinitiating systems in classical polymerization of monofunctional monomers do not provide control over the molecular weight and structure. However, they still contribute to the synthesis of various macromolecular structures. In particular, block and graft copolymers can be prepared by using main chain and side chain polymeric photoinitiators, respectively (Scheme 7). By photolysis, active sites are produced at the chain ends or side chains, which serve as initiating moieties in the polymerization of a second monomer. In this manner, copolymers with almost quantitative block or graft yields can be obtained, for the fact that side reactions and, thus, homopolymer formation are minimized as a result of the low polymerization temperature. A wide range of monomer combinations have been studied, and the detailed strategies and mechanisms were discussed.^[18–20] Herein, we present recent examples to demonstrate the versatility of the light induced processes for block, graft and star copolymer formation.



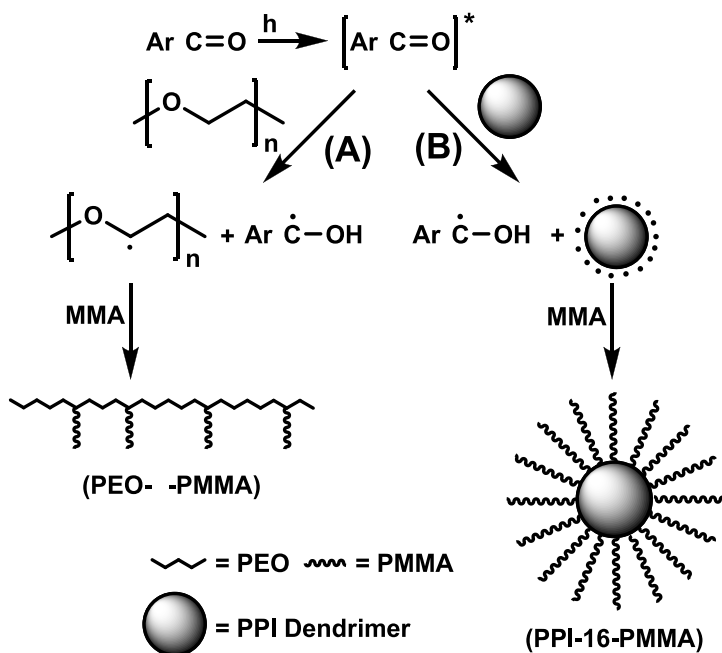
In block copolymerization the most important step is the incorporation of photoactive groups at polymer chain ends. For this purpose, usually controlled polymerization methods were employed as they yield polymers with well-defined structure and desired functionality. In a recent study,^[21] photoactive morpholine-4-dithiocarbamate terminated polystyrene was prepared by the reaction of dibrominated polystyrene, obtained by Atom Transfer Radical Polymerization (ATRP), with morpholine-4-dithiocarbamate sodium salt in dimethyl formamide. The capability of this photoactive precursor polymer to act as a photoinitiator for the block copolymerization of methyl acrylate (MA) was examined (Scheme 8).^[21] Polymerization shows a “living” character at up to 25% conversions and produces well-defined polymers with molecular weights

close to those predicted from theory and relatively narrow polydispersities ($M_w/M_n \sim 1.40$). Both functionalization and light induced steps involve controlled polymerization processes.



Scheme 8. Block copolymerization of polystyrene with methyl acrylate by photoiniferter process.

When poly(ethylene oxide) (PEO) is used as hydrogen donors in photoinitiated free radical polymerization of methyl methacrylate by using benzophenone or thioxanthone as photosensitizers, graft copolymers consisting of hydrophilic backbone and hydrophobic side chains are readily formed (*Scheme 9A*).^[22] A similar hydrogen abstraction strategy was applied to exterior methylenes of poly(propylene imine) based dendrimers yielding star copolymers (*Scheme 9B*).^[23]



Scheme 9. Synthesis of graft and star copolymers by light induced hydrogen abstraction process.

The effect of generation number of the dendrimer on photoinitiation efficiency and molecular weight of the resulting polymers was investigated. Glass transition temperatures and particle size measurements of the resulting polymers indicated the presence of nearly stretched polymer chains around the dendrimers.

2.4. LIGHT INDUCED SYNTHESIS OF METAL/POLYMER NANOCOMPOSITES

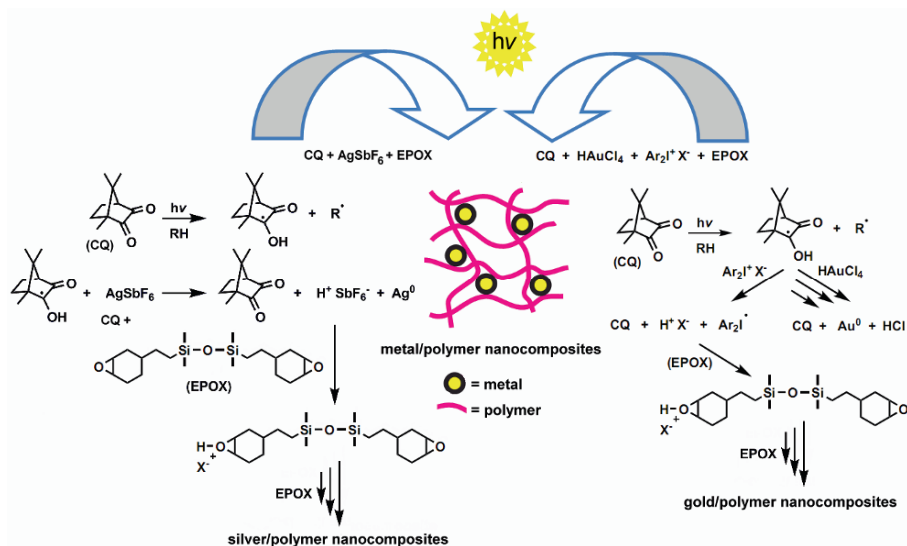
Nanocomposite materials containing metal nanoparticles and polymer matrix may exhibit novel physical and chemical properties that are of high scientific and technological importance. These materials combine the physical properties of small size metal nanoparticles with those of polymeric materials in a beneficial manner. Many advanced optoelectronic and sensor devices are based on the fabrication of these materials.^[24–27] Because of their high surface free energy, nanoparticles tend to agglomerate. A key challenge for a potential technological use is the achievement of homogeneous dispersion of the thermodynamically unstable nanoparticles. Various methods have been applied. Generally, applied methodology is detaining nanoparticles during the preparation by adding protecting agents or setting them in an inert environment. Among them, photochemical methods involving light induced reduction of metal ions such as Ag and Au complexes are of particular interest as they find a wide range of application including synthesis of metallic colloids, and metallization and patterning of films.

Recently, we have introduced a novel approach for the preparation of metal–polymer nanocomposites, in which nanoparticle formation and UV crosslinking process were accomplished in one pot by simply irradiating appropriate formulations, obtaining the homogeneous distribution of the nanoparticles within the polymer network without any macroscopic agglomeration. Silver or gold nanoparticles and initiating species were formed in a single redox process. Acrylate and epoxy resins polymerizing by free radical and cationic mechanisms, respectively, were successfully used in the preparation of such composites (Table 2).

TABLE 2. Light induced synthesis of metal/polymer nanocomposites.

Polymer matrix	Metal nanoparticle	Photoinitiator	Polymerization mechanism	Ref.
Epoxy	Silver	DMPA-AgSbF ₆	Cationic	[28]
Silicon epoxy	Silver	CQ/Amine-AgSbF ₆	Cationic	[29]
Acrylate	Gold	Irgacure 2959	Radical	[30]
Silicon epoxy	Gold	CQ/Amine-Rhodorsil	Cationic	[31]

Scheme 10 shows typical reactions for the *in situ* synthesis of silver and gold-cross-linked epoxy nanocomposites by photoinduced electron transfer and cationic polymerization processes. Simply irradiating the mixture containing epoxy resin and metallic salt the presence of a visible light photoinitiator, camphorequinone (CQ) without necessity of an external reducing agent, leads to the formation of desired composites. Compared to chemical cross-linking of metal nanoparticle decorated polymer matrices, the method described here is quite attractive since it allows for simultaneous metal nanoparticle and network formation which secures the resulting structure, and permits long-term stability.

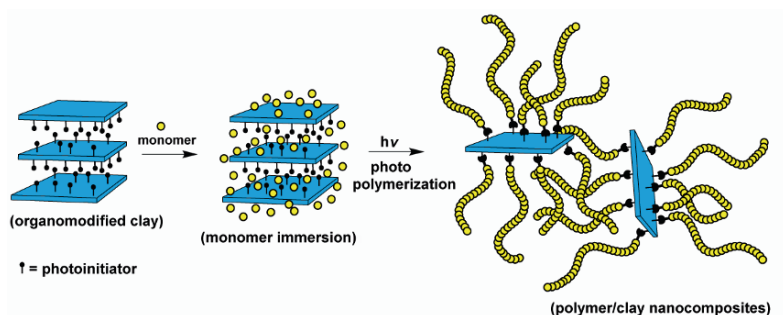


Scheme 10. Light induced synthesis of metal/epoxy nanocomposites.

2.5. LIGHT INDUCED SYNTHESIS OF CLAY/POLYMER NANOCOMPOSITES

Polymer-layered clay nanocomposites receive interest because of their improved physical and chemical properties due to small size or large surface area of the clay with nanoscale dimension.^[32–34] Although many methods have been tested, the dispersing *in situ* polymerization may be the most desirable method for preparing nanocomposites because the types of nanoparticles and the nature of polymer precursors can be selected. Photopolymerization methodology allows *in situ* synthesis of polymer nanocomposites using organophilic montmorillonite (MMT) as the layered clay. MMT clay was ion-exchanged with photosensitive molecule which acts as both suitable intercalant- and photo-initiator. These modified clays were then dispersed in a selected monomer in different loading

degrees to facilitate in situ photopolymerization.^[35] The overall process is presented in [Scheme 11](#).



Scheme 11. Light induced synthesis of clay/polymer nanocomposites.

Versatility and convenience of the method was recently demonstrated by using organo modified clay with N-phenacyl,N,N-dimethylanilinium hexafluoro phosphate (PDA) in the polymerization of methyl methacrylate. Polymerization through the interlayer galleries of clay resulted in the formation of exfoliation/intercalation structures.

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