

Review

Photochemical Production of Interpenetrating Polymer Networks; Simultaneous Initiation of Radical and Cationic Polymerization Reactions

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Abstract: In this paper, we propose to review the ways to produce, through photopolymerization, interpenetrating polymer networks (IPN) based, e.g., on acrylate/epoxide or acrylate/vinylether blends and to outline the recent developments that allows a one-step procedure (concomitant radical/cationic polymerization), under air or in laminate, under various irradiation conditions (UV/visible/near IR; high/low intensity sources; monochromatic/polychromatic sources; household lamps/laser diodes/Light Emitting Diodes (LEDs)). The paper illustrates the encountered mechanisms and the polymerization profiles. A short survey on the available monomer systems and some brief examples of the attained final properties of the IPNs is also provided.

Keywords: interpenetrating polymer networks; radical initiators; photopolymerization; photoinitiators

Glossary of Terms

Light Emitting Diode	LED
Interpenetrating polymer networks	IPNs
Semi-interpenetrating polymer networks	SIPN
Hexanediol diacrylate	HDDA
3,4-epoxycyclohexylmethyl-3'4' epoxycyclohexyl carboxylate	EPOX
Trimethylolpropane triacrylate	TMPTA
Tri(ethylene glycol) divinyl ether	DVE-3
4-cyclo-hexane dimethanol divinyl ether	CHVE
diglycidyl ether of bisphenol A based epoxy resin	EP
Poly(ethylene glycol) diacrylate	PEGDA
Photoinitiating systems	PIS
Diphenyliodonium salts	DPI
Triarylsulfonium salts	TAS
Cationic Polymerization	CP
Free Radical Polymerization	FRP
Photoinitiating system	PIS
Photoinitiator	PI

1. Introduction

Interpenetrating polymer networks (IPNs) consist in two or more chemically different networks which are at least partially interlaced on a polymer scale but, in theory, are not covalently bonded to each other, although in practice some type of grafting between the networks invariably occurs. One can also define: (i) semi-interpenetrating polymer networks SIPN (they contain networks and linear or branched polymer(s) that can be separated) and (ii) sequential semi-interpenetrating polymer networks. IPNs and SIPNs can be formed simultaneously or sequentially [1–5]. All these arrangements belong to hybrid systems (systems that contain two or more different chemical functionalities) and lead to novel properties resulting from the physico-chemical nature of the monomer/polymer used and the degree of phase separation, the formed polymers being not miscible.

IPNs have applications, e.g., as sound- and vibration-damping materials over a broad temperature and frequency range (IPNs often result in a 10–100 nm finely-dispersed phase but, when the micro-heterogeneous phase domains are in the 10–20 nm range, the glass transition is relatively broad and leads to materials that can absorb energy), in impact resistant materials, toughened plastics, membranes, ion-exchange resins, pH-sensitive systems, electrical insulation, coatings and encapsulants, adhesives, bearers of medicines, biomedical purposes, hydrogels, and materials for optics.

IPNs are synthesized from a blend of two multifunctional monomers that polymerize through two different routes (e.g., radical and cationic). This usually occurs according to a thermal process. On the other hand, photopolymerization techniques (as extensively described in [6–17]) are very well known for applications in various areas. They have also been proposed to produce IPNs, the environmentally-friendly character of this process (no volatile organic compounds released, room temperature operation, energy saving), the high polymerization rates attained under relatively intense UV irradiation and the easy triggering of the reaction (light on/off) being the main practical advantages [18].

A photoinitiating system (PIS) containing at least one or two photoinitiators PI is used to start the polymerization reactions (see below).

In this paper, as a matter of introduction, we will provide a short survey on the examples of available monomer blends suitable for the manufacture of IPNs under light exposures as well as some brief examples of the final properties of the IPNs that can be attained. Then, considering mostly acrylate/epoxide or acrylate/(di)vinylether blends as the starting materials, we will recall the different strategies for getting the photopolymerization reaction (one-step or two-step procedures) and stress again the traditional use of high intensity UV sources. We wish to focus the paper, however, on the particular recent research developments that open novel possibilities for the synthesis of IPNs as they allow a concomitant radical/cationic polymerization through an easy one-step (simultaneous) procedure under various irradiation conditions in term of lights (near UV/visible/near IR wavelength ranges, high/low intensity; monochromatic/polychromatic illumination) and irradiation devices (household lamps and light emitting diode (LEDs), laser diodes, LEDs for industrial applications). The reaction mechanisms as well as the achieved polymerization performance will be detailed.

2. Monomers for the Manufacture of IPNs through Photopolymerization

Various monomer blends have been applied for the manufacture of IPNs. Different examples can be given: acrylate/epoxide, (e.g., hexanediol diacrylate (HDDA)/3,4-epoxycyclohexylmethyl-3'4'-epoxycyclohexyl carboxylate (EPOX)), trimethylolpropane triacrylate (TMPTA)/EPOX, TMPTA/diglycidyl ether of bisphenol A based epoxy resin EP, TMPTA/tri(ethylene glycol) divinyl ether (DVE-3), TMPTA/4-cyclo-hexane dimethanol divinyl ether (CHVE), fluorinated acrylate/epoxide, vinylether/acrylate, vinylether/maleate, vinylether/maleimide or oxetane/acrylate blends, (see e.g., in [19–35]) anthracene-labeled polystyrene/methyl methacrylate MMA/ethylene glycol dimethacrylate [36], polyisobutene/polystyrene [37], polyacrylate/polybenzoxazine [38], acrylic/liquid crystals [39,40], 2-hydroxyethyl methacrylate/*N*-vinyl-2-pyrrolidone [41], polyurethane/poly(2-hydroxyethyl methacrylate) [42], calcium alginate/dextran-HEMA [43].

The photopolymerization of bisphenol-*A*-diglycidyl dimethacrylate/bisphenol-*A*-diglycidylether/tetrakis (methacryloxy ethoxy) silane [44,45], siloxane or silsesquioxane/ α,ω -nonconjugated dienes [46] leads to organic-inorganic IPNs. It should be noted that tetrakis (methacryloxy ethoxy) silane only forms an inorganic material after hydrolysis.

Semi-interpenetrating polymer networks have also been obtained by UV curing of, e.g., acrylate monomers dispersed in a polymer matrix (polyurethane, polyvinyl chloride, polymethyl methacrylate, polybutadiene, polyisoprene) [47], hyaluronic acid/hydroxyethyl methacrylate derivatized dextran (usable in 3D hydrogel bioprinted constructs) [48]. IPNs from acrylate/epoxidised polyisoprene blends have been reported [49].

IPNs have been prepared, e.g., from a trifunctional thiol/poly (ethylene glycol) (PEG)-diallyl blend via a thiol-ene coupling reaction [50].

A mixture of poly (ethylene glycol) diacrylate (PEGDA) and hexanediol diacrylate (HDDA) monomers polymerized within a hexagonal liquid crystalline template may form an IPN-type material [51]. Other systems where the characteristics or the properties in term of IPNs are not (totally) established have been only described as (i) hybrid polymers, e.g., materials derived from a thiol-ene and cationic

polymerization using two Photoinitiators (PIs) [52] or one PI [53], cycloaliphatic epoxide/acrylate monomers [54–57], 3,4-epoxy-cyclohexyl-methyl methacrylate hybrid monomers [58], multifunctional glycidyl ether (or 3,3-disubstituted oxetane)/acrylate blends [59], thiol-epoxy/thiol-acrylate hybrids [60] or (ii) dual cure systems (they contain two or more different functionalities that polymerize using two different curing processes such as thermal/photochemical or photochemical/air drying), e.g., polymers formed from a glycidyl methacrylate/trimethylolpropane oxetane/acrylate blend [61].

Although most of works are carried in film matrix, other media can be used such as microemulsions [62]. Some kinetic studies on the photoinduced quasi-simultaneous IPN synthesis have been published [63–65]. Structure–property relationships in acrylate/epoxy IPNs have been investigated as a function of the reaction sequence and composition (the relationships between phase morphology, processing and physical properties of the IPNs are claimed as complex and not predictable *a priori*) [66].

3. Examples of Final Properties for Photochemically Produced IPNs

The monomer composition has a great importance in controlling the final conversion and the glass transition temperature of the polymer. The photocuring sequence and mode affect the final resin conversion and the morphology of the final material. Light induced polymerization of monomer blends have led to IPNs exhibiting interesting tailor-made properties. Some examples are shown here.

A high-damping effect, a lower shrinkage and a better adhesion was noted in acrylate/epoxide IPNs [28]. The reduction of the shrinkage limits the buildup of the internal stress and improves the adhesion. For example, the percentage shrinkage is 89.89 vs. –13.25 and the adhesion tape is 100% vs. 0% for HDDA/EPOX (50/50) and HDDA, respectively (100% adhesion for EPOX alone) [28]. Broad T_g peaks are observed: 153, 140 and 190 °C for HDDA/EPOX, HDDA and EPOX, respectively. Low shrinkage materials are of interest in applications where length variation should be avoided as far as possible (e.g., in 3D modelling, preparation of composites or in the manufacture of optical elements). In the same way, a reduced volume shrinkage in holographic photopolymers based on organic/inorganic hybrid IPNs [67] was achieved; thiol-ene/thiol-epoxy hybrid networks [68] led to a significantly reduced shrinkage and stress, a highly crosslinked and high T_g polymer as well as robust mechanical properties.

High surface hydrophobicity for the films together with good adhesion properties can be obtained on polar substrates. This is exemplified [68] by the observed contact angles (water; 110°, 78° and 115°) for the EP/fluorinated acrylate (FA) (50/50) IPN, EP and FA, respectively.

Both hardness and flexibility have been obtained in IPNs for coating applications [29]. Persoz hardness of 300 s can be reached. For example, IPNs that combine a stiff and glassy polyacrylate with a highly flexible and elastomeric polyvinylether are well adapted for applications where an ultrafast process and specific properties (hardness, elasticity and chemical resistance, *etc.*) are required.

Interesting extracting properties, e.g., selective solid phase extraction of Cd^{2+} with ion-imprinted IPN gel [69] and enhanced heavy metal ion removal [70] have been mentioned. Spatially graded morphology was shown in polystyrene/poly (methyl methacrylate) IPNs [71].

Hydrogels have received a considerable attention for use in tissue engineering scaffolds (with gelatin methacrylamide/PEG [72], silk fibroin/poly(vinyl alcohol) [73], silk fibroin/gelatin [74] or others [75]), cartilage tissue engineering (with poly (ethylene glycol)/agarose [76]), vascular tissue

engineering (dextran/gelatin [77]). Mechanically enhanced properties (e.g., Young's moduli) rivaling those of natural load-bearing tissues was found in a poly (acrylic acid)/end-linked poly (ethylene glycol) crosslinked material [78]. A larger domain of tensile modulus (192–889 kPa compared to 175–555 kPa for single corresponding networks) [50] can be covered in systems used as scaffolds for the preparation of hydrogels. Poly (ethylene glycol)/poly (acrylamide) hydrogels can serve as a support of enzyme immobilization [79]. The polymerization of amphiphilic hydrogels under visible and UV light is interesting as the process conditions are very mild and the reaction can be carried out in direct contact with drugs, cells and tissues. Injectable hydrogels provide an effective and convenient way to administer a wide variety of bioactive agents such as proteins, genes, and even living cells [80]. Drug delivery purposes can be achieved with e.g., poly (*N*-isopropylacrylamide)-modified poly(2-hydroxyethyl acrylate) hydrogels [81], poly (ethylene glycol)-*co*-poly (*e*-caprolactone) diacrylate macromer and hydroxypropyl guar gum [82]. A recent review on the design and the applications of IPN hydrogels has been published [83].

The high stiffness, the ultimate strength and strain, and the high stability of methacrylic alginate IPN gel beads are highly useful in designing encapsulation devices with improved structural durability for a broad array of prokaryotic and eukaryotic cells used in biochemical and industrial applications [84]. Photopolymerization provides a unique way to form an IPN gel in a fast and controllable manner usable for the direct photoencapsulation of cells. Gels can be formed *in situ*, providing an easy *in vivo* placement that can be of benefit for applications in tissue engineering. Photopolymerization can also be used to create scaffolds with specific nanoscale topography to promote control of cell migration and function [85].

Among other properties of UV produced IPNs, one can cite biocidal properties using a poly(ethylene terephthalate)/polyamide IPN [86], durable hemocompatibility [87], shape-memory properties (e.g., strain fixity rate and strain recovery rate above 93% using polyesterurethane/poly (ethyleneglycol) dimethacrylate IPNs; the hydrophilicity, transition temperatures and mechanical properties of the IPNs can be easily adjusted through the network compositions so that promising potential clinical or medical application are expected [88], bioactivity (corneal epithelial wound healing) [89], using fibrin–polyethylene oxide IPNs [90], construction of multilayer ultrathin films (with poly (vinylpyrrolidone)/poly (urushiol) [91]), gradient property in polyurethane/poly(2-hydroxyethyl methacrylate semi-IPNs usable in biomedical applications [92].

Photochemically synthesized IPNs can also be used in the generation of nanostructures [93,94], as p and n dopable films for organic photovoltaic devices [95], in the surface modification of polyethylene terephthalate angioplasty balloons (hydrophilic poly (acrylamide-*co*-ethylene glycol) IPN coating [96]), for cell adhesion and proliferation *in vitro* allowing a robust biomaterial (poly (ethylene glycol)/collagen IPNs) for elastomeric tissue scaffold applications [97], in dentistry (for getting teeth protection from acid demineralization [98] or the reinforcement of restorative composites [99]).

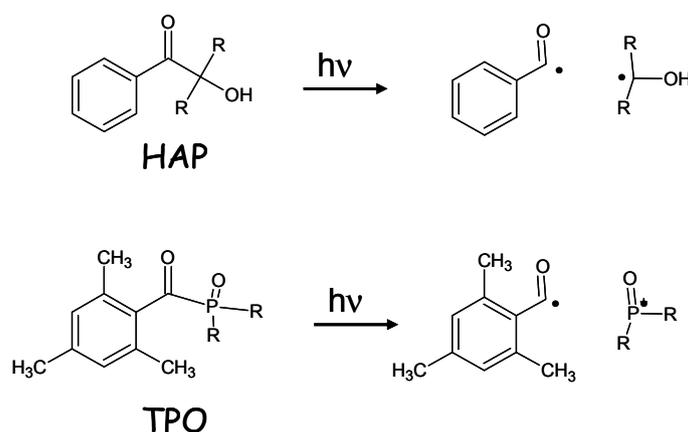
4. Short Backgrounds on PIs and PISs

The practical efficiency of a PIS in polymerization reactions under given experimental conditions is expressed in terms of polymerization rate R_p and final conversion. It depends on (i) the amount of absorbed light I_{abs} which is a function of both the absorption properties of the PI (wavelengths λ

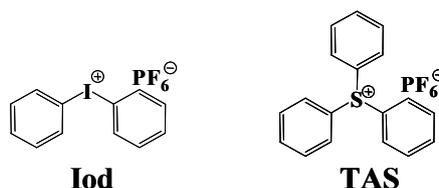
and molar extinction coefficients (ϵ) and the intensity I_0 of the light source and (ii) the photochemical/chemical reactivity of the PIS (expressed by the initiation quantum yield Φ_i that depends on the encountered excited state processes); for example, in a radical photopolymerization, R_p is proportional to the square root of $\Phi_i I_{abs}$ (for systems which have bimolecular termination such as most radical polymerizations) [100]. Therefore, a high efficiency of a given system is connected with high Φ_i and I_{abs} . However, a low Φ_i and a high I_{abs} can lead to the same performance as a high Φ_i and a low I_{abs} . Improving the reactivity (Φ_i) and designing PISs with better absorption properties (λ , ϵ) leads to enhanced polymerization efficiencies and provides the possibility to use lower light intensities I_0 .

Examples of usual radical PIs are cleavable compounds that undergo a fast breaking of a C–P (in phosphineoxide derivatives such as phosphineoxide (TPO) or a C–C bond (in hydroxyalkyl ketones such as hydroxyacetophenone (HAP)) as shown in Scheme 1 [100–103]. Widely used cationic photoinitiators are iodonium (DPI) and sulfonium (TAS) salts (Scheme 2) [100,102].

Scheme 1. Usual Type I photoinitiators (e.g., HAP, TPO), R stands for a phenyl ring in TPO and a methyl group in HAP.



Scheme 2. Examples of Cationic Initiators (iodonium and triarylsulfonium TAS).



5. Photochemical Production of IPNs: Mechanisms

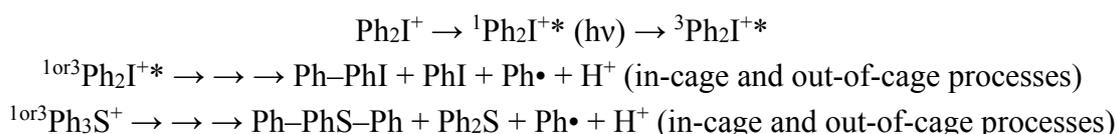
5.1. Intense UV Light Exposure

The main advantage of using UV lights in the polymerization of IPNs is the high polymerization rates that can be reached under usual Hg sources allowing an intense UV rich polychromatic illumination. The main drawback is the harmful character of the UV B and UV C rays delivered by these lamps. The photoinitiating system can consist in one or two PI that can be simultaneously or sequentially excited.

5.1.1. One-Photoinitiator Containing System

An example relates to the use of diphenyliodonium salts DPI (Ph_2I^+) or triarylsulfonium salts TAS (Ph_3S^+) that are able to generate both free radicals and protonic acids (Scheme 3). This requires an excitation at 254 nm (DPI) or 254/313 nm (TAS) and a high intensity as these systems are not extraordinarily reactive to initiate both a radical and a cationic polymerization. This strategy has been applied to the synthesis of, e.g., semi-IPNs from an EP/acrylated urethane oligomer blend using TAS under the intense UV light of a mercury lamp [104].

Scheme 3. Reaction sequence for cationic initiators.



Another example concerns the photopolymerization of a vinyl ether/acrylate blend [47]. When exposed to UV light (Hg lamp, 50 mW/cm²), the 1/1 mixture of DVE-3 and TMPTA in the presence of 2 wt% TAS readily polymerizes: almost 100% conversion for both the vinyl ether and the acrylate are reached within a few seconds. This unusual high conversion of TMPTA was attributed to a plasticizing effect of the cationic monomer. Other examples can be found, e.g., in [53].

5.1.2. Two-Photoinitiator Containing Systems and One-Step Exposure

In that case, two PIs are introduced into the formulation. For example, a radical PI such as HAP and a cationic PI such as TAS (concentrations: 2 wt%) allow the photopolymerization of a HDDA/EPOX blend (100 μm thick) under a Hg lamp in air (very high intensity: 350 mW/cm²) [28]. Free radicals originate from the photolysis of HAP (Scheme 1); protons are formed during the photolysis of TAS (Scheme 3). Conversions of 80% (HDDA) and 50% (EPOX) at $t = 120$ s are reached.

Various UV-initiated polymerizations of TMPTA/EPOX, urethane acrylate/CHVE, TMPTA/CHVE blends in the presence of 1-hydroxy-cyclohexyl-phenyl ketone HCAP (it works as HAP) and DPI were also observed; the addition of isopropylthioxanthone (ITX) enhances the rate of polymerization and the surface curing; acrylates polymerize faster than epoxides and vinyl ethers [24]. Other examples can be found, e.g., in [44,61].

In the same way, using HAP and TAS, a blend of HDDA and a renewable epoxy monomer (epoxidized soybean oil ESO (50:50) exposed to an intense UV illumination (600 mW/cm²) was cured in less than 3 s under air (conversions: HDDA ~100%, ESO ~80%) [29]. A HDDA/EP based IPN can also be obtained in the presence of HCAP and DPI [29]. The oxygen inhibition of the radical polymerization is reduced here as (i) the high photon flux generates a high amount of radical initiating species and (ii) the early buildup of the epoxy network leads to a strong increase of the viscosity and slows down the diffusion of oxygen into the sample (which thereby reduces the scavenging of the free radicals and the formation of peroxy radicals).

5.1.3. Sequential Production of IPNs Using Two Different Lights

Photoinitiation for the synthesis of IPNs has the unique advantage to also allow a sequential build-up of the two polymer networks. This can be achieved by a proper selection of the photoinitiators and the irradiation wavelengths (see a review on early experiments in [29] and references therein). The two PIs should be excited in two different wavelength ranges where the absorption spectra must have a minimum of overlap. Due to (i) the absorption of both PIs in the short UV wavelengths and (ii) the additional absorption of the radical PI in the near UV-visible part of the spectrum, one has to start first the polymerization of the acrylate under a filtered light. To avoid the oxygen inhibition (see above), high light intensities or/and viscous matrixes have to be used. For example, an acrylate/epoxidized polyisoprene IPN was created using TPO and TAS through the following procedure. A first intense irradiation at 365 nm or >350 nm (filtered light) using TPO (TAS does not absorb in that case) creates a semi-IPN where the acrylate network (almost 95% conversion within 5 s; lamp intensity: 30 mW/cm²) is embedded in the epoxidized polyisoprene. A second irradiation at $\lambda > 250$ nm (unfiltered UV light; TAS and the remaining TPO are excited) transforms the semi-IPN into a true IPN (~100% and ~80% conversion for the acrylate and the epoxide, respectively after 5 s exposure to light) thanks to the cationic polymerization through the epoxy groups. Other examples can be found, e.g., in [52,61].

5.2. UV-Thermal Dual Curing

Combining a thermal treatment with a UV irradiation could be useful to cure coatings on three-dimensional objects where shadow areas can exist. Such a treatment was applied to acrylate/oxetane blends [27]: the polyacrylate network is formed at 80 °C (44% conversion); a subsequent 1 min of irradiation leads to a substantial oxetane conversion (about 74%). The broad $\tan \delta$ curve (from 60 °C up to 200 °C) allows a broad damping effect of the final material. Other examples can be found in [105].

5.3. Visible Light Curing of IPNs

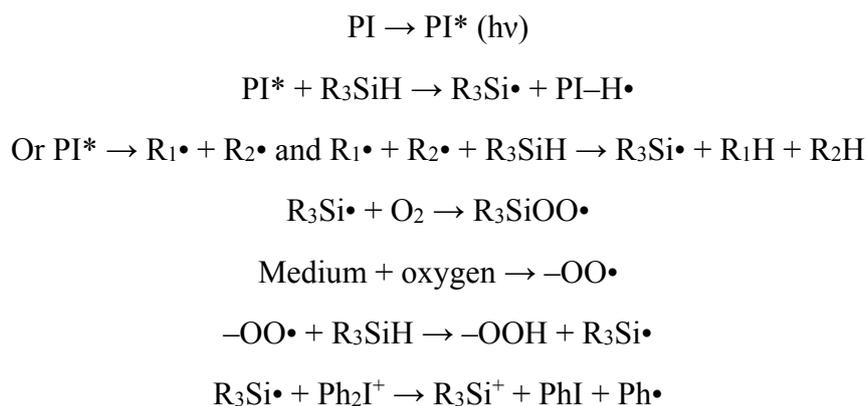
When using visible light sources (doped Hg lamps, Xe–Hg or Xe lamps), less UV lights are available and the intensities delivered at a function of the wavelength are often very different and lower. As a consequence, the I_{abs} quantities absorbed by each PI can also be different which has a strong influence on the polymerization profiles. The same holds true with usual Hg lamps where less visible lights are available. Moreover, the use of (quasi) monochromatic visible sources is usually rather difficult, as in any case, the presence of UV lights is required to get a satisfactorily excitation of the available cationic photoinitiators. Moreover, the oxygen inhibition effect increases when the light intensities decrease. Therefore, up until recently, the free radical/cationic hybrid polymerization under visible lights was hardly carried out and restricted to the use of systems absorbing in the near UV/visible wavelength range (see e.g., [106]).

5.4. Recent Design of Dual Photoinitiating Systems Operating under Visible Lights

To overcome these above mentioned limitations, one has to design a system that (i) contains one photosensitive compound (PI) and suitable additives, (ii) simultaneously generates radicals and cations (or radical cations), (iii) limits the oxygen inhibition effect and (iv) allows an excitation in the visible wavelength range.

We have recently designed such systems (see references below) that contain a reactive visible light absorbing PI, an iodonium salt Ph_2I^+ and a silane R_3SiH (or *N*-vinyl carbazole NVK) and work according to Scheme 4. The striking features are (i) the formation of the same cation R_3Si^+ and the same radicals $\text{R}_3\text{Si}\cdot$, $\text{Ph}\cdot$ whatever PI (*i.e.*, whatever the excitation wavelength), (ii) the high efficiency of these produced cations and radicals for the initiation of CP and FRP, respectively, and (iii) the role of the silane in the consumption of oxygen, the scavenging of the peroxy radicals and the re-generation of new silyls. The phenyls and silyls as well as the silyliums are used to initiate separately but concomitantly the free radical polymerization FRP and the cationic polymerization CP process within a one-step sequence. The final coatings are tack-free.

Scheme 4. Reaction sequence in the presence of a silane.



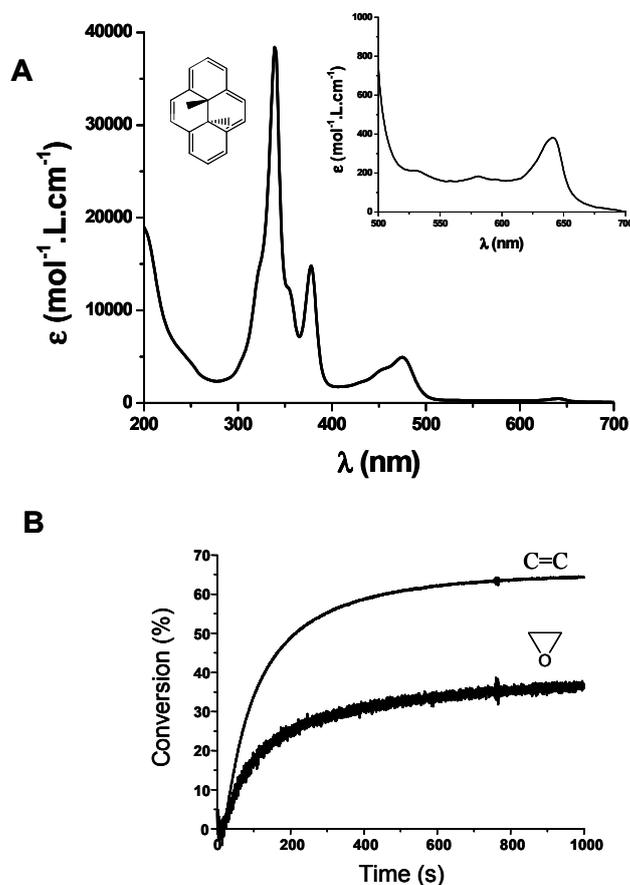
Such useful PIs in these novel dual photoinitiating systems are derived from dye structures and include e.g., diketopyrrolopyrrole-thiophene derivatives [107], mono and polyfunctional thiophene derivatives [108], indanedione skeleton [109], naphthalene scaffold [110], naphthalimide and naphthalic anhydride derivatives [111], anthraquinone derivatives [112], chalcone derivatives [113], push-pull malonate and malonitrile based compounds [114], naphthalimide based methacrylated derivatives [115], α -silicon polyoxomolybdate [116], acridinediones [117], difunctional acridinediones [118], Keggin-type polyoxometalate ion [119], push-pull structured indandiones [120], dimethyldihydropyrene [121], chromone based compounds [122], perylene bis-dicarboximides [123], pyrene derivatives [124], zinc complexes [125], pyridinium salts [126], pyrromethenes [127], trifunctional triazines [128], cyclometallated Pt(II) complexes [129], polyaromatic structures [130], and phenanthroline ligand containing Ru complex [131].

These systems are really versatile and have allowed the manufacture of IPNs under air at any wavelength (blue to red) depending only on the dye. The high reactivity of the photoinitiating systems is exemplified by the fact that low viscosity formulations where oxygen inhibition is much more important can be used (e.g., acrylate (TMPTA)/epoxide (EPOX), acrylate (TMPTA)/divinylether

(DVE), thiol (trimethylolpropane tris (3-mercaptopropionate) TMSH)/divinylether (DVE)). For example, the manufacture of IPN materials can be carried out under exposure to a large variety of wavelengths delivered by a Hg–Xe lamp (intensity $\sim 40 \text{ mW/cm}^2$) [116,119,128,130] or laser diodes (intensity $\sim 80 \text{ mW/cm}^2$) at 385–405 nm [110], 457 nm [108,111,113–115,122,124], 473 nm [127], 473 nm (and likely 532, 635 nm) [120], 532 nm [107,123], 635 nm [112], from 473 up to 635 nm [121]. This was achieved under air (for EPOX/TMPTA blends) or in laminate (for EPOX/DVE blends as seen, e.g., in [124,125,127,128]).

The attained performance can be exemplified here by the striking recent results obtained in the photopolymerization of a TMPTA/EPOX blend upon a blue to red light irradiation (Figure 1). For example, 2,7-di-tert-butylidimethyldihydropyrene (DHP) behaves as a panchromatic PI exhibiting good light absorption properties in the 400–700 nm range (Figure 1A) [121]. The synthesis of IPNs was easily carried out using DHP/DPI/NVK as PIS. Representative polymerization profiles of TMPTA/EPOX upon a red light are displayed in Figure 1B.

Figure 1. (A) UV-visible ground state spectrum of DHP in acetonitrile. (B) Photopolymerization profiles of a TMPTA/EPOX blend (50%/50%) under air using the DHP/DPI/NVK system (1%/2%/3% w/w/w) upon a laser diode exposure at 635 nm (the conversions for double bond (for TMPTA) and epoxy (for EPOX) were followed by FTIR spectroscopy as presented in [121]).



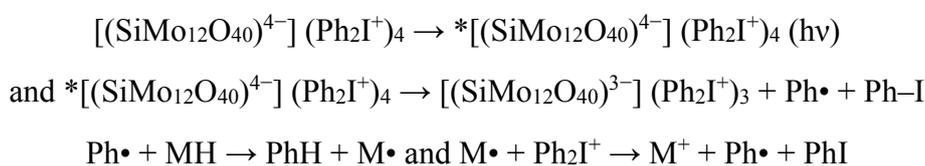
Thanks to the numerous original PIs recently designed [107–131], such IPN synthesis can be performed today with any selected irradiation devices: LEDs, laser diodes, laser beams, continuous

lamps (halogen lamp, Xe, Xe–Hg lamps, *etc.*). The novel commercial and industrially used LED arrangements (with high intensities in the visible) can obviously operate and, of course, more viscous films should also easily be photopolymerized (as the oxygen inhibition is less detrimental).

As expected, novel surface and bulk properties are obtained, e.g., in epoxide/acrylate IPNs compared to those of the bulk polyether or polyacrylate. For example (see in [130]; Hg–Xe lamp exposure), the contact angle on the surface of the EPOX/TMPTA (50%/50%) IPN film (water/polymer) is 62° which can be compared to those of neat TMPTA (49°) and neat EPOX (67°): both the polyether and polyacrylate networks are thus present at the surface. DMA analysis leads to one T_g value (148 °C) suggesting that a phase separation is avoided (or at least limited) and supporting a good compatibility between the two chemical networks.

Attempts have been made to design one-component PIs that are able to generate both radicals and cationic species. This way is, however, rather hard. A newly synthesized iodonium polyoxomolybdate $[(\text{SiMo}_{12}\text{O}_{40})^{4-}](\text{Ph}_2\text{I}^+)_4$ plays this role for the TMPTA/EPOX blend polymerization upon a Xe–Hg lamp exposure. Initiating phenyls $\text{Ph}\cdot$ and cations M^+ are formed (Scheme 5; MH being the cationic monomer). As before, excellent monomer conversions are obtained: 67% for EPOX and 78% for TMPTA under air (1000 s of UV light irradiation; tack free coatings). This way might be of interest as it avoids the introduction of several compounds (e.g., the silane or the iodonium salt in the above described three-component PISs) but the drawbacks are the design of suitable cationic moieties for a nice tuning of the absorption and the requirement of more or less complicated synthetic procedures.

Scheme 5. Chemical mechanisms involved in an iodonium polyoxomolybdate.



5.5. Photocuring of IPNs under Soft Conditions

The PI/iodonium salt/silane (or NVK) systems can also work for the simultaneous photocuring of IPNs under soft conditions (under air, under visible lights, under low light intensity). For example, various low viscosity blends of e.g., TMPTA/EPOX, TMPTA/DVE, TMSH/DVE can be polymerized under exposure to low intensity lights (intensity $< 8 \text{ mW/cm}^2$) emitted by household devices such as a halogen lamp [117,118,125,126,129], a fluorescent bulb (peaks at 430, 550 nm) [131], a blue led at 462 nm [109,132] and even sunlight (intensity $\sim 2 \text{ mW/cm}^2$).

Three representative examples are the following. When the polyaromatic chromophore depicted in Figure 2a is used in combination with DPI and a silane (or NVK) under a halogen lamp, an efficient simultaneous TMPTA/EPOX polymerization with final conversions of 55% (EPOX) and 75% (TMPTA) is readily achieved [130].

Different PIs (Anth, Napht and Pent) exhibit a suitable visible light absorption (Figure 3 [132]); upon very soft blue (for Anth), green (for Napht) and yellow and red (for Pent) LED bulb exposures ($\sim 10 \text{ mW/cm}^2$) good polymerization processes can be observed for EPOX/TMPTA blends using these PIs/DPI/silane photoinitiating systems.

Figure 2. Structure of (a) T_1 and (b) conversion profiles for the epoxy and acrylate double bond functions for an EPOX/TMPTA blend (50%/50% w/w) upon halogen lamp; irradiation under air in the presence of T_1/(TMS)₃Si–H/Ph₂I⁺ (0.2%/3%/2% w/w/w).

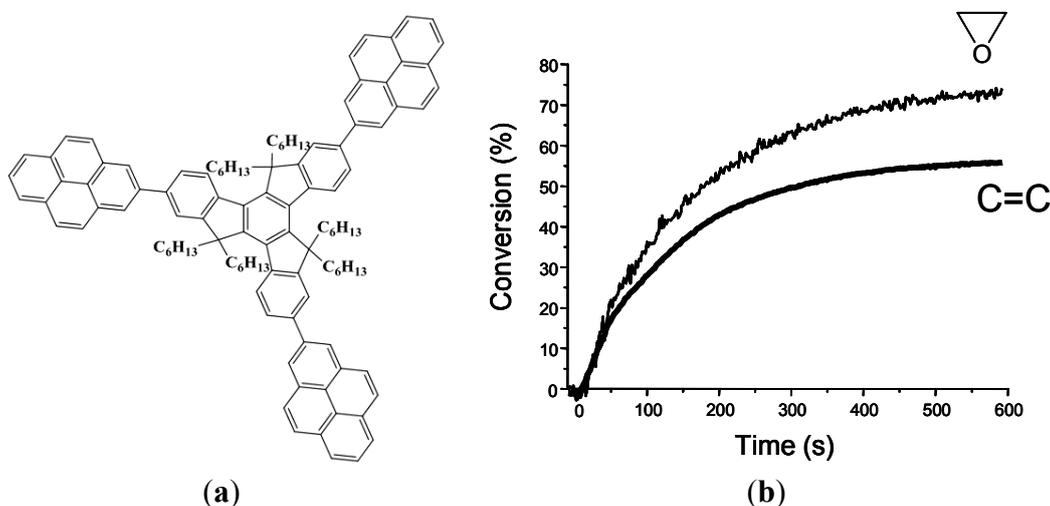
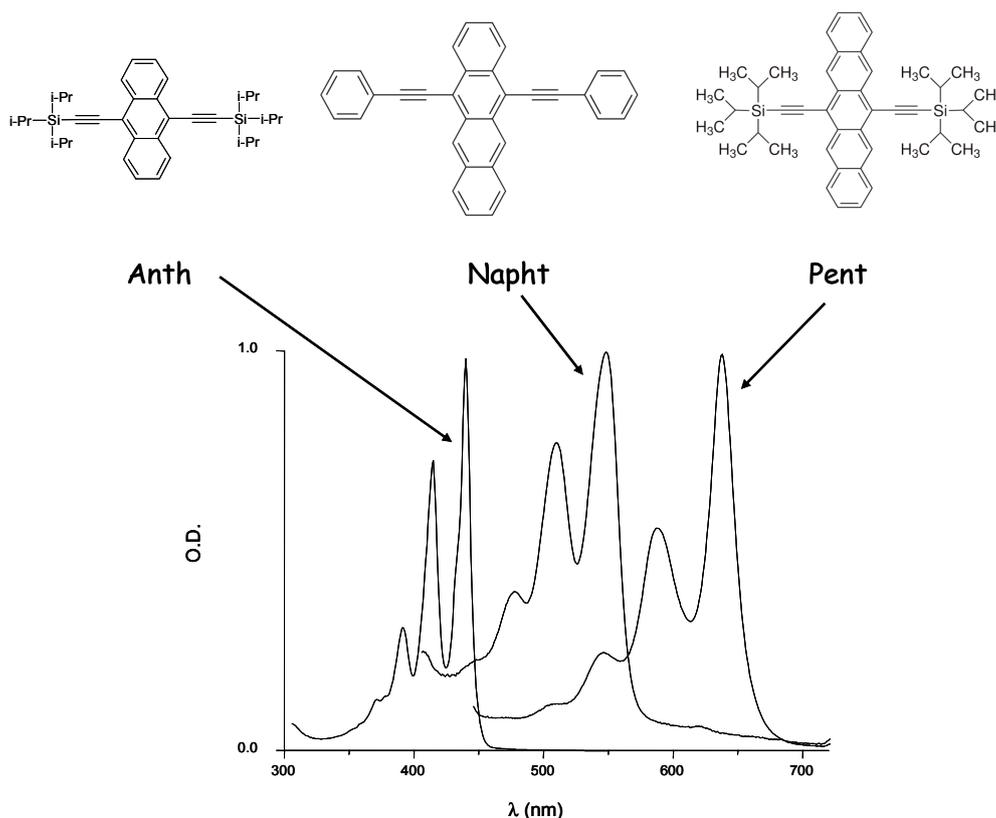


Figure 3. Visible light absorption spectra (O.D. for Optical Density) of different photoinitiators (Anth, Napht and Pent) in acetonitrile.



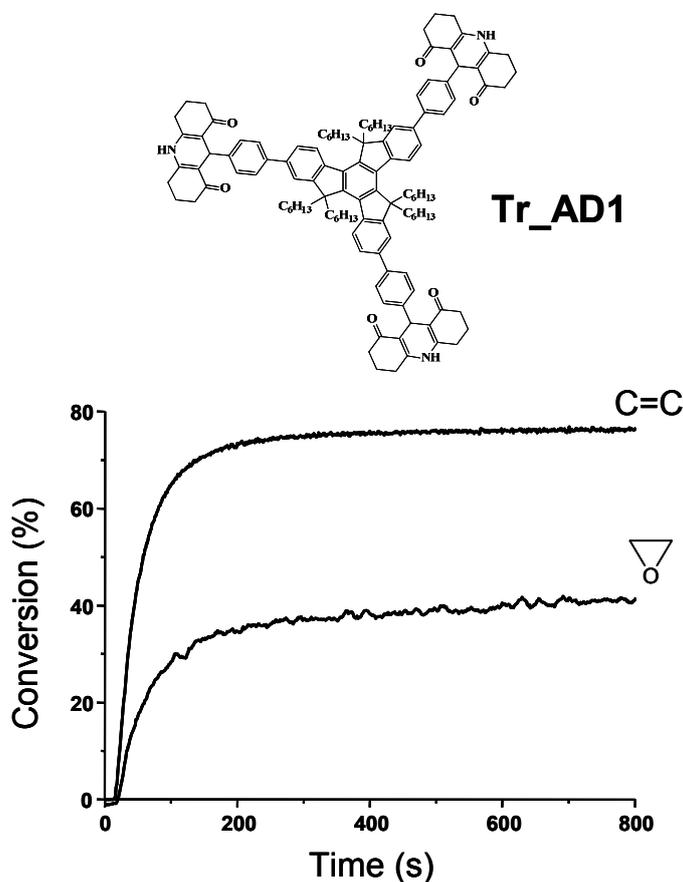
Similarly, under a polychromatic irradiation (halogen lamp; intensity ~ 12 mW/cm²), a truxene acridinedione (Tr_AD1)/DPI recently proposed PIS [120] is also very efficient (Figure 4).

These results confirm that quite high EPOX and TMPTA conversions in the formed IPNs can be obtained even under soft experimental conditions. Moreover, a noticeable difference is noted when the photopolymerization is conducted under air or in laminate. For example, when using a benzophenone

derivative/DPI/NVK system upon exposure to a household blue led at 462 nm [133], conversions of 63% (EPOX) and 56% (TMPTA) under air and 43% (EPOX) and 78% (TMPTA) in laminate are reached. This behavior is ascribed to the fact that the EPOX conversion is lower in laminate because the reduced oxygen inhibition effect and the predominant consumption of radicals in the FRP of TMPTA (rather than by the CP/FRPCP of EPOX).

The polymerization of TMPTA/DVE blends (50%/50%) in laminate leads to conversions of, e.g., 85% DVE and 55% TMPTA (see in [127]; 457 nm laser diode or halogen lamp); no IPN can be formed under air as DVE alone is unable to polymerize in such selected experimental conditions. The different TMPTA and DVE conversions are accounted for by the formation of several polymers: a vinyl ether homopolymer through the CP of vinyl ether units (i), an acrylate/vinyl ether copolymer (ii) (where the initiating radicals add both to the acrylate and the vinyl ether double bond) and a copolymer structure (iii) resulting from the difunctional character of DVE that allows a combination of the (i) and (ii) processes. In DSC (differential scanning calorimeter) experiments, two T_g values are measured. The low T_g (-11 °C) is mainly ascribed to the homopolymer (i) as the T_g of polymerized neat DVE is <30 °C); it ensures a high flexibility of the final material even at room temperature. The high T_g (111 °C) is attributed to the acrylate/vinyl ether network (ii, iii) and ensures the high hardness of the IPN. Other PISs can lead to similar DVE and TMPTA conversions (80%) [125].

Figure 4. Conversions of the acrylate double bond and the epoxide during the photopolymerization of a TMPTA/EPOX blend (50%/50%) in laminate upon a halogen lamp irradiation in the presence of Tr_AD1/DPI initiating system (0.5%/3% w/w).



The hybrid cure of EPOX/NVK blends and thiol (TMSH)/acrylate (TMPTA) media is also feasible using three-component PI/silane/iodonium salt PISs [112,113].

The reactivity/efficiency difference of these novel PISs compared with previously used PIs, two examples can be highlighted by the following results. Twenty years ago, semi IPNs based on an acrylate monomers dispersed in a solid matrix (such as polymethyl methacrylate or in a styrene-butadiene rubber) [134] and IPNs formed from an acrylate and an epoxidized natural rubber [135] have been synthesized under sunlight under air within minutes using conventional PIs (such as TPO): this was possible owing to the high matrix viscosity and, as a consequence, the reduction of the oxygen inhibition. In contrary, other low viscosity radical/cationic matrices cannot be photopolymerized except when using a two-step procedure where the first irradiation of the epoxide produces a viscous matrix in which the acrylate can further polymerize [134,135]. Nowadays, however, even low viscosity TMPTA, EPOX or TMPTA/EPOX blends that are easily polymerized under very low intensity artificial sources under air in the presence of our newly developed PISs (see above) should also be polymerized under sunlight. This has been confirmed with the DHP/DPI/NVK system presented above for the manufacture of an acrylate/epoxy blend. Interesting reviews about possibilities and interests of IPNs can also be found in [136–140].

6. Conclusions

This paper has shown what has been done up to now in the manufacture of IPNs using a photochemical technology. The versatility of the light induced processes for the initiation of radical and cationic polymerizations reactions is certainly a decisive factor in the choice or the possibilities of applications. A significant progress in the design of photoinitiating systems allowing the simultaneous formation of both networks under low intensity visible lights (and under air with acrylate/epoxide) is clearly observed, but improvements are still expected (for example, in the control of the monomer conversions, the access of other functionalities (e.g., caprolactone, lactide, *etc.*). A forthcoming challenge might be the proposal of photoinitiating systems being able to sequentially operate in the same experimental conditions. This could still be useful in further fine tuning the final properties (mechanical properties, chemical properties, *etc.*). Among others, the recent works carried out in low viscosity media under soft irradiation conditions are promising for a lot of applications in various areas as they should likely be transposed to other photopolymerizable monomer blends, thereby opening up new opportunities.

Conflicts of Interest

The authors declare no conflict of interest.

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